

**PERFLUORINATED COMPOUNDS IN LANDFILL LEACHATE AND THEIR EFFECT
ON THE PERFORMANCE OF SODIUM BENTONITE LANDFILL LINERS**

by

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B.A.Sc., The University of Northern British Columbia and The University of British Columbia,
2009

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in

The Faculty of Graduate Studies

(Civil Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA
(Vancouver)

August 2011

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Abstract

Perfluorinated compounds (PFCs) are a class of persistent organic pollutants (POPs) with potential major health and environmental concerns. PFCs are thermally and chemically stable, and do not readily degrade in the environment. PFCs have been detected in numerous environmental matrices, including surface water, ground water and sediment. PFCs are used for surface treatments for paper and textiles, industrial surfactants, insecticides and fire-fighting foams. Given their widespread use, products that contain PFCs have been, and continue to be disposed in landfills after their useful lives. Typical landfills have liners made of compacted clay (e.g. sodium bentonite) to prevent contaminants in leachate from migrating into the surrounding environment. Research was conducted to characterize geographic and temporal distributions of PFCs in landfill leachate in Canada and to investigate PFC retention on sodium bentonite.

Landfill leachate was collected from 29 landfills across Canada and analyzed for up to 18 PFCs. PFCs were ubiquitous in landfill leachate samples from across Canada and varied considerably with concentrations, generally being lower in the North than in the South. At one landfill, PFCs were analyzed in landfill gas condensate and water from a nearby river. Concentrations in both of these matrices were less than the landfill leachate. At another landfill, PFCs in landfill leachate were monitored for five months. Some PFCs varied temporally, whereas others remained relatively constant. The temporal variations were attributed to the presence of PFC precursors. There were strong correlations between PFC precursors and corresponding major degradation end-products. PFCs of similar size were also well-correlated with each other.

Batch adsorption tests were conducted in which sodium bentonite was contacted with water and landfill leachate spiked with PFCs to measure the sorption of PFCs on sodium bentonite. PFCs in landfill leachate do not readily bind to sodium bentonite. Leaching cell tests were conducted in which compacted sand-bentonite admix columns were permeated with water, landfill leachate and PFC spiked landfill leachate. Similar hydraulic conductivity values were produced under each condition, indicating that PFCs do not significantly compromise the performance of bentonite liners. The sand-bentonite admix also appears to retain PFCs under the leaching cell test conditions.

Preface

Sampling for cross-Canada landfill leachate samples was conducted by landfill operators and Dr. Monica Danon-Schaffer. Sample extraction, clean-up and PFC analyses using liquid chromatography-tandem mass spectrometry (LC/MS/MS) were performed by AXYS Analytical Services Ltd. in Sidney, British Columbia. I was responsible for data analyses and interpretation.

Sample extraction, clean-up and PFC analyses using LC/MS/MS for all other samples were conducted at the Fisheries and Oceans Canada Institute of Ocean Sciences in Sidney, British Columbia by Dr. Jonathan Benskin, Dr. Xiangjun Liao and Belinda Li under the guidance of Dr. Michael Ikononou. I was responsible for sample extraction, clean-up and assisting with preparing samples for LC/MS/MS. Dr. Jonathan Benskin and Dr. Xiangjun Liao performed LC/MS/MS analyses and data processing. I performed data analyses and interpretation with the guidance of Dr. Jonathan Benskin, Dr. Xiangjun Liao, and Dr. Michael Ikononou.

A version of chapter 4 relating to the cross-Canada landfill leachate samples has been published. Li, L.Y., Danon-Schaffer, M.N., **Li, B.**, Ikononou, M.G., and Grace, J.R. (2010). PFAs and PBDEs in Landfill Leachates from across Canada. Proceedings of the 1st International Conference on Final Sinks. I conducted statistical analyses and prepared tables and figures for the publication.

A version of chapter 4 relating to landfill leachate samples from landfills A and B is in preparation for publication. Benskin, J.P., **Li, B.**, Ikononou, M.G., Grace, J.R., and Li, L.Y. (2011). Sources of polyfluorinated compounds in landfill leachate. I conducted sampling, sample extraction, clean-up and assisted with preparing the manuscript.

A version of chapter 5 has been submitted as a report to Environment Canada. **Li, B.**, Ikononou, M.G, Li, L.Y., and Grace, J.R. (2011). Batch adsorption tests on bentonite with perfluorinated compounds in landfill leachate. I conducted all experimental work and wrote most of the report with guidance from Dr. Loretta Li, Dr. John Grace and Dr. Michael Ikononou.

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List of Abbreviations

ASTM	American Society for Testing and Materials
BAT	batch adsorption test
BC	British Columbia
DFO-IOS	Fisheries and Oceans Canada Institute of Ocean Sciences
ECF	electrochemical fluorination
EPA	United States Environmental Protection Agency
HDPE	high-density polyethylene
IDL	instrument detection limit
IUPAC	International Union of Pure and Applied Chemistry
k	hydraulic conductivity
k _{oc}	binding affinity to organic carbon
LCT	leaching cell test
LCRS	leachate collection and removal system
LC/MS/MS	liquid chromatography-tandem mass spectrometry
MDL	method detection limit
MRM	multiple reaction monitoring
p	probability value
PFC	perfluorinated compound
POP	persistent organic pollutant
R ²	Pearson's correlation coefficient
RSD	relative standard deviation
TOC	total organic carbon
TSS	total suspended solids
UBC	University of British Columbia
XRD	X-ray diffraction

List of Chemicals

6:2 FTUA	6:2 fluorotelomer unsaturated acid
8:2 FTUA	8:2 fluorotelomer unsaturated acid
10:2 FTUA	10:2 fluorotelomer unsaturated acid
PFBA	perfluorobutanoic acid
PFBS	perfluorobutane sulfonate
PFDA	perfluorodecanoic acid
PFD _o A	perfluoroundecanoic acid
PFDS	perfluorodecane sulfonate
PFHpA	perfluoroheptanoic acid
PFH _x A	perfluorohexanoic acid
PFH _x S	perfluorohexane sulfonate
PFNA	perfluorononanoic acid
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonate
PFOSA	perfluorooctane sulfonamide
PFPeA	perfluoropentanoic acid
PFTA	perfluorotetradecanoic acid
PFUnA	perfluoroundecanoic acid
POSF	perfluorooctanesulfonyl fluoride

Acknowledgements

Dr. Loretta Li and Dr. John Grace, my research supervisors: Thank you for your guidance, patience, and encouragement throughout the course of this research. This was an ambitious project and I am grateful for all the support you have provided to make it happen. Despite your busy schedules and frequent travels to conferences around the world, I greatly appreciate your willingness to review my countless pages of writing from time zones away.

Dr. Michael Ikononou, Dr. Jonathan Benskin, Dr. Xiangjun Liao and the staff of the Fisheries and Oceans Institute of Ocean Sciences (DFO-IOS): Thank you for your knowledgeable advice, laboratory assistance, and providing valuable lab space for this project. I would not have gone this far with my research without your patience in teaching me about analytical methods and answering my many questions over emails about PFCs and analytical chemistry. I learned more in the weeks I spent at the DFO-IOS than I have throughout my entire Masters program.

Paula Parkinson, Timothy Ma, Bill Leung, and the staff of the UBC Civil Environmental Engineering Lab and Workshop: Thank you for providing me with advice and assistance with my lab work at UBC. From figuring out how to build a column apparatus to troubleshooting broken compressors, your practical knowledge on how to make these research plans work in real-life is invaluable.

Joan Trill, my couchsurfing host in Sidney: Thank you for welcoming and "adopting" me into your home for so many weeks so I could work on my research at the DFO-IOS. To Emma, the most excitable host dog and fetching champion, thank you for keeping my spirits up after long days at the lab.

Dr. Monica Danon-Schaffer: Your research inspired me to pursue this challenging topic in the first place. I appreciate your sage advice and all the effort you put into blazing the trail for this project before I even considered doing a Masters. I owe this thesis to you.

The staff at the landfills: I cannot mention your names, but you know who you are. Thank you for your assistance with collecting landfill leachate samples from your landfills. I could not have done any of my research without your help and support.

Sara Pour: Thank you for keeping my experiments running in the lab, being there when I need a break from research, and enthusiastically joining me in the pursuit of extra-curricular projects. You've added so much fun to my graduate student experience. I wish you the best in getting those rain barrels installed!

Susana Harder, my APEGBC P.Eng. Mentor: Thank you for the invaluable career advice, insights on everything related to solid waste, and guidance on getting through the Engineer-In-Training program. Your real-world, outside of academia perspectives on my research have helped me broaden my approach to analyzing problems.

Susan and Sam Li, my parents: Thank you for supporting me throughout my education and encouraging me to do my best no matter what. Your hard-working attitude has certainly inspired me, and I am grateful for everything you have done to shape me into who I am today.

Kamil Kisiel, my partner: I couldn't have done this Masters without you. Thank you for proof-reading my writing despite the fact that the acronyms make no sense to you, helping me move samples and containers on weekends and evenings when you could have been doing something else, and acting as my personal Python/data processing consultant.

This research was made possible by the financial support of:

- Environment Canada
- Natural Sciences and Engineering Research Council of Canada for research funding and the Alexander Graham Bell Canada Graduate Scholarship
- University of British Columbia Faculty of Applied Science Graduate Scholarship
- Solid Waste Association of North America (SWANA) Pacific Chapter BC and Yukon Scholarship
- Contaminated Sites Approved Professionals (CSAP) Graduate Scholarship
- Girl Guides of Canada-Guides du Canada Energizer Canada Now That's Positivenergy National Science Scholarship

Chapter 1: Introduction

1.1 Problem statement

Perfluorinated compounds (PFCs) are a class of synthetic chemicals used in fire-fighting foams, industrial surfactants, insecticides, and surface treatments for paper and textiles (Paul et al., 2009, Prevedouros et al., 2006, Hekster et al., 2003). All PFCs consist of a fluorinated carbon chain attached to one or more functional groups (Parsons et al., 2008). The stability in the fluorine-carbon bond gives these compounds unique properties. PFCs are thermally and chemically stable, and therefore they are environmentally persistent (Parsons et al., 2008, Prevedouros et al., 2006, Sinclair & Kannan, 2006). They are found globally in all environmental matrices, such as surface water, ground water, and sediment, including remote locations such as the Arctic (Murakami et al., 2009, Becker et al., 2008, Young et al., 2007, Giesy & Kannan, 2002). Negative health effects on humans and animals resulting from long-term exposure to PFCs include developmental toxicity such as low birth weight, and endocrine disruption in the regulation of sex hormones (Jensen & Leffers, 2008, Lau et al., 2007, Alexander et al., 2003, Austin et al., 2003). Due to their environmental persistence, widespread occurrence and toxicity, PFCs are persistent organic pollutants (POPs) (Karrman et al., 2006). The two classes of PFCs of greatest concern are perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonates (PFSAs) as they are the final degradation products of most commercial PFCs (Giesy & Kannan, 2002). The most widely studied compounds are perfluorooctane sulfonate (PFOS), a PFSA, and perfluorooctanoic acid (PFOA), a PFCA (Vestergren et al., 2008). The Stockholm Convention on Persistent Organic Pollutants is a global treaty ratified by 172 countries, including Canada, to eliminate or reduce the use of POPs to prevent release into the environment (Stockholm Convention, 2009). The PFCs listed under the Stockholm Convention are perfluorooctane sulfonic acid, its salts, and perfluorooctane sulfonyl fluoride.

The largest emissions of PFCs are from direct sources, such as fluorochemical manufacturing facilities (Prevedouros et al., 2006). Indirect sources, such as chemical reaction impurities and degradation precursors account for a smaller portion of historical emissions but are more difficult to control because they are widely dispersed. Given their widespread use, products that contain

PFCs have been, and continue to be, disposed in landfills after their useful lives. Due to their environmental persistence, PFCs will exist in landfills for decades. PFCs from landfilled materials may leach into landfill leachate, which is treated on-site or off-site (e.g. directed to a wastewater treatment plant) and eventually released into the environment. This creates a potential long-term source of PFCs in the environment. Thus, it is important to determine the extent of PFC contamination in landfills through examining their concentrations in landfill leachate. Data on PFCs in landfill leachates are sparse, with only a handful of studies characterizing PFCs (Huset et al., 2011, Kallenborn et al., 2004, Busch et al., 2010a, Oliaei et al., 2006) in landfill leachates. No research has been reported on PFCs in Canadian landfills.

Landfill leachates are created from precipitation falling on the landfill, moisture in waste that trickles through the landfill, and leaching contaminants from the waste. Typical landfills have liners to prevent contaminants in landfill leachate from migrating into the surrounding environment. The landfill liners are made from compacted clay, geosynthetics, or a combination of the above (Sharma & Lewis, 1994). Landfill leachate is typically managed by a collection system that sends it to on-site treatment before being released to the environment, or directs it to the sewer system to be treated by a wastewater treatment plant. If a landfill liner fails by developing a hole, fissure or crack, then landfill leachate and its contaminants can spread into the surrounding environment.

Sodium bentonite is a clay commonly used for landfill liners (Sharma & Lewis, 1994). The major mineral constituent of sodium bentonite is montmorillonite, a very soft clay with high swelling potential (Sharma & Lewis, 1994). Hence, it is a favourable material for low-permeability landfill liners. Montmorillonite also has a large specific surface area and high cation-exchange capacity (He et al., 2001). This allows common contaminants such as metals to be immobilized in a landfill liner made with sodium bentonite through adsorption (Li & Li, 2001). However, hydrophobic organic contaminants cannot be readily adsorbed because sodium bentonite is hydrophilic (Li & Denham, 2000). Perfluorinated compounds are generally hydrophobic. However, they do have hydrophilic functional groups (Parsons et al., 2008), so there is some potential for them to adsorb onto sodium bentonite. One study (Zhou et al., 2010) has shown some sorption of PFCs on pure montmorillonite. There have been no studies published so far on the sorption of PFCs contained in landfill leachate and on sodium bentonite.

1.2 Objectives

The goal of this study was to determine the extent of contamination of PFCs in landfill leachate from landfills in Canada and to gain preliminary insight on the interaction of PFCs with landfill liners. The specific objectives of this study were:

- To characterize field samples (landfill leachate, water) and experimental materials (sodium bentonite, Ottawa sand) in terms of physical and chemical properties.
- To examine geographic and temporal distributions of PFCs in leachate, soil, and surface water by:
 - Characterizing PFC concentrations in Cross-Canada landfill leachate
 - Characterizing PFC concentrations in landfill leachate, landfill gas condensate and river water collected within 10 km downstream of one landfill site (landfill A)
 - Monitoring temporal variations in PFC concentrations over a five-month period at another landfill site (landfill B)
- To determine the sorption capacity of bentonite for PFCs by conducting batch adsorption tests.
- To determine the sorption capacity of sand/bentonite admix for PFCs under simulated field conditions by conducting leaching cell tests.

1.3 Analytes of interest

The PFCs examined in the study include 4 to 12 and 14 carbon straight-chain perfluoroalkyl carboxylic acids (PFCAs), 4, 6, 8, and 10 carbon straight-chain perfluoroalkyl sulfonates (PFSAs), and a select number of precursors. The precursors examined in this study are perfluorooctane sulfonamide (PFOSA), a fluorinated sulfonamide (FOSA), 6:2, 8:2, and 10:2 fluorotelomer unsaturated acids (FTUAs). The physical and chemical properties of the compounds analyzed in this study are discussed in section 2.1.

1.4 Research plan

A research plan of field and laboratory work was developed to achieve the objectives of this study. A flowchart of this research plan is shown in Figure 1.1.

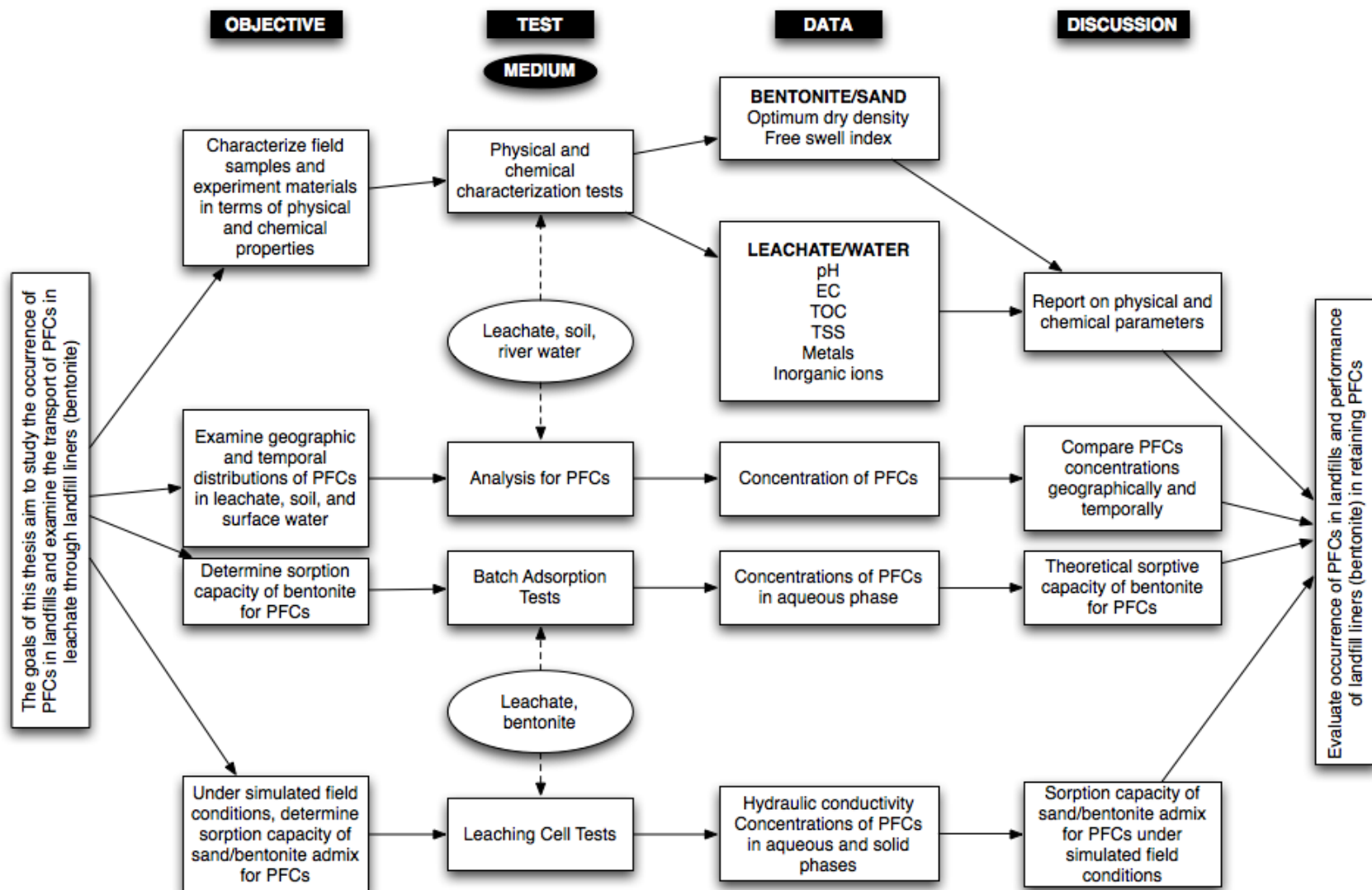


Figure 1.1: Research plan

1.5 Research contributions

This study provides a comprehensive overview of PFC concentrations in landfill leachate across Canada, temporal variations at one landfill site, and comparison of PFC concentrations in various aqueous media at another landfill site. These results will contribute to a better understanding of which landfill parameters may influence the presence of PFCs in landfill leachate, as well as whether the materials disposed in landfills are a significant source of PFCs to the environment. The batch adsorption tests and leaching cell tests provide a preliminary assessment of the ability of sodium bentonite landfill liners to retain PFCs and reduce their migration into the surrounding environment. By better understanding potential effects of PFCs on the performance of landfill liners, these results can aid decisions on the handling of solid waste at landfills, design of landfills, and landfill leachate management.

Chapter 2: Background and literature review

2.1 Physical and chemical properties

Perfluorinated compounds (PFCs) are synthetic compounds that consist of a fluorinated, hydrophobic alkyl chain between 4 to 16 carbons attached to one or more hydrophilic functional groups (Parsons et al., 2008). The chemical structures of the classes of PFCs included in this study are illustrated in Figure 2.1. The PFCs analyzed in this study, IUPAC names, acronyms, and Chemical Abstracts Service (CAS) numbers are listed in Table 2.1. It is important to note that for the acids (Figure 1a-b), once they are released in the environment, they are likely to be present in their anionic forms (i.e. with O⁻ instead of OH) (Goss, 2008).

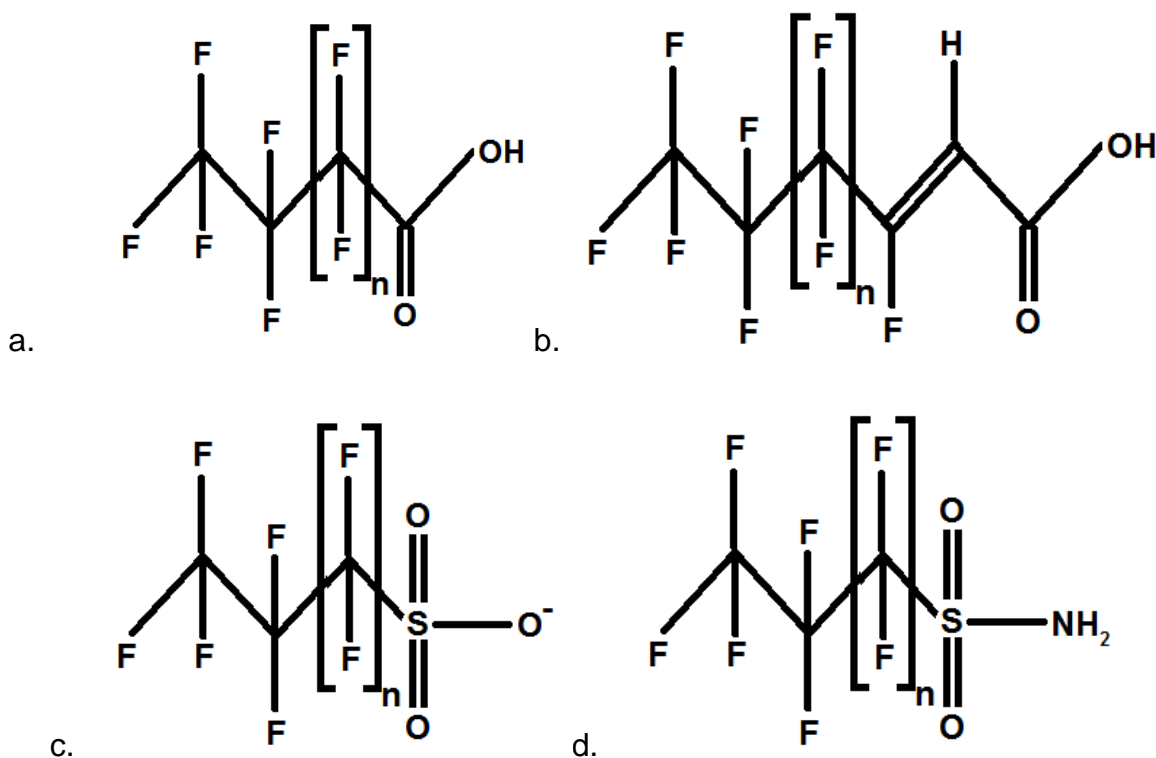


Figure 2.1: Chemical structures of (a) perfluoroalkyl carboxylic acid, (b) fluorotelomer unsaturated acid, (c) perfluoroalkyl sulfonate, and (d) fluoroalkyl sulfonamide (adapted from American Chemical Society, n.d.)

Table 2.1: Perfluorinated compounds analyzed in this study grouped by class (American Chemical Society, n.d.)

Name	IUPAC name	Acronym	CAS number
Perfluoroalkyl carboxylic acid		PFCA	
Perfluorobutanoic acid	2,2,3,3,4,4,4-heptafluorobutanoic acid	PFBA	375-22-4
Perfluoropentanoic acid	2,2,3,3,4,4,5,5,5-nonafluoropentanoic acid	PFPeA	2706-90-3
Perfluorohexanoic acid	2,2,3,3,4,4,5,5,6,6,6-undecafluorohexanoic acid	PFHxA	307-24-4
Perfluoroheptanoic acid	2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptanoic acid	PFHpA	6130-43-4
Perfluorooctanoic acid	2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanoic acid	PFOA	335-67-1
Perfluorononanoic acid	2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononanoic acid	PFNA	375-95-1
Perfluorodecanoic acid	2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-nonadecafluorodecanoic acid	PFDA	335-76-2
Perfluoroundecanoic acid	2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heneicosafluoroundecanoic acid	PFUnA	2058-94-8
Perfluorododecanoic acid	2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-tricosafluorododecanoic acid	PFDoA	307-55-1
Perfluorotetradecanoic acid	2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptacosafuorotetradecanoic acid	PFTA	376-06-7
Perfluoroalkyl sulfonate		PFSA	
Perfluorobutane sulfonate	1,1,2,2,3,3,4,4,4-nonafluoro-1-butanefluoronic acid	PFBS	375-73-5
Perfluorohexane sulfonate	1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-1-hexanesulfonic acid	PFHxS	355-46-4
Perfluorooctane sulfonate	1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-1-octanesulfonic acid	PFOS	1763-23-1
Perfluorodecane sulfonate	1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heneicosafluoro-1-decanesulfonic acid	PFDS	335-77-3

Table 2.1 continued.

Name	IUPAC Name	Acronym	CAS Number
Fluoroalkyl sulfonamide		FOSA	
Perfluorooctane sulfonamide	1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-1-octanesulfonamide	PFOSA	754-91-6
Fluorotelomer unsaturated acid		FTUA	
6:2 Fluorotelomer unsaturated acid	3,4,4,5,5,6,6,7,7,8,8,8-dodecafluoro-2-octenoic acid	6:2 FTUA	70887-88-6
8:2 Fluorotelomer unsaturated acid	3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-2-decenoic acid	8:2 FTUA	70887-84-2
10:2 Fluorotelomer unsaturated acid	3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-eicosfluoro-2-dodecenoic acid	10:2 FTUA	70887-94-4

The carbon-fluorine bond found in all PFCs is one of the strongest in nature (460 kJ/mol) (3M Company, 1999a, O'Hagan, 2008). This bond gives PFCs thermal and chemical stability, but also leads to persistence in the environment. The chemical properties of PFCs depend on the length of the carbon chain and the functional end groups. Selected properties of PFCs analyzed in this study are listed in Table 2.2. For each class of compounds, mass solubility decreases with fluorinated carbon chain length. The organic carbon normalized sorption coefficient (k_{oc}) increases exponentially with fluorinated carbon chain length. Note that all of these properties were estimated using software (American Chemical Society, n.d.), not empirically measured and assume conditions at 25°C and a pH of 7. In any case, the properties shown in Table 2.2 give some insight into how these compounds behave relative to each other in the environment.

Table 2.2: Properties of PFCs (American Chemical Society, n.d.)

PFC	Molecular weight (g/mol)	Mass solubility (g/L)	k_{oc}
PFBA	214.04	327	1.0
PFPeA	264.05	13	3.2
PFHxA	314.05	1.2	7.5
PFHpA	364.06	0.073	22.8
PFOA	414.07	5.00×10^{-3}	69.6
PFNA	464.08	3.60×10^{-4}	212
PFDA	514.08	2.40×10^{-5}	645
PFUnA	564.09	1.70×10^{-6}	1970
PFDoA	614.10	1.20×10^{-7}	5980
PFTA	714.11	6.70×10^{-10}	55500
PFBS	300.10	110	1.0
PFHxS	400.11	1.6	5.43
PFOS	500.13	0.019	50.4
PFDS	600.14	2.30×10^{-4}	467
PFOSA	499.14	1.20×10^{-7}	1.74×10^5
6:2 FTUA	358.08	999	1.0
8:2 FTUA	458.10	110	4.43
10:2 FTUA	558.11	5.6	27.8
k_{oc} : organic carbon normalized sorption coefficient			

Though experimentally derived values for some properties of PFCs are available, properties of PFCs are an emerging research field, as their properties change according to physical and

chemical conditions (Giesy et al., 2006). Furthermore, studies typically focus only on PFOS and PFOA. As this study focuses on PFCs in landfill leachate and interactions with landfill liner materials, k_{oc} is an important factor in explaining the partitioning behaviour of PFCs to particulates in landfill leachate and landfill liners. For ease of comparison, one typically refers to $\log k_{oc}$ instead of k_{oc} . Rayne and Forest (2009) and Higgins and Luthy (2006) calculated $\log k_{oc}$ values from several experimental studies. These are plotted with computationally-derived values from Table 2.2 in Figure 2.2. Although the values of $\log k_{oc}$ vary among experimental studies, the overall trend is that $\log k_{oc}$ increases with longer carbon chain lengths, consistent with the computational values. The only experimental study to compare several compounds is Higgins and Luthy (2006), and their PFOA and PFOS $\log k_{oc}$ values lie between other experimentally derived values at 2.11 and 2.68 respectively.

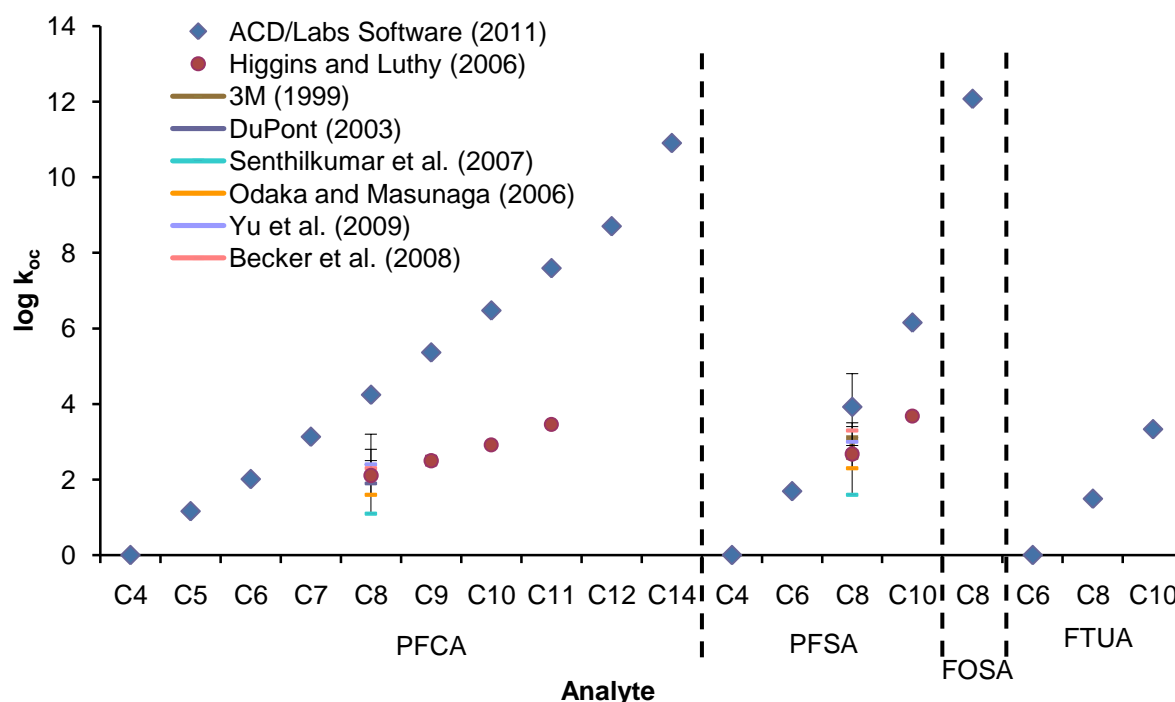


Figure 2.2: Comparison of experimentally and computationally derived organic carbon normalized sorption coefficients (k_{oc}) for PFCs analyzed in this study. PFCs are grouped by class and arranged in increasing order of fluorinated carbon chain. $\log k_{oc}$ values for 3M Company (1999) and Dupont (2003) were cited from Higgins and Luthy (2006). $\log k_{oc}$ values for Senthilkumar et al. (2007), Odaka and Masunaga (2006), Yu et al. (2009) and Becker et al. (2008) were cited from and calculated by Rayne and Forest (2009).

2.2 Synthesis

There are two major manufacturing processes to produce PFCs: electrochemical fluorination (ECF) and telomerization. ECF was developed in the 1940s by Joseph Simons at Penn State University (3M Company, 1999a). This technology is used by 3M Company, the largest fluorochemical manufacturer in the world. The production process involves running an electric current through an organic feedstock dispersed in liquid with anhydrous hydrogen fluoride. The hydrogen atoms are replaced with fluorine in the reaction. The dominant product from this reaction is a compound with the same carbon skeletal arrangement as the organic feedstock with all hydrogen atoms replaced with fluorine. Byproducts include cleaved, branched, and cyclic structures formed through fragmentation and rearrangement of the carbon skeleton. Until the product was phased out in 2002, 3M Company produced perfluorooctanesulfonyl fluoride (POSF) in the highest volumes, as it was a building block for most of 3M Company's fluorochemical products. The straight-chain (normal) POSF yield is approximately 35-40%. The composition of products from the ECF process are listed in Table 2.3. The two major classes of products derived by 3M from POSF were N-alkylperfluorooctane sulfonamide (FOSA) and N-alkylperfluorooctane sulfonamidoethanol (FOSE).

Table 2.3: Electrochemical fluorination product composition (3M Company, 1999a)

Product	Percentage
Straight-chain (normal) POSF ($C_8F_{17}SO_2F$)	35-40%
Higher and lower straight-chain perfluoroalkylsulfonyl fluorides (e.g. $C_6F_{13}SO_2F$, $C_7F_{15}SO_2F$)	7%
Branch-chained, perfluoroalkylsulfonyl fluorides with various chain lengths	18-20%
Straight-chain, branched, and cyclic perfluoroalkanes and ethers	20-25%
"Tars" (high molecular weight fluorochemical byproducts), other byproducts	10-15%

Telomerization is a process that reacts a telogen (e.g. perfluoroethyl iodide) with one or more taxogens (unsaturated molecules, e.g. tetrafluoroethylene) (Lehmle, 2005). Other common taxogens include vinylidene fluoride, chlorotrifluoroethylene, trifluoroethylene, and hexafluoropropene. The products of the reaction are even-carbon-chain telomers (e.g. $F(CF_2CF_2)_n + 1I$), the first intermediate compound of the process. These telomers are further

reacted with compounds such as ethylene to produce intermediate products such as perfluoroalkyl iodides. These compounds are then converted into other fluorinated intermediates such as olefins, fluorinated carboxylic acids, and fluorotelomer alcohols. Note that unlike ECF, the odd-numbered carbon chain and branched intermediates cannot be produced in the telomerization process (D'eon & Mabury, 2011). This is important for characterizing the source of PFCs in environmental samples as the dominance of straight-chained, even-numbered carbon PFCs is an indicator of telomerization-produced compounds.

2.3 Applications

The major commercial applications of PFCs are surface treatments, paper and packaging protectors, and performance chemicals (Paul et al., 2009, Prevedouros et al., 2006, 3M Company, 1999a, 3M Company, 1999b). Based on information from 3M Company (1999a, 1999b), surface treatment products are categorized as industrial, retail, and commercial. Industrial products are applied during the manufacture of carpets, upholstery, and clothing for soil, stain and water resistance. Retail products include aerosol can spray cleaners and protectors for consumer use. Commercial products are used by commercial cleaning services and film processing facilities. Paper and packaging protectors are used by paper mills and packaging manufacturers to add grease, oil, and water resistance to paper and packaging products. These products are used for both food contact (e.g. plates, containers, bags, wraps) and non-food applications. Performance chemicals take advantage of the surfactant properties of PFCs. Aqueous film forming foams (AFFFs) are a major group of performance chemicals containing PFCs. These are used to extinguish fires in a variety of places, including chemical and petroleum plants, fire departments, oil drilling platforms, and military operations. The mining and oil industries use PFC-based surfactants to enhance metal and oil recovery. Other performance chemical applications include metal plating and electronic etching surfactants, household additives (e.g. cleaners, floor polishes, shampoos), chemical intermediates for fluoropolymer production, carpet spot cleaners, and insecticides.

2.4 PFCs in Canada

Approximately 600 tonnes of PFCs were imported into Canada from 1997 to 2000, based on the Canadian Environmental Protection Agency (CEPA) Screening Assessment on Perfluorooctane

Sulfonate (Environment Canada, 2006). Historical data before 1997 are not available. As these compounds are not manufactured in Canada, the sole source is through imports. Approximately 43% (258 tonnes) of the PFCs were PFOS, its salts and precursors. Since 3M phased out its production of PFOS in 2002 (3M Company, 2011), the use of PFOS, its salts and precursors within Canada has ceased for the most part. However, other PFCs may still be imported and used. The primary uses of PFOS, its salts and precursors in Canada are the following:

- Surface treatment (water, oil, soil and grease repellents) for fabric, leather, packaging and rugs and carpet
- Surfactants/detergents
- Emulsifiers
- Wetting agents
- Dispersants
- Fire-fighting foams.

The surface treatment applications in Canada are of particular interest as these products (e.g. carpets, packaging) are typically disposed in landfills after their useful lives. According to Environment Canada (2001, cited in Environment Canada, 2006), there may have been significant releases of PFOS to the environment from water, oil, soil and grease repellents for packaging. However, data on the use and disposal are not available.

On April 17, 2008, the Perfluorooctane Sulfonate Virtual Elimination Act received Royal Assent and became law (Government of Canada, 2009). This Act "requires Ministers of the Environment and of Health to make a regulation to add perfluorooctane sulfonate (PFOS) and its salts to the Virtual Elimination List within nine months after the coming into force of the Act".

2.5 Health effects and toxicology

PFCAs and PFSAAs with carbon chains greater than six or seven have bioaccumulation potential and biomagnify through food chains (Conder et al., 2008, Haukas et al., 2007, Houde et al., 2008). Conder et al. (2008) found that bioconcentration and bioaccumulation potential are directly related to the length of the fluorinated carbon chain and that PFSAAs are more bioaccumulative than PFCAs. Haukas et al. (2007) studied the biomagnification of PFCs in a

Barents Sea food web and reported biomagnification factors greater than one for PFHxS, PFNA, and PFOS. Houde et al. (2008) investigated bioaccumulation of PFOS isomers in a Lake Ontario food web. The bioaccumulation factor for PFOS was 3.4×10^4 L/kg (mg/kg PFOS in fish tissue per mg/L PFOS in water) for lake trout.

Negative health effects on humans and animals resulting from long-term exposure to PFCs have been documented in numerous studies (Webster, 2011, Jensen & Leffers, 2008, Lau et al., 2007, Joensen et al., 2009, Fei et al., 2007, Alexander et al., 2003, Austin et al., 2003, Case et al., 2001). PFOS and PFOA are most widely studied in toxicological studies (Jensen & Leffers, 2008, Lau et al., 2007). Unlike other persistent organic pollutants, which are fat-soluble, PFOS and PFOA are unique because they bind to serum proteins in blood (Jensen & Leffers, 2008) and accumulate in the kidney and liver (Lau et al., 2007). PFOS and PFOA are potential endocrine disruptors in sex hormone production as they appear to lower testosterone levels and raise oestradiol levels (Jensen & Leffers, 2008, Joensen et al., 2009). In a Danish study (Joensen et al., 2009), males with high levels of PFOS and PFOA in serum had lower total sperm counts. In another Danish study (Fei et al., 2007), maternal plasma levels of PFOA were inversely associated with birth weight. Webster (2011) investigated thyroid effects of PFCs during pregnancy and found significant negative relationships between several PFCs in maternal serum and maternal free thyroxine, and positive relationships with maternal thyroid stimulating hormone in women with autoimmune hypothyroidism. Alexander et al. (2003) observed potential carcinogenic effects in workers from a POSF manufacturing facility as workers in high exposure jobs appeared to have an increased number of deaths from bladder cancer. Animal toxicological studies conducted by Austin et al. (2003) found neuroendocrine effects of PFOS on rats. Female rats exposed to 10 mg PFOS/kg body weight over a two week period exhibited decreased food intake, increased stress, and inhibited reproduction.

2.6 Environmental fate and occurrence

Direct sources, such as fluorochemical manufacturing facilities are the largest sources of PFCs to the environment, with an estimated 3,200 to 6,900 tonnes emitted globally from 1951-2004 (Prevedouros et al., 2006). 3M Company (1999a) estimated that 85% of emissions of POSF-derived products are from losses from consumer products during use and disposal (e.g. from carpets, clothing, paper, and packaging, etc.). Indirect sources, such as environmental

degradation of fluorotelomers, contributed 30-350 tonnes from 1960-2004. Although the amount of PFCs released from indirect sources is much smaller than from direct sources, there is more uncertainty in their emissions as they are more difficult to control. The manufacturing process of commercial PFCs produces numerous byproducts, and the degradation pathways of environmentally-persistent PFC precursors are complex (D'eon & Mabury, 2011, Washington et al., 2009, Parsons et al., 2008). The two major degradation pathways of fluorotelomers are biodegradation and atmospheric oxidation (photolysis) (D'eon & Mabury, 2011). However, these pathways are still not completely understood due to their complexities. Though it is important to understand degradation pathways to elucidate sources of PFCs from materials in landfills, it is beyond the scope of this study to go into detail on degradation as only a small portion of the precursors were monitored in the landfill leachate samples. In general, primary biodegradation products of precursors are compounds with the same number of fluorinated carbons (e.g. 8:2 FTOH to PFOA) (D'eon & Mabury, 2011). When biodegradation is the main pathway, even-chain PFCs tend to dominate. On the other hand, the products of atmospheric transformation are split into even-odd pairs such that they have the same number or one additional fluorinated carbon compared to the precursor. For example, 8:2 FTOA transforms into PFOA and PFNA and $PFOA \approx PFNA$. Based on this information, potentially applicable pathways for precursor and degradation products of PFCs analyzed in this study are summarized in Table 2.4.

Table 2.4: Potential degradation pathways applicable to PFCs analyzed in this study (based on D'eon & Mabury, 2011)

Type of Pathway	Precursor(s)	Primary degradation product(s)
Biodegradation	6:2 FTUA	PFHxA
Atmospheric oxidation	6:2 FTUA	PFHxA, PFHpA
Biodegradation	8:2 FTUA	PFOA
Atmospheric oxidation	8:2 FTUA	PFOA, PFNA
Biodegradation	10:2 FTUA	PFDA
Atmospheric oxidation	10:2 FTUA	PFDA, PFUnA
Biodegradation	PFOSA	PFOS
Atmospheric	PFOSA	PFOS

An example degradation pathway is illustrated in Figure 2.3. This is a proposed degradation pathway for 8:2 fluorotelomer alcohol (8:2 FTOH), a precursor to PFOA (Wang et al., 2005). The intermediate steps in the degradation pathway include conversion of the alcohol to an

aldehyde, a saturated acid, unsaturated acids, olefins, and alcohols of varying fluorinated carbon chain lengths, before reaching PFOA, the final degradation product.

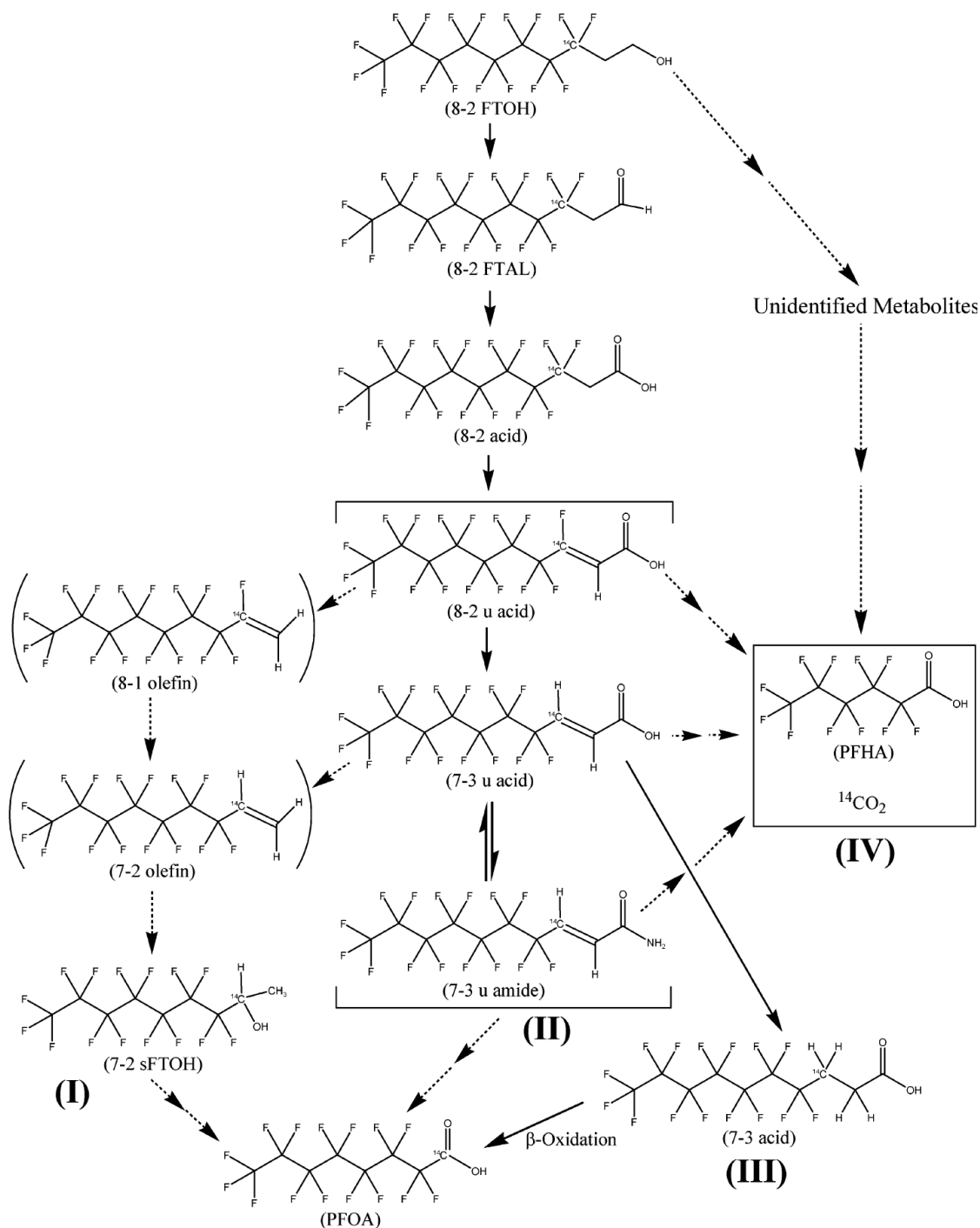


Figure 2.3: Proposed biodegradation pathway and products of 8:2 fluorotelomer alcohol (8:2 FTOH) to PFOA. (Reprinted with permission from Wang et al., 2005. Copyright 2005 American Chemical Society.)

PFCs have been measured in biota (mostly aquatic organisms and birds) in various parts of the world, including North America (Giesy & Kannan, 2002, Sinclair et al., 2006), the Mediterranean Sea (Nania et al., 2009), Korea and Japan (Taniyasu et al., 2003, Kannan et al., 2002), and the Arctic (Martin et al., 2004, Haukas et al., 2007, Kelly et al., 2009). PFCs have been found in several environmental compartments and are distributed globally (Giesy & Kannan, 2002, Fujii et al., 2007). Since most studies report on concentrations of PFOS and PFOA, the range of concentrations of these compounds in environmental samples are summarized in Table 2.5. There were large variations in concentrations of PFOS and PFOA in all environmental samples. In solid samples, it appears that PFOS and PFOA concentrate in sewage sludge, with concentrations up to 5,383 and 4,591 ng/g, respectively. Concentrations of PFOS and PFOA in sediment were much lower than in sewage sludge, up to 11 and 3.9 ng/g, respectively. In aqueous samples, the highest concentrations of PFOS and PFOA were in surface water in Germany, up to 5.9 and 33.9 ppb, respectively (Skutlarek et al., 2006). These concentrations were measured in a creek contaminated by fluorochemicals. The next highest concentrations were in landfill leachates, up to 0.235 and 0.926 ppb for PFOS and PFOA, respectively. Landfills are the ultimate destination of many PFC-containing materials and typically also receive PFC-containing sludge from wastewater treatment plants. PFCs may leach from refuse and sludge into landfill leachate. PFOA levels in untreated wastewater were up to 0.184 ppb, whereas PFOS levels were up to 0.085 ppb. Though drinking water generally contained the lowest levels of PFOS and PFOA, their concentrations were up to 0.022 and 0.519 ppb, respectively in Germany at a source close to the contaminated creek mentioned above (Skutlarek et al., 2006).

Table 2.5: Range of PFOS and PFOA concentrations in environmental samples from published studies

Type of sample	Location	Units	PFOS		PFOA		n	Source
			Low	High	Low	High		
Landfill leachate	Germany	ppb	0.0001	0.235	0.00056	0.926	20	Busch et al., 2010a
	USA	ppb	0.038	0.16	0.13	1.1	12	Huset et al., 2011
	Nordic countries	ppb	0.0302	0.187	0.0913	0.516	6	Kallenborn et al., 2004
Untreated wastewater	Kentucky, USA	ppb	0.007	0.016	0.022	0.184	4	Loganathan et al., 2007
	Georgia, USA	ppb	0.0025	0.0079	0.002	0.05	3	Loganathan et al., 2007
	Germany	ppb	0.033	0.085	0.0018	0.04	6	Becker et al., 2008
Sewage sludge	New York, USA	ng/g	26	34	18	241	10	Sinclair & Kannan, 2006
	USA	ng/g	14.4	2610	5.2	29.4	13	Higgins et al., 2005
	China	ng/g	280	5383	492	4591	16	Guo et al., 2008
Surface water	Japan	ppb	0.0171	0.6122	0.0112	0.0198	13	Zushi et al., 2008
	Germany	ppb	0.0008	0.006	0.0008	0.0028	6	Becker et al., 2008
	Tennessee, USA	ppb	0.0168	0.144	0.14	0.598	40	Hansen et al., 2002
	China	ppb	0.00015	0.099	0.00085	0.26	34	So et al., 2007
	Germany	ppb	0.002	5.9	0.002	33.9	79	Skutlarek et al., 2006
	New York, USA	ppb	0.00008	1.09	0.01	0.173	51	Sinclair et al., 2006
Drinking water	Germany	ppb	0.003	0.022	0.02	0.519	28	Skutlarek et al., 2006
	Europe	ppb	0.002	0.004	0.005	0.006	15	Skutlarek et al., 2006
	China	ppb	0.0002	0.0148	0.0001	0.0459	24	Jin et al., 2009
Sediment	USA	ng/g	0.248	1.4	0.184	0.625	17	Higgins et al., 2005
	Germany	ng/g	0.05	0.537	0.026	0.175	11	Becker et al., 2008
	Japan	ng/g	3.8	11	1.3	3.9	9	Senthilkumar et al., 2007

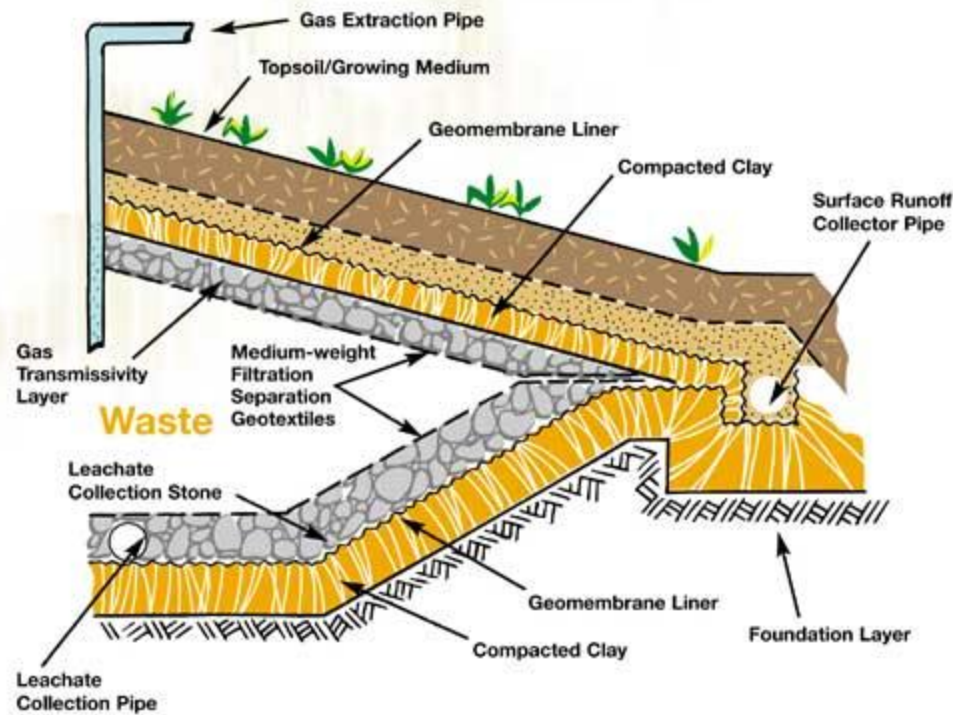
2.7 Landfill design and leachate management

Landfills are designed to contain waste and protect the surrounding environment from contaminants that may be contained in waste materials. Landfill leachate is generated when precipitation and moisture from waste percolates through layers of waste. Contaminants leach out of waste and into landfill leachate. The composition of landfill leachate varies among landfills depending on factors such as waste composition, climatic conditions, and age of the landfill (Wreford et al., 2000, Blight et al., 1999). Common contaminants found in landfill leachate include halogenated aliphatic compounds, benzene and alkylated benzenes, phenol and alkylated phenols, ethoxylates, polycyclic aromatic compounds, phthalic esters, chlorinated benzenes, chlorinated phenols, polychlorinated biphenyls, chlorinated dioxins and chlorinated furans, bromated flame-retardants, pesticides, organic tin, methyl mercury and heavy metals (Oman & Junestedt, 2008). The physiochemical parameters and contaminants in landfill leachate from a comprehensive characterization study conducted by Oman & Junestedt (2008) are listed in Table 2.6.

A typical landfill design is illustrated in Figure 2.4. Typical landfills have engineered clay liners and landfill leachate collection and removal systems to contain landfill leachate and prevent it from migrating into the surrounding environment. They also have landfill gas collection systems to manage volatile components and drainage ditches to manage surface water runoff. In some landfills, the drainage ditches are combined with the landfill leachate drainage system.

Table 2.6: Selected physiochemical parameters in landfill leachate from 12 landfills in Sweden (Oman & Junestedt, 2008)

Parameter	Mean concentration or value (n = 12)
pH	7.6
Conductivity	870 mS/m
Suspended solids	196 mg/L
Total organic carbon	220 mg/L
Chloride (Cl ⁻)	1,471 mg/L
Fluoride (F ⁻)	8.7 mg/L
Sulphate (SO ₄ ²⁻)	215 mg/L
Bicarbonate (HCO ₃ ⁻)	2,284 mg/L
N-ammonium (NH ₄ ⁺)	260 mg/L
N-NO ₂ ⁻ and NO ₃ ⁻	7.5 mg/L
P-Phosphate (PO ₄ ²⁻)	0.9 mg/L
Metals ^a	26 mg/L
Halogenated aliphatic compounds ^a	1,400 ng/L
Benzenes and alkylated benzenes ^a	20,700 ng/L
Phenol and alkylated phenols ^a	960 ng/L
Polycyclic aromatic compounds ^a	2,600 ng/L
Phthalate esters ^a	1,700 ng/L
Chlorinated benzenes ^a	605 ng/L
Chlorinated phenols ^a	750 ng/L
Bromated flame retardants ^a	4,200 ng/L
Pesticides ^a	10,700 ng/L
Metal organic compounds ^a	26 ng/L
^a Total concentrations reported for these contaminant classes	
n = number of samples	



A cross-section of a best practice landfill cell

Figure 2.4: Typical landfill design (Latrobe City, 2005)

Landfill liners are made from compacted clay, geosynthetics, or a composite of the above (Sharma & Lewis, 1994). A leachate collection and removal system (LCRS) made of higher hydraulic conductivity granular or geosynthetic materials overlays the liner. Examples of landfill liner systems are illustrated in Figure 2.5. Landfill leachate is typically managed by a directing it through pipes in the LCRS and collected in a central location such as a well or lagoon. The landfill leachate is then treated on-site treatment before being released to the environment or directed it to the sewer system to be treated by a wastewater treatment plant.

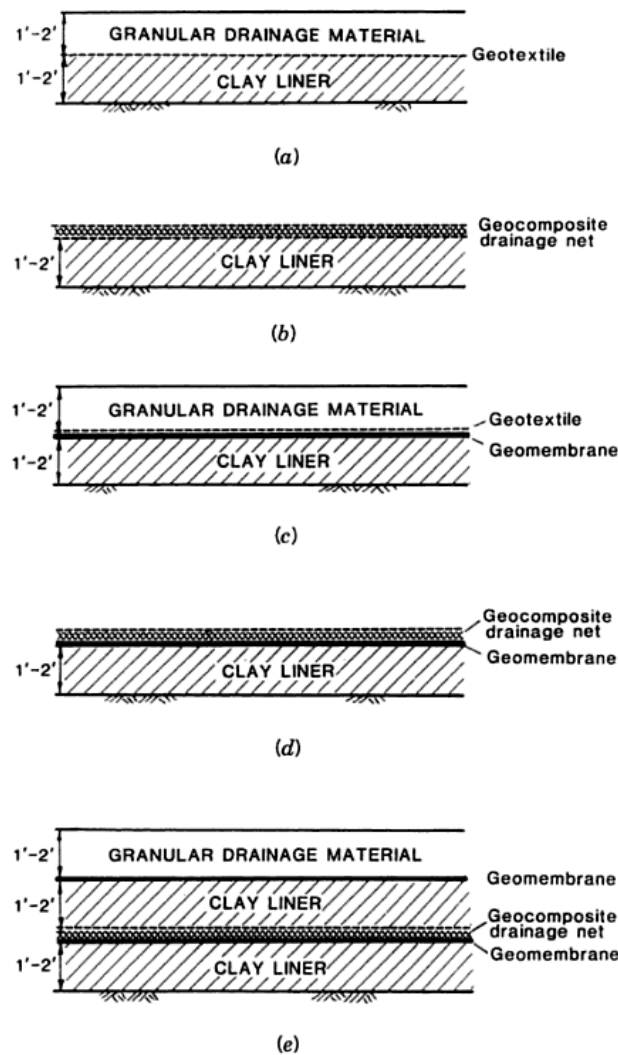


Figure 2.5: Types of landfill liner systems: (a) soil liner with leachate collection and removal system (LCRS), (b) soil liner with geosynthetic LCRS, (c) composite liner with LCRS, (d) composite liner with geosynthetic LCRS, (e) double composite liner (Sharma & Lewis, 1994).

The clays used for landfill liners are either mined from local sources or purchased from a commercial producer. Sodium bentonite is a clay commonly used for landfill liners because its major mineral constituent is montmorillonite, a very soft clay with high swelling potential (Sharma & Lewis, 1994). Swollen sodium bentonite possesses a very low hydraulic conductivity, making it a favourable material for low-permeability landfill liners. In British Columbia, environmental regulations require the hydraulic conductivity of an engineered clay liner to be less than 1×10^{-7} cm/s (Ministry of Environment, 2005). Even if a landfill liner meets the specifications set out by law, they are never completely impermeable to landfill leachate due to

heterogeneities in soil and uneven clay compaction. If a fissure or crack develops in a landfill liner, landfill leachate and its contaminants can spread into the surrounding environment.

Montmorillonite also has a large specific surface area and high cation-exchange capacity (He et al., 2001). This allows common contaminants such as metals to be immobilized in a landfill liner made with sodium bentonite through adsorption (Li & Li, 2001). However, hydrophobic organic contaminants cannot be readily adsorbed because sodium bentonite is hydrophilic (Li & Denham, 2000). Perfluorinated compounds are generally hydrophobic, but they also have hydrophilic functional groups (Parsons et al., 2008), so there is some potential for them to adsorb onto sodium bentonite. One study (Zhou et al., 2010) has shown some sorption of PFCs on pure montmorillonite. No studies have been published so far on the sorption of PFCs contained in landfill leachate on sodium bentonite.

Chapter 3: Materials and methods

3.1 Field sampling

3.1.1 Landfill leachate from cross-Canada landfill sites

Twenty-seven landfill leachate samples were collected (Danon-Schaffer, 2010) from landfills and northern dumpsites from across Canada (coast-to-coast-to-coast, most provinces and all three territories) between 2005 and 2006. The identity of the landfills cannot be disclosed because of a confidentiality agreement with the landfill operators. Sampling regions were divided into North (three Canadian territories) and South (six provinces). All samples were collected in solvent-washed amber glass bottles. Samples from the South were collected by the landfill operators using their own methodologies (Appendix A, Table A.1), whereas those from the North were collected by Danon-Schaffer (2010), with additional details reported therein. Samples were shipped from the sampling site in coolers packed with ice to the Fisheries and Oceans Canada Institute of Ocean Sciences (DFO-IOS) in Sidney, BC, Canada. Samples were either stored in a fridge at 4°C or frozen at -30°C until analysis.

3.1.2 Sampling at landfill A

Landfill leachate, soil, and condensate samples were collected from a regional landfill on August 18, 2009. This landfill is referred to as landfill A. This landfill services between 50,000 to 100,000 people. At the request of the operator, this landfill cannot be identified. In preparation for sampling, high-density polyethylene (HDPE) bottles were rinsed three times with HPLC grade methanol and air-dried. Three 500-mL HDPE bottles were filled with de-ionized water as trip blanks. During sampling, nitrile gloves were worn to handle samples. Gloves, scoops, and bailers were rinsed with methanol before sampling.

Landfill leachate samples from the leachate lift station (a sump that collects leachate from the drainage layer of a landfill) were collected using a HDPE bailer. Samples were transferred into twenty-two 500-mL and five 4-L HDPE bottles. Sample bottles were filled to approximately 80% of their capacity to allow for expansion during storage (described below). Landfill gas condensate was collected from the condensate trap using a HDPE bailer. One 4-L HDPE bottle

was filled with condensate. Soil samples were collected from the cover soil borrow pit. The face of the pit where samples were collected was first cleaned off with a metal shovel. Samples were collected using polypropylene scoops into eight 500-mL HDPE bottles. Landfill soil samples were collected from the top of the leachate recirculation field. The roots and organic layers were cleared using a metal shovel to a depth of approximately 30 cm. Soil was collected using polypropylene scoops into eight 500-mL HDPE bottles. In addition to the samples collected at the landfill, river water samples from a river less than 10 km downstream of the landfill were collected directly into six 500-mL HDPE bottles from the riverbank on the same day. These river water samples are hereafter referred to as river A.

All samples were placed in coolers filled with ice for transport to the University of British Columbia (UBC) in Vancouver, BC, Canada where all samples were stored in a fridge. As this was a walk-in fridge, the temperature fluctuated from 4 to 6°C. All samples were transferred to a freezer at a temperature of -20°C in October 2009 until they were transported to the DFO-IOS in coolers packed with ice for analysis.

3.1.3 Sampling at landfill B

Between December 2009 and March 2011, landfill leachate samples were collected from an urban landfill, which cannot be identified at the request of the operator. This landfill is referred to as landfill B. This landfill services more than one million people. All sampling and sub-sampling containers were rinsed with methanol followed by deionized water, then air-dried before sampling. Latex gloves were worn to handle samples. During sampling, all sampling containers were filled to approximately 80% of their capacity to leave headspace for expansion when the samples were stored in a freezer.

On December 2, 2009, landfill leachate samples were collected via a pump (Isco 6712) fitted with food-grade vinyl tubing located approximately 30 cm from the bottom of the leachate well. The pump was flushed for approximately 10 seconds before pumping landfill leachate into ten 20-L polypropylene carboys. Samples were surrounded by ice packs and transported to UBC. Two samples were stored in a freezer at -20°C, and the remaining samples were stored in a walk-in fridge between 4 and 6°C. Again, the fridge temperature fluctuated because it is a walk-in fridge. As the 20-L carboys were too large to transport to the DFO-IOS, sub-sampling was done

at UBC. The carboys were thawed (if necessary) and shaken for approximately 30 seconds before 500 mL aliquots were collected in 500-mL or 1-L HDPE bottles. These aliquots were transported to the DFO-IOS in coolers packed with ice for analysis.

Landfill leachate was sampled once every two weeks between February 2, 2010 and June 22, 2010, as well as once on March 22, 2011. Landfill leachate was collected using a methanol-rinsed stainless steel bucket on a rope. A bucket was dipped into the leachate well and submerged approximately 50 cm. A landfill leachate sample was lifted out and transferred to a 4-L polypropylene bottle via a polypropylene funnel. On June 22, 2010, four 1-L polypropylene bottles were instead used as sampling bottles. To compare sampling methods (i.e. bucket versus pump), on March 2, 2010, one additional sample was collected using the pump from December 2, 2009. Samples were transported in coolers with ice packs to UBC. All samples were stored in a freezer at -20°C until they were transported to the DFO-IOS in coolers packed with ice for analysis.

3.2 Physical and chemical characterization

The UBC Civil Environmental Engineering Laboratory (Vancouver, BC) provided analytical services for metals, total organic carbon (TOC), phosphate (PO_4^{3-}), sulphate (SO_4^{2-}), ammonia (NH_3) and nitrite/nitrates (NO_x). Maxxam Analytics (Burnaby, BC) provided analytical services for chloride (Cl^-), fluoride (F^-) and bromide (Br^-). Total suspended solids (TSS), pH and electrical conductivity (EC) were determined by the author. Standard methods, either from Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (EPA, 2009) or Standard Methods for the Examination of Water and Wastewater (APHA et al., 2005) were followed to analyze landfill leachate samples for physical and chemical parameters, listed in Table 3.1.

Table 3.1: Methods for physical and chemical characterization of landfill leachate samples (APHA et al., 2005, EPA, 2009)

Parameter	Method (revision year)
pH	EPA SW-846 9040c (2004)
Electrical conductivity (EC)	EPA SW-846 9050a (1996)
Metals	Standard Method 3120 (1999)
Total organic carbon (TOC)	Standard Method 5310B (2000)
Total suspended solids (TSS)	Standard Method 2540D (1997)
Chloride (Cl ⁻)	EPA 9251 (1986)
Fluoride (F ⁻)	Standard Method 4500-F C (1997)
Bromide (Br ⁻)	EPA 9211 (1996)
Phosphate (PO ₄ ³⁻)	Standard Method 4500-P G (1999)
Sulphate (SO ₄ ²⁻)	Standard Method 4500- SO ₄ ²⁻ G (1997)
Ammonia (NH ₃)	Standard Method 4500-NH ₃ H (2000)
Nitrites/nitrates (NO _x)	Standard Method M 4500-N B (1997)

3.3 Field sample preparation

3.3.1 Aqueous samples

Cross-Canada landfill leachate samples were extracted by AXYS Analytical Services Ltd. (Sidney, BC) by solid phase extraction (SPE). All other aqueous samples were first processed at the DFO-IOIS by liquid-liquid extraction. Since the detection limits for the liquid-liquid extraction method were not low enough to yield enough accurate data for analysis, samples were processed by SPE. Samples were processed in duplicate or triplicate wherever possible.

For all three methods, if samples were frozen, they were first thawed at room temperature. Samples were then mixed thoroughly before sub-sampling to ensure adequate distribution of particulate in the sample and a representative presence in each of the aliquots.

3.3.1.1. Solid phase extraction (AXYS)

AXYS used an in-house solid phase extraction (SPE) method to extract PFCs from the landfill leachate samples. Two aliquots were taken from each of the samples for these analyses. An aliquot of approximately 200 to 500 mL of leachate samples was processed for PFCs. A Nalgene, 500-mL filtration unit equipped with a 75 mm diameter 0.45 µm Nylon filter was used to filter the aliquot. Subsequently, the aliquot was spiked with the internal standard spiking

solution ($^{13}\text{C}_4$ PFBA, $^{13}\text{C}_2$ PFHxA, $^{13}\text{C}_2$ PFOA, $^{13}\text{C}_5$ PFNA, $^{13}\text{C}_2$ PFDA, $^{13}\text{C}_2$ PFDoA, and $^{13}\text{C}_4$ PFOS). After shaking, the samples were extracted by SPE using disposable cartridges (Waters Oasis WAX, 6 cc/150 mg) containing a weak anion exchange sorbent. The solvent used for the SPE extraction was methanolic ammonium hydroxide. Post extraction, the extracts were spiked with the recovery standard ($^{13}\text{C}_4$ -PFOA) and the final volume was made to 4 mL with methanol, from which 300 μL was taken for instrumental analysis. Calibration solutions were processed through SPE in the same way as the samples. Six calibration solutions were prepared within the range of 0.2 to 100 ng/sample.

3.3.1.2. Liquid-liquid extraction

The liquid-liquid extraction method was based on Higgins et al. (2005). 15 mL aliquots of landfill leachate were collected in 15-mL centrifuge tubes. They were centrifuged for 20 minutes at 4,185 G. 1 mL aliquots of the supernatant were transferred to 1.5-mL microcentrifuge tubes. These aliquots were centrifuged for 20 minutes at 12,800 G. 250 μL aliquots were transferred from each microcentrifuge tube into polypropylene HPLC vials. 250 μL of HPLC-grade methanol was added and 50 μL of internal and recovery standard spiking solution (1 ppb of each internal standard $^{13}\text{C}_4$ PFBA, $^{13}\text{C}_2$ PFHxA, $^{13}\text{C}_4$ PFOA, $^{13}\text{C}_5$ PFNA, $^{13}\text{C}_2$ PFDA, , $^{13}\text{C}_4$ PFOS, $^{13}\text{C}_2$ FDUEA, and recovery standard $^{13}\text{C}_2$ PFOA) were added to each vial. For spike recovery samples, a native standard solution (PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTA, PFBS, PFHxS, PFOS, PFOSA, plus PFBA, PFDS, FHUEA, FOUEA, FDUEA when available) was also added to the samples to yield a final concentration of 0.05 to 10 ppb in the extract. The vial was then sealed with a polypropylene cap and agitated on a vortex mixer for approximately 10 s.

3.3.1.3. Solid phase extraction (DFO-IOS)

The extraction method was adapted from Ahrens et al. (2009) and Busch et al. (2010a). For water and condensate, an aliquot of approximately 200 to 700 mL was processed. For landfill leachate, aliquots of 45 to 50 mL were processed. Exact volumes were determined by weighing the samples before and after extraction. 10 μL of internal standard spiking solution (50 ppb of each $^{13}\text{C}_4$ PFBA, $^{13}\text{C}_2$ PFHxA, $^{13}\text{C}_4$ PFOA, $^{13}\text{C}_5$ PFNA, $^{13}\text{C}_2$ PFDA, , $^{13}\text{C}_4$ PFOS, and $^{13}\text{C}_2$ FDUEA) was added to each aliquot. For spike recovery samples, a native standard solution

(PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTA, PFBS, PFHxS, PFOS, PFDS, PFOSA, FHUEA, FOUEA, and FDUEA) was also added to the samples to yield 25 to 250 ng/sample. All samples were thoroughly shaken to disperse the internal standard. A piece of glass wool was placed in the bottom of each solid phase extraction (SPE) cartridge (Waters Oasis WAX, 6cc/150 mg) to capture particulates which would otherwise clog the cartridge. For water and condensate, SPE cartridges were conditioned with 5 mL of methanol, followed by 5 mL of deionized water. For landfill leachate, SPE cartridges were conditioned with 5 mL of 0.1% ammonium hydroxide in methanol followed by 5 mL of methanol and 5 mL of deionized water. Cartridges were loaded with samples at a rate of 2 drops/second in a vacuum manifold set at approximately -1 to -2 kPa. For water and condensate samples, the cartridges were washed with 5 mL of 0.1% formic acid in deionized water after loading. For landfill leachate samples, the cartridges were washed with 5 mL of 0.1% ammonium hydroxide in deionized water. The cartridges were dried for 5 minutes under vacuum suction. The cartridges were next eluted with 14 mL of acetonitrile followed by 5 mL of 0.1% ammonium hydroxide in methanol. Eluates were collected in two 15-mL polypropylene centrifuge tubes. Eluates were then placed in a 50 to 60°C water bath and reduced under a gentle nitrogen stream. The eluates were combined by rinsing the contents of one tube into another with methanol and then reduced to dryness. Methanol was added to yield a final extract volume of 500 µL. Extracts were centrifuged at 2,900 G for 5 minutes. 450 µL aliquots of each extract were finally transferred to polypropylene HPLC vials.

3.3.2 Soil and sand-bentonite admix samples

Soil and sand-bentonite admix samples were processed at the DFO-IOS. One or both of the two methods described below were used. Samples were processed in duplicate or triplicate wherever possible.

If samples were frozen, they were thawed at room temperature. Samples were dried in a desiccator for at least 24 h, or until their weight changed by less than 0.01 g. Then 1.0 ± 0.01 g of each air-dried sample was weighed in a plastic weigh boat and transferred into a 50-mL polypropylene centrifuge tube.

3.3.2.1. Method A

Method A was adapted from Higgins et al. (2005). Samples were spiked with 200 μL of internal and recovery standard spiking solution (500 ppb of each internal standard $^{13}\text{C}_4$ PFBA, $^{13}\text{C}_2$ PFHxA, $^{13}\text{C}_4$ PFOA, $^{13}\text{C}_5$ PFNA, $^{13}\text{C}_2$ PFDA, , $^{13}\text{C}_4$ PFOS, $^{13}\text{C}_2$ FDUEA, and recovery standard $^{13}\text{C}_2$ PFOA) and agitated on a vortex mixer for approximately 30 s. For spike recovery samples, a native standard solution (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDaA, PFTA, PFBS, PFHxS, PFOS, PFDS, PFOSA, FHUEA, FOUEA, and FDUEA) was also added to the samples to yield 0.25 to 5 ppb in the final extract. The amount of standard varied as the stock solutions were at different concentrations. They were then left at room temperature for 1 h. Two solutions for the extraction were prepared. Solution A was a 1% acetic acid wash in HPLC grade water, whereas Solution B was an extraction solution containing a 90:10 (v/v) mixture of HPLC grade methanol and solution A.

The washing and extraction steps consisted of repeated washes with solution A and extractions with solution B. 10 mL of solution A was added to each sample and agitated on a vortex mixer for approximately 10 s. They were then placed in a sonication bath set at a temperature of 60°C for 15 minutes. The contents were centrifuged at 4,185 G for 15 minutes. The supernatant was decanted into a second polypropylene tube, which contained all the combined washes and extracts. 2.5 mL of solution B was added to the first centrifuge tube. The agitation, sonication, centrifugation, and decanting steps mentioned above were repeated. The solution A wash/solution B extraction process was repeated once, followed by a final wash with solution A. The total wash and extract volume was approximately 35 mL. HPLC-grade methanol was added to the combined washes and extracts to make a final volume of 50 mL. The combined washes and extracts were centrifuged at 4,185 G for 15 minutes. 1 mL was transferred into a microcentrifuge tube. These aliquots were centrifuged for 20 minutes at 12,800 G. 500 μL aliquots were transferred into polypropylene HPLC vials.

3.3.2.2. Method B

This method was adapted from Powley et al. (2005). Samples were spiked with 20 μL of internal standard spiking solution (50 ppb of each $^{13}\text{C}_4$ PFBA, $^{13}\text{C}_2$ PFHxA, $^{13}\text{C}_4$ PFOA, $^{13}\text{C}_5$ PFNA, $^{13}\text{C}_2$ PFDA, , $^{13}\text{C}_4$ PFOS, and $^{13}\text{C}_2$ FDUEA) and agitated on a vortex mixer for approximately 30 s.

10 mL of 1% ammonium hydroxide in methanol were added and the contents were shaken for approximately 30 s. The contents were then centrifuged (VWR Clinical 2000) at 6,000 RPM (4,185 G) for 3 minutes. The supernatant was decanted into a second polypropylene tube, which contained all the combined extracts. This extraction procedure was repeated twice. For the final repeat, before centrifugation, the samples were placed in a sonication bath at a temperature of 60°C for 10 minutes. The final extract volume was 30 mL. 300 µL of glacial acetic acid was added to each extract. The extracts were next placed in a 50 to 60°C water bath and reduced in volume to 500 µL by evaporation under a gentle nitrogen stream blowing on the surface of the extract. An additional 500 µL of methanol was used to rinse the tube containing the extract to make a final volume of 1 mL. The extracts were transferred to 1.5-mL microcentrifuge tubes. Approximately 25 mg of Envi-Carb was added to clean up the extracts. The contents in the tubes were briefly mixed and centrifuged for 30 minutes at 12,800 G. 500 µL aliquots of each extract were then transferred to polypropylene HPLC vials.

3.4 Batch adsorption test

3.4.1 Chemical standards and solutions

One combined stock solution containing 500 ppb each of PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTA, PFBS, PFHxS, PFOS, and PFOSA in methanol was prepared. This is referred to hereafter as Σ PFC1. As there was a low stock of PFBA, a second solution (Σ PFC2) containing 500 ppb of all the above compounds in methanol except PFBA was also prepared. Single PFC stock solutions at 500 ppb were made for PFBA, PFHxA, PFOA, PFBS, and PFOS in methanol. These 500 ppb stock solutions were then used to make spiked landfill leachate and water for the batch adsorption tests. The landfill leachate was an aliquot of the sample collected from landfill A. Based on the results in section 4.4.1 on concentrations of PFCs in landfill leachate, 10 ppb was chosen as the PFC spike concentration for landfill leachate and water. As a result, small variations in PFC concentrations in the landfill leachate will not be significant, as they are all less than about 5% of the PFC spike.

3.4.2 Sodium bentonite

Envirogel® MSW 10, a chemically and polymerically treated sodium bentonite for environmental sealing (personal communication with Norman Pelak of Wyo-Ben, Inc.) was

obtained from Wyo-Ben, Inc (Billings, Montana, USA). The UBC Earth and Ocean Sciences Laboratory (Vancouver, BC) determined the mineral components of Envirogel® MSW 10 listed in Table 3.2 using the X-ray powder diffraction analysis (XRD) method described by Raudsepp and Pani (2003). Step-scan XRD data were collected over a range of 3-80°2θ with CoKα radiation on a Bruker D8 Focus Bragg-Brentano diffractometer equipped with an Fe monochromator foil, 0.6 mm (0.3°) divergence slit, incident- and diffracted-beam Soller slits and a LynxEye detector. The long fine-focus Co X-ray tube was operated at 35 kV and 40 mA, using a take-off angle of 6°. The XRD pattern is plotted in Figure A.1. Key physical and chemical properties are listed in Table 3.3.

Table 3.2: Mineral components of Envirogel® MSW 10

Mineral	Chemical formula	Percentage
Quartz	SiO ₂	26.0
Montmorillonite	(Na,Ca) _{0.3} (Al,Mg) ₂ Si ₄ O ₁₀ (OH) ₂ ·nH ₂ O	55.0
Muscovite	KAl ₂ AlSi ₃ O ₁₀ (OH) ₂	6.3
Plagioclase	NaAlSi ₃ O ₈ – CaAl ₂ Si ₂ O ₈	4.8
K-feldspar	KAlSi ₃ O ₈	4.2
Gypsum	CaSO ₄ ·2H ₂ O	1.3
Stellerite	CaAl ₂ Si ₇ O ₁₈ ·7(H ₂ O)	1.5
Analcime	Na[AlSi ₂ O ₆]·H ₂ O	0.9

Table 3.3: Key physical and chemical properties of Envirogel® MSW 10

Property	Value ^a														
Specific gravity	2.55 ± 0.1														
Surface area	800 m ² /g														
pH	9.1 ± 0.4														
Cation exchange capacity	70-90 CEC meq/100 g														
Free swell index	22 ± 2 cm ³ /2 g														
Moisture content	6-9%														
Particle size distribution	<table><tr><td>Sieve size</td><td>% passing</td></tr><tr><td>8 (2360 µm)</td><td>99.46</td></tr><tr><td>10 (2000 µm)</td><td>95.69</td></tr><tr><td>20 (850 µm)</td><td>62.82</td></tr><tr><td>60 (250 µm)</td><td>29.54</td></tr><tr><td>100 (150 µm)</td><td>24.14</td></tr><tr><td>200 (75 µm)</td><td>18.54</td></tr></table>	Sieve size	% passing	8 (2360 µm)	99.46	10 (2000 µm)	95.69	20 (850 µm)	62.82	60 (250 µm)	29.54	100 (150 µm)	24.14	200 (75 µm)	18.54
Sieve size	% passing														
8 (2360 µm)	99.46														
10 (2000 µm)	95.69														
20 (850 µm)	62.82														
60 (250 µm)	29.54														
100 (150 µm)	24.14														
200 (75 µm)	18.54														
^a Obtained through personal communication with Norman Pelak of Wyo-Ben, Inc.															

3.4.3 Experimental set-up

All experiments were conducted in triplicate or quadruplicate. Varying amounts (0.1, 0.2, or 0.4 g) of sodium bentonite were dispersed into 40 mL of 10 ppb PFC spiked landfill leachate or water in 50-mL polypropylene centrifuge tubes. These are referred to here as test experiments. To fully disperse the sodium bentonite, approximately 0.1 g of sodium bentonite was added to approximately 10-20 mL of spiked water or landfill leachate to allow it to fully hydrate. The tube was then shaken on a vortex mixer for 30 s. This was repeated until all the sodium bentonite had been added. The spiked water or landfill leachate was topped up to 40 mL and the centrifuge tube was capped. As a control experiment, 40 mL of 10 ppb spiked landfill leachate or water were dispensed into clean 50-mL polypropylene centrifuge tubes without sodium bentonite. Lab blanks of 40 mL of HPLC water were processed with the BAT samples. All centrifuge tubes were rotated at 21 rpm for 24 h in a mechanical rotator at room temperature (22°C). For ease of identification in this report, each experiment (sorted by type of solution and analyte in the spike) is assigned a number referred to from this point forward and given in Table 3.4.

Table 3.4: Summary of batch adsorption test experiments

Experiment Number	Liquid	PFC
1	Landfill leachate	Σ PFC1
2	Water	Σ PFC2
3	Landfill leachate	Single PFCs: PFBA, PFHxA, PFOA, PFBS, PFOS
4	Water	Single PFCs: PFBA, PFHxA, PFOA, PFBS, PFOS

3.4.4 Extraction

After the 24 h period of rotation, the centrifuge tubes containing the landfill leachate or water and sodium bentonite (if applicable) were centrifuged at 4,185 G for 5 minutes. To facilitate filtration of the water samples, as they do not have sufficient ions to wet the filter membrane, approximately 0.1 g of ammonium acetate was added to all water samples. Ammonium acetate is an additive in LC/MS/MS and does not interfere with the analytes of interest. A 5 mL portion of HPLC grade methanol was added to a 0.2 μ m syringeless filter with polypropylene filter media (Whatman AV125EPP). A 5 mL aliquot of the 40 mL of supernatant was transferred from each centrifuge tube to the filter. The methanol-supernatant mixture was filtered to remove sodium bentonite particles, and 10 mL of filtrate was transferred into a 15-mL polypropylene centrifuge tube.

A 500 μ L aliquot of the 10 mL of filtrate was transferred to a polypropylene HPLC vial. Then, 50 μ L of internal and recovery standard spiking solution (1 ppb of each internal standard $^{13}\text{C}_4$ PFBA, $^{13}\text{C}_2$ PFHxA, $^{13}\text{C}_4$ PFOA, $^{13}\text{C}_5$ PFNA, $^{13}\text{C}_2$ PFDA, $^{13}\text{C}_4$ PFOS, $^{13}\text{C}_2$ FDUEA, and recovery standard $^{13}\text{C}_2$ PFOA) was added. The final volume of extract for chemical analysis was 550 μ L. The HPLC vial was sealed with a polypropylene cap and shaken on a vortex mixer for approximately 10 s to thoroughly disperse the mass-labelled internal standard.

3.4.5 Rinse solutions

To check for PFCs that may have adhered to the walls of the centrifuge tubes, these tubes were rinsed with a solution of 1:1 HPLC grade methanol and landfill leachate. The rinse solutions

were then analyzed for PFCs. If the PFCs adhered to the wall of the centrifuge tubes, they would be present in the rinse solutions. To carry out this test, the contents of one tube from each set of samples in experiments 1 and 2 were transferred into another clean centrifuge tube. The original tubes were then filled with 20 mL of the corresponding matrix (HPLC grade water or landfill leachate) and 20 mL of HPLC grade methanol, to make a total volume of 40 mL of rinsing solution. These tubes were sonicated for 10 minutes, and then centrifuged for 5 minutes at 4,185 G. A 1 mL aliquot of the 40 mL of supernatant was collected from each tube and transferred to 1.5-mL microcentrifuge tubes. These were centrifuged for 20 minutes at 12,800 G. Then, 500 μ L of the 1 mL aliquots was transferred into a polypropylene HPLC vial, and 50 μ L of the internal and recovery standard spiking solution described in section 3.4.4 was added. The vial was sealed with a polypropylene cap and shaken on a vortex mixer for approximately 10 s.

3.5 Treatment of analytical data

As discussed in section 3.7.2 below, when mass-labelled internal standards are used to quantify non-corresponding analytes (e.g. using $^{13}\text{C}_4$ -PFOS to quantify PFBS), the mass-labelled internal standards do not behave exactly the same way as these other analytes, and may lead to larger variations in the results. These variations were evident in the results for the batch adsorption tests (BATs). Therefore, the analytes were split into the two groups, as shown in Table 3.5, for the discussion of the results from experiments 1 and 2. Group A consists of analytes quantified using corresponding mass-labelled internal standards. All other analytes constitute Group B.

None of the analytes were detected above the instrument detection limits (IDLs) in the blanks; therefore, blank corrections were not necessary for this data set. Method detection limits (MDLs) were set at twice the IDLs, as discussed in section 3.7.2. Detection limits for all analytes are listed in Table 3.5.

Table 3.5: Detection limits and data groups

PFC	Group	IDL (ppb)	MDL (ppb)
PFBA	A ^a	0.14	0.28
PFHxA	A	0.03	0.06
PFOA	A	0.07	0.14
PFNA	A	0.03	0.06
PFDA	A	0.03	0.06
PFOS	A	0.02	0.04
PFPeA	B	0.07	0.14
PFHpA	B	0.14	0.28
PFUnA	B	0.03	0.06
PFDaA	B	0.03	0.06
PFTA	B	0.01	0.02
PFBS	B	0.01	0.02
PFHxS	B	0.02	0.04
PFOSA	B	0.02	0.04
^a PFBA was not included in Σ PFC mix for experiment 2.			

To determine whether there was significant statistical variation between the PFC concentrations in the control experiments (no sodium bentonite added to landfill leachate or water) and test experiments (0.1 g, 0.2 g, or 0.4 g sodium bentonite added to 40 mL of landfill leachate or water), the two-tailed Student t-test was employed with the following hypotheses and a level of significance (p-value) of 0.05:

$$H_0: [PFC]_0 \leq [PFC]_t \quad 3.1$$

$$H_a: [PFC]_0 > [PFC]_t \quad 3.2$$

Here H_0 is the null hypothesis, H_a is the alternative hypothesis, $[PFC]_0$ is the average concentration of an analyte in the control experiment after 24 h of contacting time, and $[PFC]_t$ is the average concentration of an analyte in one test experiment after 24 h of contacting. The Student t-test method is described in standard statistical textbooks such as Dixon and Massey (1983).

3.6 Leaching cell test

3.6.1 Chemical standards and solutions

The Σ PFC2 mixture described in section 3.4.1 was added to spike an aliquot of landfill leachate sample from landfill A at 10 ppb for the leaching cell test. Unspiked landfill leachate and tap water were the liquids tested in the other leaching cell tests.

3.6.2 Sand-bentonite admix

The sodium bentonite used in leaching cell tests was a blend of 60:40 (w/w) Envirogel® MSW 10 and sodium bentonite from Canadian Clay Products, Wilcox, Saskatchewan, Canada. The UBC Earth and Ocean Sciences Laboratory (Vancouver, BC) determined the bentonite mineral components listed in Tables 3.2 and 3.6 using the X-ray powder diffraction (XRD) analysis method outlined by Raudsepp and Pani (2003). The XRD pattern is plotted in Figure A.2. The physical and chemical properties are listed in Tables 3.3 and 3.7. ASTM C778 graded Ottawa sand was obtained from U.S. Silica, Ottawa, Illinois, USA. The physical properties of the ASTM C778 graded Ottawa sand are listed in Table 3.9.

Table 3.6: Mineral components of sodium bentonite from Canadian Clay Products

Mineral	Chemical formula	Percentage
Quartz	SiO_2	14.1
Montmorillonite	$(\text{Na,Ca})_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$	74.2
Plagioclase	$\text{NaAlSi}_3\text{O}_8 - \text{CaAl}_2\text{Si}_2\text{O}_8$	6.6
K-feldspar	KAlSi_3O_8	5.1

Table 3.7: Key physical and chemical properties of sodium bentonite from Canadian Clay Products (Li, 1999)

Property	Value ^a												
Specific gravity	2.64												
Surface area	462 m ² /g												
pH	8.38												
Cation exchange capacity	59.7 meq/100 g												
Moisture content	6.8%												
Particle size distribution (approximate)	<table> <tr> <td>Sieve size</td><td>% passing</td></tr> <tr> <td>50 (300 µm)</td><td>100</td></tr> <tr> <td>60 (250 µm)</td><td>99</td></tr> <tr> <td>100 (150 µm)</td><td>97</td></tr> <tr> <td>75 (200 µm)</td><td>91</td></tr> <tr> <td>25 (500 µm)</td><td>83</td></tr> </table>	Sieve size	% passing	50 (300 µm)	100	60 (250 µm)	99	100 (150 µm)	97	75 (200 µm)	91	25 (500 µm)	83
Sieve size	% passing												
50 (300 µm)	100												
60 (250 µm)	99												
100 (150 µm)	97												
75 (200 µm)	91												
25 (500 µm)	83												

Table 3.8: Mineral components of ASTM C778 graded Ottawa sand

Mineral	Chemical formula	Percentage ^a
Quartz	SiO ₂	99.7
Iron oxide	Fe ₂ O ₃	0.020
Aluminum oxide	Al ₂ O ₃	0.06
Titanium dioxide	TiO ₂	0.01
Calcium oxide	CaO	<0.01
Magnesium oxide	MgO	<0.01
Sodium oxide	Na ₂ O	<0.01
Potassium oxide	K ₂ O	<0.01

^a Obtained from Product Data Sheet provided by U.S. Silica Company.

Table 3.9: Physical properties of ASTM C778 graded Ottawa sand

Property	Value ^a												
Colour	White												
Grain shape	Round												
Hardness	7 mohs												
Melting point	1704°C												
Specific gravity	2.65												
pH	7												
Particle size distribution	<table> <tr> <th>Sieve size</th><th>% passing</th></tr> <tr> <td>16 (1180 µm)</td><td>100.0</td></tr> <tr> <td>30 (600 µm)</td><td>98.0</td></tr> <tr> <td>40 (425 µm)</td><td>70.0</td></tr> <tr> <td>50 (300 µm)</td><td>25.0</td></tr> <tr> <td>100 (150 µm)</td><td>2.0</td></tr> </table>	Sieve size	% passing	16 (1180 µm)	100.0	30 (600 µm)	98.0	40 (425 µm)	70.0	50 (300 µm)	25.0	100 (150 µm)	2.0
Sieve size	% passing												
16 (1180 µm)	100.0												
30 (600 µm)	98.0												
40 (425 µm)	70.0												
50 (300 µm)	25.0												
100 (150 µm)	2.0												
^a Obtained from Product Data Sheet provided by U.S. Silica Company.													

The sand-bentonite admix was prepared to contain 92.5% sand and 7.5% bentonite by dry weight. Latex gloves were worn to handle the admix. All labware and tools were rinsed with methanol before use. The optimum dry density of the sand-bentonite admix was determined by following the Laboratory Compaction Characteristics of Soil Using Standard Effort (ASTM D698-07) method (ASTM International, n.d.a), also known as the Standard Proctor Compaction Test. The compaction curve is plotted in Appendix E, Figure E.1. The optimum dry density was 1.8 g/cm³ and the optimum water content was 13%.

After weighing out the appropriate amount of sand and bentonite, each batch was divided into three portions. Each portion of bentonite was blended with each portion of sand, and then all the portions were combined to ensure even distribution of the bentonite. A HDPE spray bottle was used to distribute deionized water into the sand-bentonite admix to yield a moisture content of approximately 16%, about 3% greater than the optimum dry density to ensure saturated flow conditions in the leaching cells. To achieve even wetting of the admix, it was thoroughly blended by hand throughout the process. The admix was left at room temperature for at least 24 h in a 100% humidity box (sealed storage bin containing several cups of water) to allow the water to equilibrate throughout the admix. Before using the admix for the leaching cell test, the moisture

content of the admix was checked by weighing approximately 100 g of admix before and after drying in an oven at 60°C and taking the difference of the two weights.

To prevent sidewall leakage during the leaching cell test, the inner walls of the stainless steel leaching cells were smeared with a thin layer of bentonite slurry (prepared with deionized water to a moisture content of 200%). The sand-bentonite admix was compacted in the leaching cells by following sections 10.1 to 10.4.8 of method ASTM D698-07 (ASTM International, n.d.a) with the following modifications:

- The height of the compaction mold was 50.8 mm, not 114.3 mm
- The number of layers was two, not three
- The number of blows per layer was 15, not 25

These modifications were made to accommodate the smaller compaction cell used for the leaching cell tests so that the total energy input from compaction would be similar to that of the Standard Proctor Compaction Test (600 kN/m³). The energy input from the compaction conducted in this study was 540 kN/m³.

3.6.3 Free swell test

To measure the swelling capacity of bentonite, free swell tests were conducted according to the Swell Index of Clay Mineral Component of Geosynthetic Clay Liners (ASTM D5890-06) method (ASTM International, n.d.b), with slight modifications described below. The bentonite used for this test was a blend of 60:40 (w/w) Envirogel® MSW 10 and sodium bentonite from Canadian Clay Products, Wilcox, Saskatchewan, Canada. The ΣPFC2 mixture described in section 3.4.1 was used to spike an aliquot of landfill leachate sample from landfill B and deionized water at a concentration of 10 ppb. The swelling capacity of bentonite was compared in the following liquid matrices: deionized water, landfill leachate from landfill B, spiked deionized water, and spiked landfill leachate from landfill B.

3.6.4 Experimental set-up

Prior to use, all components of the leaching cell test set-up were rinsed with methanol. Porous stones were cleaned by sonicating for 1 h at room temperature and then boiled for 30 min in deionized water to remove air pockets within the stones. An overall schematic of the experimental set-up is illustrated in Figure 3.1. The base plates of the leaching cell apparatus were connected to the bottom of an aluminum reservoir. Depending on the experiment, the reservoir was filled with tap water, landfill leachate, or spiked landfill leachate until the base plate of the leaching cells filled with liquid from the reservoir. This process helped remove air bubbles from the tubing. The leaching cell apparatus was then assembled and the collection tubes (50-mL polypropylene centrifuge tubes with holes drilled in the caps) were connected to the top plates of the leaching cell apparatus. A schematic of the leaching cell apparatus is provided in Appendix A, Figure A.3. The liquid in the reservoir was then topped up to a volume of 4 to 7 L. An aliquot of the liquid in the reservoir was collected in a 50-mL polypropylene centrifuge tube and stored in a fridge at 4 to 6°C. The reservoir was closed and pressurized air was supplied to the top of the reservoir. The pressure in the reservoir gradually increased to allow the system to equilibrate and to prevent the formation of preferential flow paths. The pressure was first increased to 5 kPa gauge; after at least 1 h, it was further increased to 15 kPa gauge. After at least a further 15 h, it was increased to 25 kPa gauge and subsequently by 5 to 10 kPa every hour to a maximum of 35 or 45 kPa. Several attempts were made to conduct leaching cell tests with landfill leachate at a pressure of 45 kPa. However, the leaching cells leaked after several days. Therefore, the pressure was reduced to 35 kPa. The leaching cell test operated in up-flow mode to reduce the number of preferential flow-paths. The experiment was left running at room temperature for 73 to 85 days. As the collection tubes filled with effluent, they were replaced with new collection tubes and the effluent was stored in a fridge at 4 to 6°C. All effluent samples were transported to the DFO-IOS in coolers packed with ice for analysis. The operating conditions of each experiment are described in Table 3.10.

Table 3.10: Operating conditions for leaching cell tests

Liquid	Maximum pressure (kPa gauge)	Duration (days)	Number of cells	Temperature (°C)
Tap water	45	73	1	$\sim 20 \pm 2$
Landfill leachate	35	85	2 ^a	$\sim 20 \pm 2$
Spiked landfill leachate	35	77	2 ^a	$\sim 20 \pm 2$

^a Initial set up with 3 cells, but one cell started to leak and was taken off line.

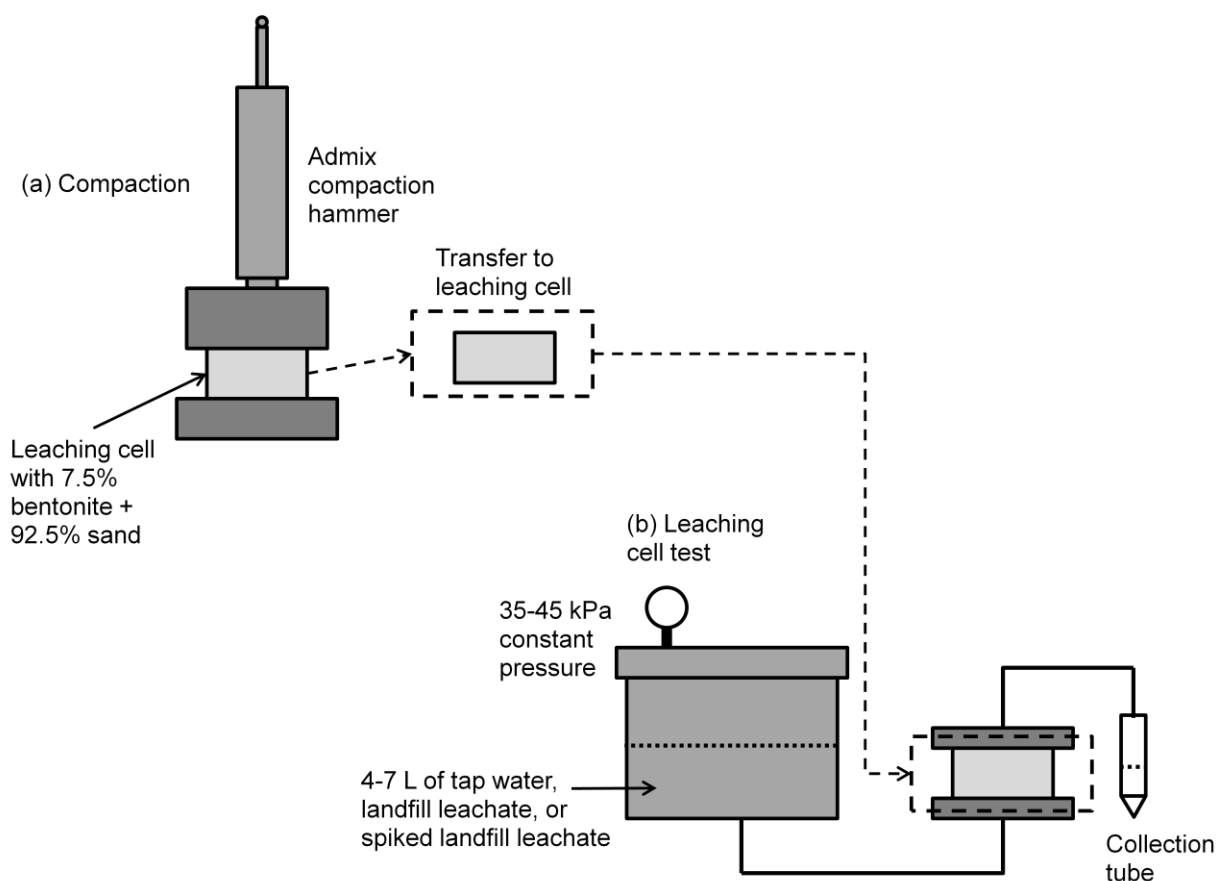


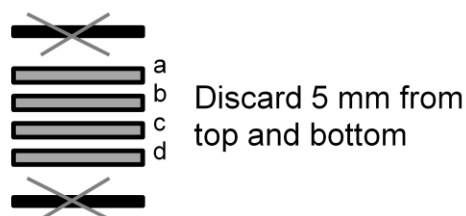
Figure 3.1: Schematic of (a) Sand-bentonite admix compaction, (b) Leaching cell test set-up.

3.6.5 Admix sampling

At the end of each leaching cell test, the apparatus was dismantled. In preparation for admix sampling, a fume hood was lined with aluminum foil and all tools were cleaned with methanol.

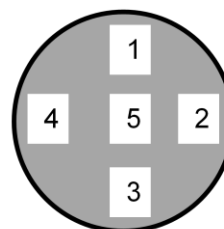
The leaching cell was weighed. The admix was extruded in the fume hood by cutting the entire column of admix out from the cell with a knife. Approximately 5 mm of admix from the edges were discarded to avoid including bentonite paste in the sample. Using a wire saw, approximately 5 mm of both the top and bottom of the admix were trimmed. The admix was then cut with a wire saw into four horizontal layers that were each approximately 10 mm thick (Figure 3.2). The wire saw was rinsed with methanol between each layer and cell. 5 g (approximate wet weight) of admix were sampled from five points (four around the edge, one in the centre) in each layer (Figure 3.2). The admix from each layer was then combined, and three 5 g (approximate wet weight) composite samples were taken. All admix samples were stored in 50-mL polypropylene centrifuge tubes in a fridge at 4 to 6°C until they were transported for analysis to the DFO-IOS in coolers packed with ice.

(a) slice sand-bentonite admix into four layers



Side view of admix slices

(b) sampling: 5 sampling points + 3 composite samples



Plan view of admix layer

Figure 3.2: Schematic of sampling of sand-bentonite admix from leaching cell tests. The sand-bentonite admix was (a) first sliced into four layers, then (b) sampled at five points within each layer and sampled as a composite.

3.7 Instrumental analysis

PFCs were analyzed by liquid chromatography tandem mass spectrometry (LC/MS/MS). Cross-Canada landfill leachate samples were analyzed at AXYS Analytical Services Ltd. All other samples were analyzed at DFO-IOS.

3.7.1 AXYS Analytical Services Ltd.

Separations of the target analytes were achieved with a Waters 2795 Alliance HPLC equipped with an Xterra C18 analytical column (3.5 μm , 2.1 mm x 100 mm) and a guard column (C18 1mm opti-guard column). Mobile phases consisted of 0.1% ammonium acetate / 0.1% acetic acid in HPLC grade water (solvent A) and 90% acetonitrile (solvent B). The gradient elution program was: 0-0.5 min, 40-70% B, 0.5-6.5 min, 70-100% B, then a 1 minute hold time, followed by a 4 min re-equilibration to starting conditions. Injection volumes were 15 μL . A Micromass Quattro Ultima tandem quadrupole mass spectrometer (Manchester, UK), equipped with Z-spray electrospray (ESI) ion source operating in negative ion multiple reaction monitoring (MRM) mode was employed for sample analysis. Desolvation and cone gas (nitrogen) flows were set at 450 L/h and 80 L/h, respectively. The ion source temperature was 120°C, and the desolvation temperature 400°C. The data system was running Waters MassLynx v.4.0 software for targeting and quantification.

For each analysis batch, calibration curves were constructed from the analysis of seven calibration solutions, ranging in concentration between 0.2 and 500 ng/mL. Concentrations were determined using weighted linear regression calibration procedures. Analyte concentrations were determined with respect to the mass-labelled quantification and internal standards using isotope dilution or internal standard quantification against matrix matched calibration standards carried through the analysis procedure alongside the samples. Recoveries of labelled surrogate standards were determined with respect to the labelled recovery standard ($^{13}\text{C}_4\text{-PFOA}$). The mass-labelled internal standards used to quantify PFCs are listed in Table 3.11. Two procedural (or method) blanks, one sample analyzed in duplicate and a spiked sample, were analyzed with every batch of 12 samples. 20 mL of water was used as the blank sample matrix, and approximately 20 μL , equivalent to 10 ng per analyte, was spiked into 20 mL of water for the spiked samples. Method detection limits (MDLs) were determined as 3 standard deviations above the mean blank levels. In cases where analyte concentrations were non-detectable in blanks, the MDL was set equal to the instrument detection limit (IDL), determined from the analyte peak response with a signal-to-noise ratio of 3:1.

Table 3.11: Mass-labelled internal standards used for quantification at AXYS Analytical Services Ltd.

PFC	Mass-labelled internal standard for quantification
PFBA	¹³ C ₄ -PFBA
PFPeA	¹³ C ₄ -PFBA
PFHxA	¹³ C ₂ -PFHxA
PFHpA	¹³ C ₂ -PFHxA
PFOA	¹³ C ₂ -PFOA
PFNA	¹³ C ₅ -PFNA
PFDA	¹³ C ₂ -PFDA
PFUnA	¹³ C ₂ -PFDA
PFDoA	¹³ C ₂ -PFDoA
PFBS	¹³ C ₄ -PFOS
PFHxS	¹³ C ₄ -PFOS
PFOS	¹³ C ₄ -PFOS
PFOSA	¹³ C ₄ -PFOS

3.7.2 DFO-IOS

Target analytes were separated with a Dionex P680 HPLC using a Waters XTerra C18 (5 µm, 4.6 mm x 30 mm) reversed phase column equipped with a Waters Opti-Guard C18 1 mm guard cartridge. Two Waters XTerra C18 (5 µm, 4.6 mm x 30 mm) columns were also linked in series and placed upstream of the injector to separate PFCs from the pump from the PFCs in the samples. Mobile phases consisted of 50:50 (v/v) methanol and acetonitrile (solvent A) and 10 mM ammonium acetate (solvent B). Initial conditions were 90% B and 10% A. The gradient elution program was: 0-0.5 min, 90% B, 0.5-5 min, 90-20% B, 5-10.5 min, holding time, 10.5-10.6 min, 20-2% B, 10.6-12 min, holding time, 12-12.1 min, return to initial conditions, 12.1-15 min, re-equilibrate to initial conditions. Injection volumes were 15 µL. The flow rate was held constant at 300 µL/min throughout. Samples were analyzed by a API 5000Q triple-quadrupole mass spectrometer (AB Sciex, Concord, ON, Canada) operating in negative ion multiple reaction monitoring (MRM) mode. One or two precursor-product transitions were monitored per analyte. A Vici Valco diverter valve diverted flow away from the mass spectrometer for the first 4.5 min of each run. The source temperature was 400°C. Analyst v. 1.5.1 software was used for targeting and quantification.

Calibration curves were constructed from the analysis of 10 to 11 calibration solutions, ranging in concentration from 0.025 to 50 ng/mL. Concentrations were determined using weighted linear regression calibration procedures. Analyte concentrations were determined with respect to the mass-labelled internal standards. Where applicable, recoveries of labelled surrogate standards were determined with respect to the labelled recovery standard ($^{13}\text{C}_4\text{-PFOA}$). The mass-labelled internal standards used to quantify PFCs are listed in Table 3.12. Each batch consisted of 9 to 12 samples, with at least one procedural blank (methanol) and one calibration check standard processed between each batch. Method detection limits (MDLs) were adopted as 3 standard deviations above the mean blank levels. In cases where analyte concentrations were non-detectable in blanks, the MDL was set equal to the instrument detection limit (IDL), determined from the analyte peak response with a signal-to-noise ratio of 3:1. For the liquid-liquid extraction samples, since the samples were diluted 1:1 (v/v) with methanol during extraction and analyte concentrations were not detectable in blanks, the MDLs were set at twice the IDLs.

To obtain highest data quality possible in ultra-trace analysis, one aims to include the maximum number of internal standards in the analysis. Ideally, each target analyte should have a mass-labelled internal standard included in the analytical procedure. This criterion becomes important in accurately quantifying target analytes. Mass-labelled internal standards respond the same way as their native counterparts throughout all analytical steps, including instrumental analysis. This facilitates adjustment of the analytical data of the native compounds according to the response of the corresponding mass-labelled internal standards. However, for some analyses, mass-labelled internal standards are not available.

Mass-labelled internal standards for corresponding analytes (e.g. using $^{13}\text{C}_4\text{-PFOS}$ to quantify PFOS) were available for 7 of the 18 PFCs examined in this study, listed in Table 3.12. These analytes with corresponding mass-labelled internal standards are expected to provide the best precision and accuracy. In the absence of mass-labelled internal standards, these standards can be used to quantify other analytes (e.g. using $^{13}\text{C}_4\text{-PFOS}$ to quantify PFBS). The internal standard-to-analyte assignments are based on the physio-chemical properties of the compounds including chemical structure, functional groups and size of the corresponding compounds. In some cases, the internal standards do not behave exactly the same way as these other analytes, possibly leading to larger variations in the results (van Leeuwen et al., 2009).

Table 3.12: Mass-labelled internal standards used for quantification at DFO-IOS.

PFC	Mass-labelled internal standard for quantification
PFBA	¹³ C ₄ -PFBA
PFPeA	¹³ C ₄ -PFBA
PFHxA	¹³ C ₂ -PFHxA
PFHpA	¹³ C ₂ -PFHxA
PFOA	¹³ C ₂ -PFOA
PFNA	¹³ C ₅ -PFNA
PFDA	¹³ C ₂ -PFDA
PFUnA	¹³ C ₂ -PFDA
PFDaA	¹³ C ₂ -PFDA
PFTA	¹³ C ₂ -PFDA
PFBS	¹³ C ₄ -PFOS
PFHxS	¹³ C ₄ -PFOS
PFOS	¹³ C ₄ -PFOS
PFOSA	¹³ C ₄ -PFOA
6:2 FTUA	¹³ C ₂ FDUEA
8:2 FTUA	¹³ C ₂ FDUEA
10:2 FTUA	¹³ C ₂ FDUEA

For the purpose of statistical analyses, any concentrations below MDLs were assigned values according to the conditions shown in Table 3.13. All data in the results are reported as means of the experimental values (n = 3 or 4).

Table 3.13: Conditions for handling results below MDL

PFC Concentration	Assigned Value
No peak or < 0	1/10 of MDL
< 0.5 MDL	1/2 of MDL
< MDL	MDL

Chapter 4: Perfluorinated compounds in landfill leachate samples

4.1 Field sample characterization

4.1.1 Landfill A samples

Results from characterization of landfill leachate and condensate from landfill A are summarized in Tables 4.1 and 4.2. The results from river water collected less than 10 km downstream of landfill A are summarized in Table 4.3. In Table 4.1, concentrations of the three metals with the highest concentrations are listed. For concentrations of other metals, see Appendix B, Table B.1.

Table 4.1: Physical and chemical parameters measured in landfill leachate from landfill A

Parameter	Mean	Standard Deviation	Range	n
pH	4.76	0.022	4.73-4.78	3
Electrical conductivity	0.88 mS/cm	0.00 mS/cm	0.88-0.88 mS/cm	3
Total organic carbon	339 mg/L	N/A	N/A	1
Calcium (Ca)	24.8 mg/L	1.24 mg/L	23.7-26.2 mg/L	3
Magnesium (Mg)	12.6 mg/L	0.80 mg/L	12.0-13.5 mg/L	3
Iron (Fe)	2.94 mg/L	0.68 mg/L	2.56-3.73 mg/L	3
n = number of samples				

Table 4.2: Physical and chemical parameters measured in landfill gas condensate from landfill A

Parameter	Mean	Standard Deviation	Range	n
pH	6.55	0.012	6.53-6.56	3
Electrical conductivity	0.11 mS/cm	0.0047 mS/cm	0.10-0.11 mS/cm	3
Total organic carbon	1,389 mg/L	N/A	N/A	1
n = number of samples				

Table 4.3: Physical and chemical parameters measured in river water collected less than 10 km downstream of landfill A

Parameter	Mean	Standard Deviation	Range	n
pH	3.32	0.033	3.27-3.34	3
Electrical conductivity	0.24	0.0050	0.23-0.24	3
Total organic carbon	16.3 mg/L	N/A	N/A	1
n = number of samples				

4.1.2 Landfill B samples

Results from characterization of landfill leachate from landfill B are summarized in Table 4.4. In this table, concentrations of the three metals with the highest concentrations are listed. For concentrations of other metals, see Appendix B, Table B.2.

Table 4.4: Physical and chemical parameters measured in landfill leachate from landfill B

Parameter	Mean	Standard Deviation	Range	n
Total suspended solids (TSS)	216 mg/L	77 mg/L	39-322 mg/L	12
Bromide	4.2 mg/L	N/A	N/A	1
Fluoride	0.11 mg/L	N/A	N/A	1
Chloride	180 mg/L	N/A	N/A	1
Sulphate	5.1 mg/L	3.7 mg/L	0.9-8.4 mg/L	5
Phosphate	0.19 mg/L	0.02 mg/L	0.17-0.22 mg/L	5
Nitrogen (NO _x)	0.50 mg/L	0.24 mg/L	0.26-0.76 mg/L	5
Ammonia	123 mg/L	54 mg/L	60-209 mg/L	5
pH	7.4	0.3	7.0-7.9	13
Electrical conductivity	2.4 mS/cm	0.7 mS/cm	1.2-3.4 mS/cm	13
Total organic carbon	113 mg/L	22 mg/L	73-152 mg/L	9
Iron (Fe)	145 mg/L	5.26 mg/L	140-151 mg/L	3
Magnesium (Mg)	142 mg/L	5.51 mg/L	138-148 mg/L	3
Potassium (K)	32.4 mg/L	0.88 mg/L	31.6-33.3 mg/L	3
n = number of samples				

4.2 Cross-Canada landfill leachate

4.2.1 PFC concentrations

PFCs were detected in all collected landfill leachate samples. PFC concentrations in collected landfill leachates are plotted in descending order of concentrations and grouped by North and South in Figure 4.1. Ten of the 13 PFCs analyzed in this study were detected in the majority (>14 of 27) of the samples. The concentrations of PFCs in the leachate samples are listed in Appendix B, Table B.3. Σ PFC varied greatly, from 27 (site 16) to 21,300 ng/L (site 9), with the mean concentration being 2,950 ng/L.

In Table 4.5, the concentration ranges, means, and method detection limits are reported for each analyte. The PFC concentrations for all of the procedural blanks were below detection limits, as shown in Appendix B, Table B.4. Therefore, blank corrections were not applied to the concentrations measured in the landfill leachate samples. PFC concentrations normalized as a percentage of Σ PFC in collected landfill leachates are plotted in descending order of concentrations in Figure 4.2. PFOA was detected in all landfill leachate samples at a mean concentration of 439 ng/L and was 16% of Σ PFC. Although one would expect PFOS to be a more dominant PFC due to the widespread use of its salts and precursors in Canada as a surface treatment for products (e.g. packaging) that are ultimately disposed in landfills (see section 2.4 for discussion), it only contributed 10% of Σ PFC (279 ng/L). PFOSA, a precursor to PFOS, was a very small fraction (0.3%) of Σ PFC at 8 ng/L. PFHxA was the dominant compound, contributing 25% of Σ PFC at 695 ng/L. The C4 to C8 perfluorocarboxylic acids (PFCAs) constituted the majority (73%) of Σ PFC. These PFCAs are degradation products of the most widely manufactured fluorotelomer-based and perfluoroalkyl sulfonyl products (Lee et al., 2010, van Zelm et al., 2008, Russell et al., 2008, Prevedouros et al., 2006, Wang et al., 2009). Van Zelm et al. (2008) estimated that two-thirds of all fluorotelomer acrylate polymers, the largest commercial category of polyfluorinated products, are ultimately disposed of in landfills. This is a substantial source of precursors that may degrade into PFCAs in landfill leachate. Information on the inventory of PFCAs is not available for Canada. Therefore, it was not possible to make a comparison of the amount of PFCAs imported with its relative concentrations in landfill leachate.

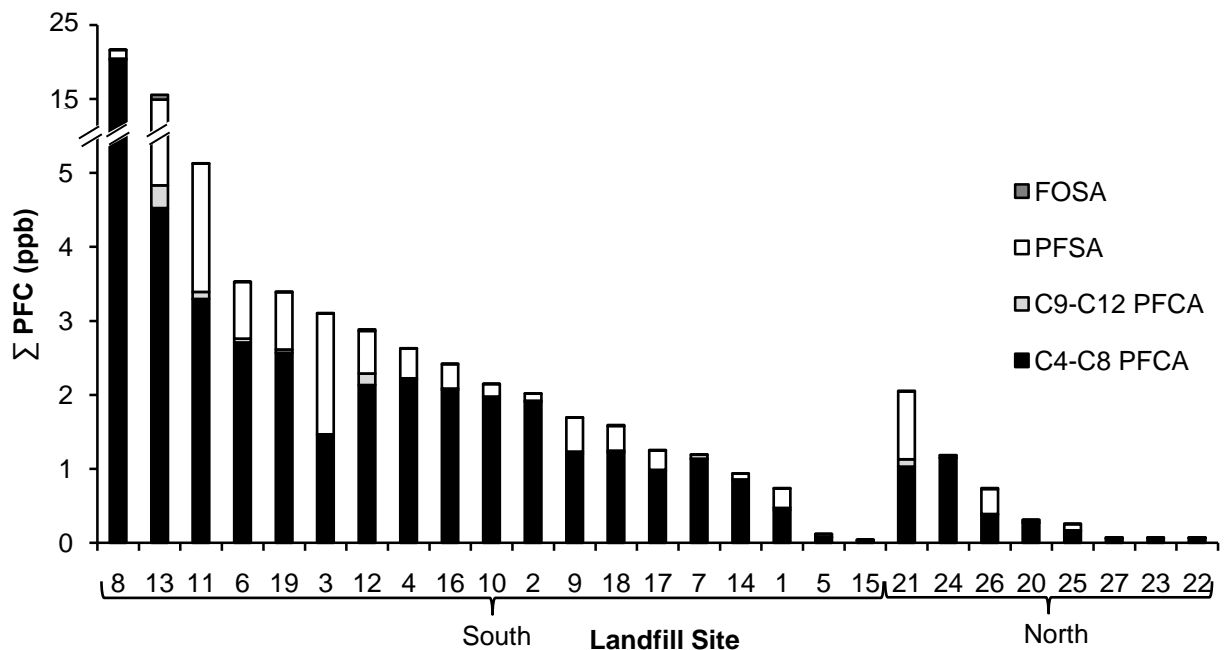


Figure 4.1: Σ PFC in cross-Canada landfill leachate. PFCs are grouped by class. PFCAs are further grouped by C4-C8 and C9-C12 compounds.

Table 4.5: Mean, range, and mean method detection limits of PFCs in cross-Canada landfill leachate

Analyte	Mean (ppb)	Range (ppb)	Mean MDL ^a (ppb)
PFBA	0.227	<MDL-3.260	0.0032
PFPeA	0.359	<MDL-3.920	0.0044
PFHxA	0.695	<MDL-7.090	0.0026
PFHpA	0.278	<MDL-2.310	0.0025
PFOA	0.439	0.006-3.450	0.0015
PFNA	0.022	<MDL-0.117	0.0108
PFDA	0.015	<MDL-0.190	0.0042
PFUnA	0.002	<MDL-0.011	0.0031
PFDoA	0.003	<MDL-0.032	0.0031
PFBS	0.114	<MDL-1.370	0.0206
PFHxS	0.300	<MDL-3.010	0.0064
PFOS	0.279	<MDL-4.840	0.0097
PFOSA	0.008	<MDL-0.063	0.0032
^a MDL: Method detection limit			

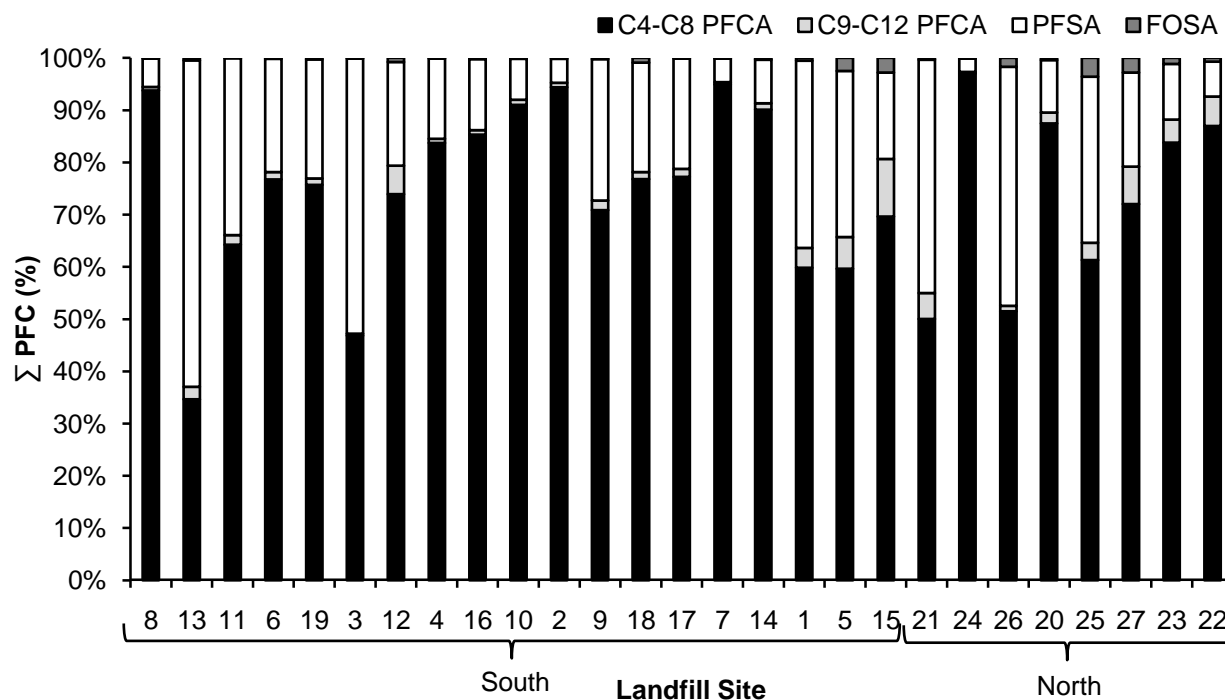


Figure 4.2: PFCs normalized as a percentage of Σ PFC in cross-Canada landfill leachate. PFCs are grouped by class. PFCAs are further grouped by C4-C8 and C9-C12 compounds.

4.2.2 Correlations between PFCs

The data are plotted on a log-log scale to improve visualization and identification of potential correlations. The R^2 values for correlations between PFCs are listed in Appendix B, Table B.5. There was some correlation between PFOA and PFOS ($R^2 = 0.25$) in landfill leachate (Figure 4.3), but it was not as strong as the correlation observed in surface water ($R^2 = 0.82$) in Europe (Pistocchi & Loos, 2009). PFOSA was moderately correlated with PFOS ($R^2 = 0.54$) (Figure 4.4). This was expected as PFOSA is a precursor to PFOS (Martin et al., 2004, Kannan et al., 2001). There were strong correlations between the concentrations of PFPeA, PFHxA, and PFHpA ($R^2 = 0.84$ - 0.97). These correlations were strongest for compounds most similar by molecular weight (e.g. $R^2 = 0.89$ for PFPeA vs PFHxA). Being similar in structure, one would expect these compounds to behave in similar ways in the environment. They have similar physical and chemical properties, as discussed in section 2.1. A strong correlation was also

observed between PFHxS and PFOA ($R^2 = 0.82$). PFHxS was moderately correlated with the other C5 to C10 PFCAs, as well as PFBS, PFOS, and PFOSA ($R^2 = 0.50$ - 0.71).

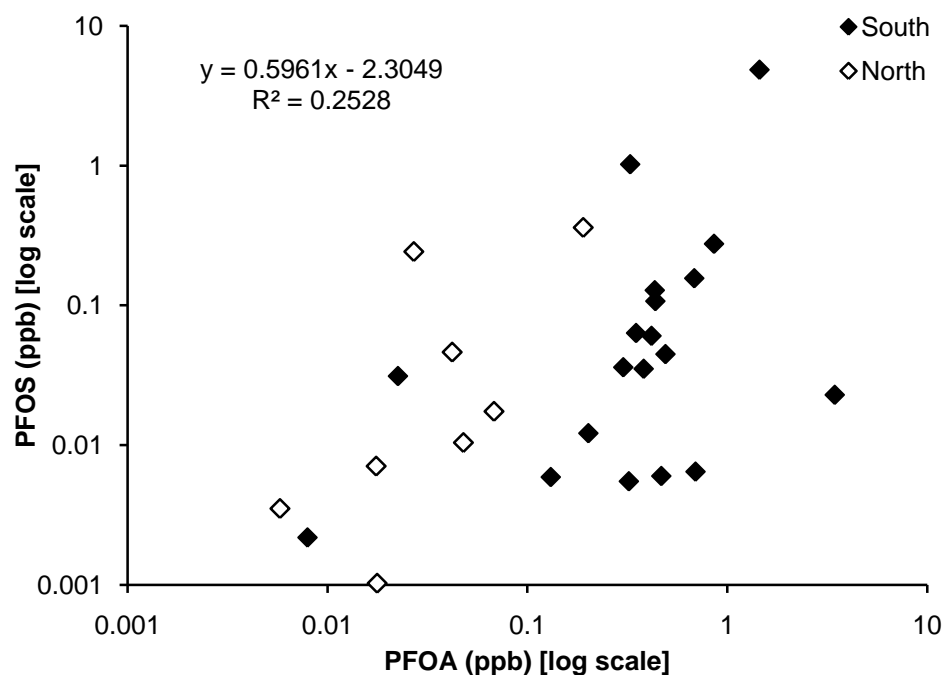


Figure 4.3: PFOS vs PFOA (log-log) in cross-Canada landfill leachate.

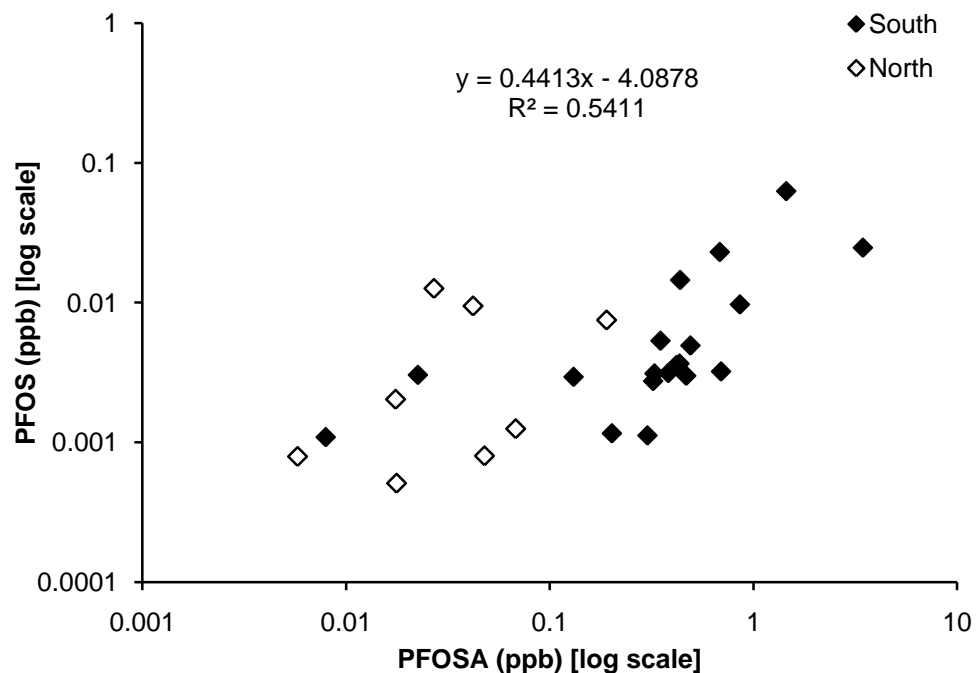


Figure 4.4: PFOS vs PFOSA (log-log) in cross-Canada landfill leachate.

4.2.3 Influences of geography, landfill size, and precipitation

Σ PFC were significantly higher ($p < 0.05$, i.e. using a null hypothesis test, the probability that Σ PFC is not statistically significant between the South and North is less than 5%) in the South than in the North. The mean Σ PFC was 3,250 ng/L in the South and 590 ng/L in the North (Table B.3). A major difference between the North and South is that the population centers are much smaller in the North. There are also fewer manufacturing industries in the North. As a result, the numbers of consumer goods and manufacturing byproducts disposed in landfills are expected to be lower in the North. Correlations of PFC concentrations with population have been observed by other studies (Murakami et al., 2009, Pistocchi & Loos, 2009). Correlation of PFCs with population was mostly weak ($R^2 < 0.33$) in this study. Other factors that may affect landfill leachate quality considered in this study were waste tonnage in landfills and precipitation; their correlations were relatively low ($R^2 < 0.40$) in comparing concentrations of PFCs with either of these factors.

4.2.4 Influence of total organic carbon

The organic carbon content of sediment and soil is a dominant factor in sorption of PFCs to sediment and soil (Higgins & Luthy, 2006). Landfill leachate contains organic carbon, of which the majority is on particulates. There is great variation in TOC and total particulates (total suspended solids) in leachate from this study, as shown in Appendix B, Table B.3. The range of TOC is 3 to 225 mg/L, with a mean of 41 mg/L. The range of total suspended solids (TSS) is 30 to 2,000 mg/L, with a mean of 400 mg/L. Both parameters are comparable in range with reported mean literature values of 220 mg/L and 196 mg/L for TOC and total suspended solids, respectively from a study comparing landfill leachate parameters from 12 landfills in Europe (Oman & Junestedt, 2008). Although PFCs are expected to bind to the organic carbon in landfill leachate, there were only weak ($R^2 < 0.28$) correlations between PFCs and TOC.

4.2.5 Other potential factors

No single landfill and landfill leachate parameters discussed in this section appears to have had a large influence on the levels of PFCs in the cross-Canada landfill leachate samples. This is likely

due to the complex matrix and heterogeneity of landfill leachate. It is likely that a combination of factors would affect the landfill leachate characteristics, suggesting the need for a more complex multi-regression and multivariate analyses. Other parameters not considered in this study that could influence PFCs levels in landfill leachate include waste composition, soil properties, rainwater chemistry, and temperature within the landfill.

4.2.6 Comparison with other countries

Three similar studies on PFCs in landfill leachate were found in the literature from the United States (Huset et al., 2011), Germany (Busch et al., 2010a), and Nordic countries (Kallenborn et al., 2004).

In the United States, landfill leachate was collected from eight landfills (Huset et al., 2011). For one, samples were collected from five different cells, yielding 12 samples in all landfills. In Germany, leachate was collected from 22 landfills (Busch et al., 2010a). However, raw data were only reported for 20 landfills. In the Nordic study, landfill leachate was collected from six landfills: one in Finland and the others in Norway (Kallenborn et al., 2004). Huset et al. (2011) and Busch et al. (2010a) extracted PFCs from landfill leachate by solid-phase extraction and analyzed by LC/MS/MS using methods similar to the analysis of the cross-Canada landfill leachates. Kallenborn et al. (2004) used accelerated solvent extraction instead and analyzed the samples with LC/MS/MS. Since Kallenborn et al. (2004) did not use the same extraction method, the results from their study are not included in the following comparison.

The PFCA class was compared between landfill leachate in the United States (Huset et al., 2011), Germany (Busch et al., 2010a), and Canada (Cross-Canada landfill leachate). The mean concentrations of PFCAs in these three studies are plotted and ordered by increasing molecular weight (Figure 4.5). The mean concentration curves for all three countries have similar patterns, even though the sources of the leachates are from diverse geographical and demographic regions. There was high variability in PFCs between individual landfills within each study, indicated by the large span of the error bars indicating the standard errors of the means. There is a common trend in the distribution between the various compounds whereby most PFCs found in these landfill leachates are in the C4-C8 range. However, the PFC concentration ranges differ. The ranges of concentrations in each study are summarized in Table 4.6. The data from this study

tend to be between those from Germany and the United States, with Germany having generally lower PFC concentrations.

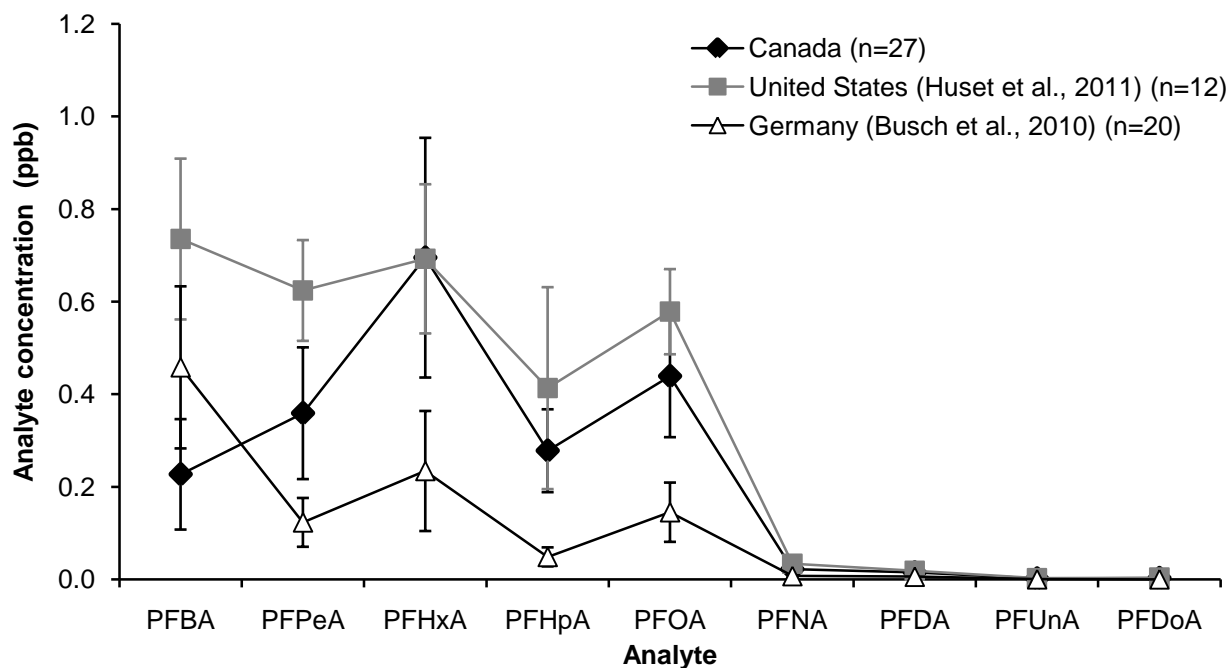


Figure 4.5: Mean concentrations of PFCAs in landfill leachates collected in the United States, Germany and Canada. PFCAs are ordered by increasing molecular weight. Error bars indicate the standard errors of the means.

Table 4.6: Range of PFC mean concentrations in landfill leachate from studies from Canada, Germany and the United States.

Author, Country	Lowest mean concentration (Compound)	Highest mean concentration (Compound)
This study, Canada	0.002 ± 0.0005 ppb (PFUnA)	0.694 ± 0.259 ppb (PFHxA)
Busch et al. (2010), Germany	0.0003 ± 0.0003 ppb (PFDoA)	0.458 ± 0.343 ppb (PFBA)
Huset et al. (2011), United States	0.0027 ± 0.0021 ppb (PFUnA)	0.735 ± 0.340 ppb (PFBA).

4.3 Landfill A PFCs

Aqueous samples analyzed by solid phase extraction are discussed in this section. The detection limits from liquid-liquid extraction were not low enough to make accurate measurements for these samples, whereas those from solid phase extraction were satisfactory. Therefore, only the results from solid phase extraction are included below. For results from analysis by liquid-liquid extraction, refer to Appendix C, Table C.1. Appendix B, Table B.6 provides the concentrations for all PFCs analyzed in these samples. Sampling and analysis methods for this set of samples are described in sections 3.1.2, 3.3.1.3, 3.3.2.2, and 3.7.2. The method detection limits are listed in Table 4.7.

Table 4.7: Method detection limits (MDLs) for landfill leachate, condensate, and water samples

Analyte	Landfill leachate MDL (ppb)	Condensate MDL (ppb)	River water MDL (ppb)
PFBA	0.018	2.6×10^{-4}	3.2×10^{-4}
PFPeA	0.042	2.0×10^{-4}	2.5×10^{-4}
PFHxA	0.017	1.5×10^{-4}	1.8×10^{-4}
PFHpA	0.0061	5.8×10^{-5}	7.1×10^{-5}
PFOA	0.0055	2.5×10^{-5}	3.1×10^{-5}
PFNA	0.028	5.1×10^{-5}	6.4×10^{-5}
PFDA	0.0050	2.7×10^{-5}	3.4×10^{-5}
PFUnA	0.030	2.1×10^{-5}	2.6×10^{-5}
PFDaA	1.7×10^{-4}	2.3×10^{-5}	2.9×10^{-5}
PFTA	2.4×10^{-4}	3.2×10^{-5}	4.0×10^{-5}
PFBS	8.4×10^{-4}	1.0×10^{-5}	1.3×10^{-5}
PFHxS	4.3×10^{-5}	5.8×10^{-6}	7.1×10^{-6}
PFOS	0.0015	7.1×10^{-6}	8.8×10^{-6}
PFDS	3.5×10^{-5}	4.7×10^{-6}	5.8×10^{-6}
PFOSA	5.0×10^{-5}	6.7×10^{-6}	8.3×10^{-6}
6:2 FTUA	3.0×10^{-5}	4.0×10^{-6}	4.9×10^{-6}
8:2 FTUA	2.0×10^{-5}	2.7×10^{-6}	3.3×10^{-6}
10:2 FTUA	3.1×10^{-5}	4.1×10^{-6}	5.0×10^{-6}

4.3.1 Landfill leachate

The mean Σ PFC of landfill leachate from landfill A was 2.8 ppb. To compare these data to the other cross-Canada landfill leachate data, Σ PFC was recalculated with PFTA, PFDS, and the

FTUAs removed. As PFTA, PFDS, and FTUAs were at very low concentrations compared to other analytes, the recalculated mean concentration was also 2.8 ppb, slightly below the cross-Canada mean of 2.9 ppb discussed in section 4.2.1. The concentration profile of the PFCs in landfill leachate from landfill A is plotted in Figure 4.6. Similar to the cross-Canada samples, PFHxA was detected at the highest concentration (mean concentration 1.07 ppb). The C5-C8 PFCAs were the dominant compounds. PFHxS and PFOS were also detected at relatively high concentrations. PFHxS was the dominant PFSA (mean concentration 0.19 ppb). Most analytes were well above their method detection limits, except for PFNA, PFUnA, PFOSA, and the FTUAs. The variation between subsamples was relatively small, as seen in the error bars in Figure 4.6. This indicates good reproducibility of the extraction and analytical method. The PFC concentrations in landfill leachate from landfill A are compared to landfill B and cross-Canada samples in section 4.4.1.1 below.

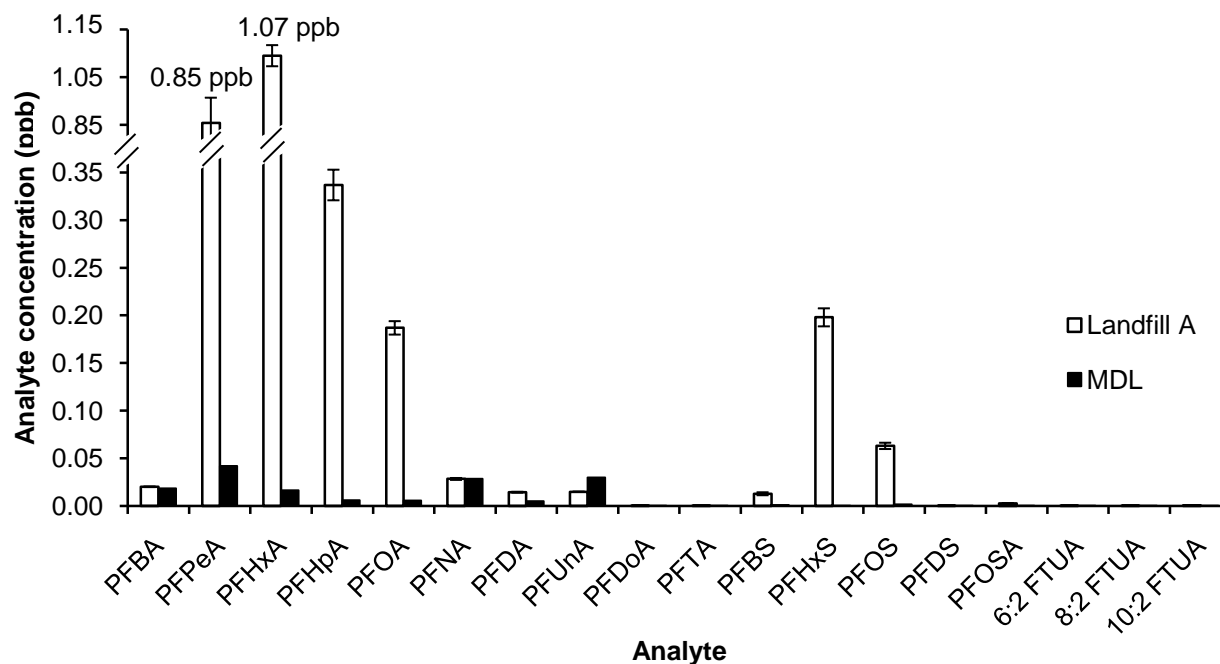


Figure 4.6: PFCs in landfill leachate samples from landfill A. Error bars indicate the standard errors of the mean (n=3).

4.3.2 Condensate

The Σ PFC of condensate from landfill A was 0.05 ppb, only 2% of the Σ PFC for landfill leachate from the same site. Condensate is formed when landfill gas within the landfill cools and condenses. The concentration profile of the PFCs in condensate from landfill A is plotted in Figure 4.7. Unlike the concentration profile of the landfill leachate, the PFSAs were at higher concentrations than the C5-C8 PFCAs. PFBS was the dominant compound (0.01 ppb), followed by PFOSA (0.007 ppb), and PFOS (0.006 ppb). All of the dominant compounds in condensate were not dominant in landfill leachate from landfill A. PFDS and the FTUAs were close to or below the MDLs, while all other analytes were well above MDLs. The condensate was acidic (mean pH 3.3). Under these conditions, PFCAs may protonate and become volatile (Goss, 2008). The PFCAs may have not condensed, and as a result, were measured to be at lower concentrations in the condensate.

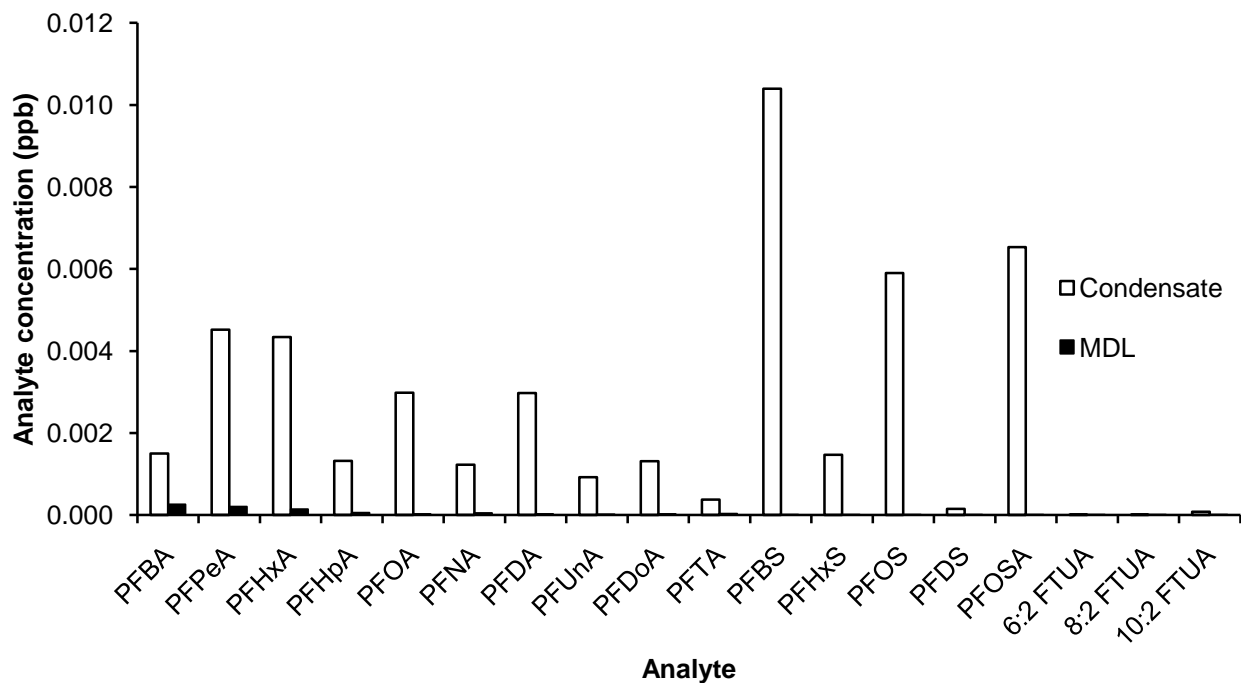


Figure 4.7: PFCs in condensate from landfill A (n=1).

4.3.3 River water

The mean Σ PFC of river water collected less than 10 km downstream of landfill A was 0.02 ppb. That is less than 1% of the Σ PFC in landfill leachate from landfill A. At the sampling point, the river was expected to be relatively pristine as there are no major wastewater treatment plants or PFC-producing industries upstream. The concentration profile of the PFCs in condensate from landfill A is plotted in Figure 4.8. The dominant PFCs were PFOA (mean concentration 0.002 ppb) and PFHxA (mean concentration 0.001 ppb). The PFSA's were lower than the PFCAs by almost one order of magnitude. PFPeA was not quantifiable because its signal peak was too small. PFBA, PFHxS, PFDS, PFOSA and the FTUAs were below or slightly above MDL while other analytes were well above MDLs.

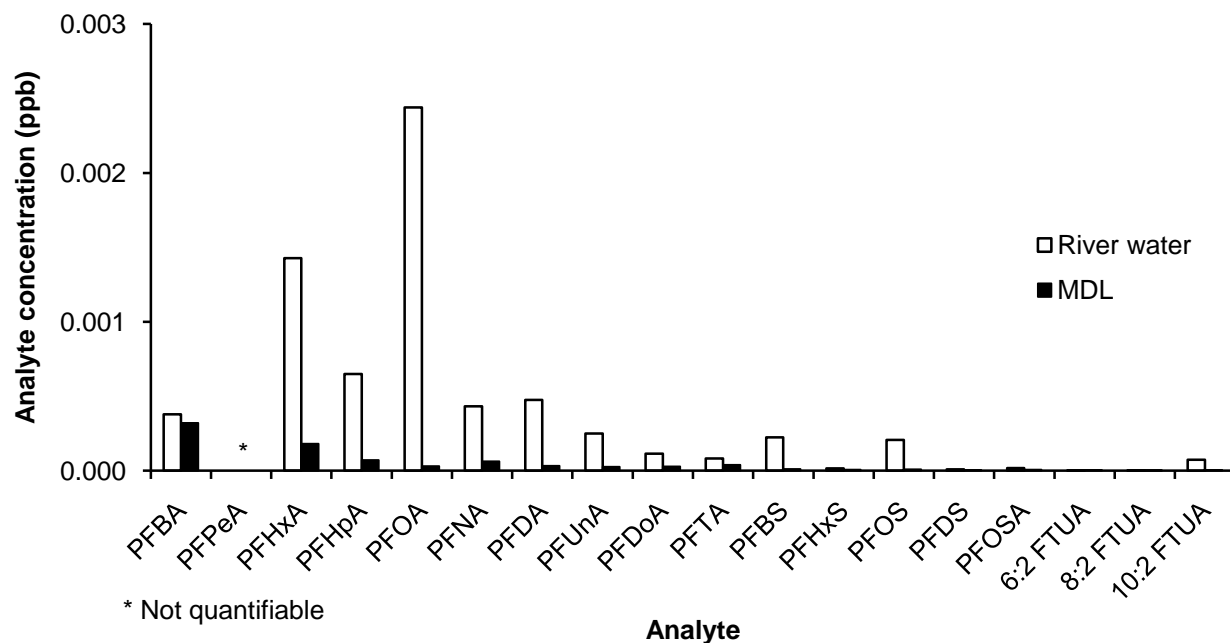


Figure 4.8: PFCs in river water samples collected within 10 km downstream of landfill A (n=2).

4.3.4 Soil

PFCs were extracted from soil samples from landfill A by Method A, described in section 3.3.2.1. The detection limits from Method A were not low enough for these samples. However, it appears that the soil samples collected by the landfill's leaching field had larger peaks in the

chromatograms from the LC/MS/MS than soil samples from the soil borrow pit. Though these peaks were not considered quantifiable because they were smaller than the noise, they indicate that there are likely more PFCs in the leaching field soil. Based on the spike recovery concentrations, it appears that the method effectively extracted eight (PFBA, PFHxA, PFHpA, PFOA, PFNA, PFBS, PFHxS, PFOS) of the 18 PFCs from soil, with recovery rates ranging from 77 to 120%. The other 10 PFCs were not effectively quantified by this method as their recovery rates deviated greatly from 100% up to 600,000%. The PFC concentrations from soil samples collected from landfill A and spike recovery samples are listed in Appendix B, Table B.7.

4.4 Landfill B PFCs

Analyses of aqueous samples subjected to solid phase extraction are discussed in this section. The detection limits from liquid-liquid extraction were not low enough to allow for these samples to be quantified accurately, whereas those from solid phase extraction were satisfactory. Therefore, only the results from solid phase extraction are included below. For results from analysis by liquid-liquid extraction, refer to Appendix C, Table C.2. Appendix B, Table B.8 summarizes the concentrations for all PFCs analyzed in these samples, whereas Appendix B, Table B.9 contains the raw data. Sampling and analysis methods for this set of samples are described in sections 3.1.3, 3.3.1.3 and 3.7.2. The method detection limits for the landfill leachates are listed in Table 4.7.

4.4.1 December 2009 samples

The mean concentrations are presented in this section for three landfill leachate sub-samples drawn from one sample, and one sub-sample drawn from each of two samples collected on December 2, 2009 from landfill B. The total number of samples collected on this sampling trip was 10. The mean Σ PFC of the landfill leachate was 3.8 ppb.

4.4.1.1. Comparison with cross-Canada and landfill A leachate samples

To compare data from landfill B to the other cross-Canada landfill leachate data, Σ PFC was recalculated with the PFTA, PFDS and FTUAs removed. As the latter were at very low concentrations compared to other analytes, the recalculated mean concentration was also 3.8 ppb. This was greater than the mean Σ PFC of the cross-Canada landfill leachate (see section 4.2.1) by

140%. The concentration profiles of the PFCs in landfill leachate from landfill B compared to landfill A and cross-Canada are plotted in Figure 4.9. PFHxA was the dominant analyte in the landfill B sample, with a mean concentration of 1.5 ppb. Most analytes were well above their method detection limits. The analyte distribution from landfill B had some similarities to that of the cross-Canada and landfill A leachates, such as the dominance of the C5-C8 PFCAs. Overall, concentrations of PFCs were higher in leachate from landfill B than in landfill A. Although correlations of PFCs with population were weak in the cross-Canada samples (section 4.2), other studies (Murakami et al., 2009, Pistocchi & Loos, 2009) have found that PFC concentrations correlate with population. Since landfill B is located in a more densely populated region (more than one million people) than landfill A (50,000 to 100,000 people), population may be one factor contributing to higher PFC concentrations. The mean concentrations of PFCs in cross-Canada samples were generally less than in landfills A and B. However, the PFOA and PFOS levels in landfill A and B samples were lower than the corresponding cross-Canada mean concentrations.

Another interesting observation was PFHxS at concentrations similar to, or higher than, PFOS in landfills A and B. The dominant perfluoroalkyl sulfonate observed in the environment is typically PFOS (see sections 2.4 and 2.6 for discussion). However, significant use of PFHxS in various surface treatments has been reported. For example, “ScotchGard Carpet and Upholstery protector containing FC-228”, a type of former post-mill application surface treatment, was reported to contain higher residuals of PFHxS than PFOS or any perfluorooctane sulfonamide (Fraunhofer ITEM, 2004). A study on house dust conducted in the Greater Vancouver Area, British Columbia (Beesoon et al., 2011) found that four of 18 dust samples contained levels of PFHxS which exceeded PFOS. Carpets are a major source of PFCs in house dust, so that the elevated levels of PFHxS may be an indicator of the dominant type of surface treatment used on carpets in a geographic area. This relationship could be further extended to explain the dominance of PFHxS in landfill leachate, as carpets are typically disposed of in landfills after their useful lives.

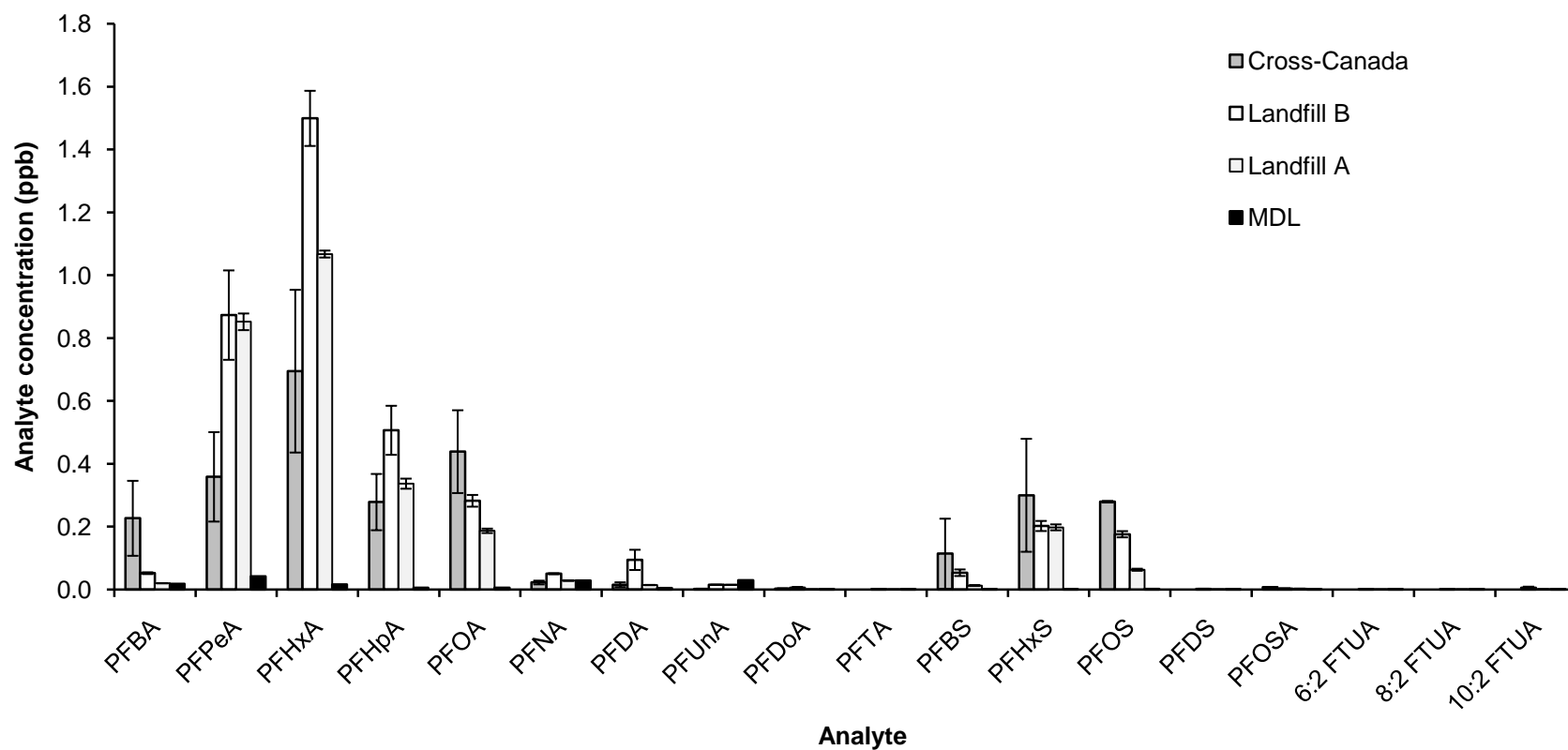


Figure 4.9: Mean concentrations of PFCs in landfill leachate samples from landfill B collected on December 2, 2009, landfill A and cross-Canada landfill leachate. Error bars indicate the standard errors of the mean (n=3).

4.4.2 Time series

The Σ PFC concentrations and general observations are discussed first in this section, with more detailed discussion on each analyte presented in the sub-sections below. For all landfill leachate samples discussed in this section, the mean concentrations are for three sub-samples drawn from one sample collected on each sampling trip every two weeks from February 22 to June 22, 2010. The only exception is the sample from March 2, 2010, when two samples were collected and three sub-samples were drawn from each sample. The mean concentrations are averages for all sub-samples from both samples.

Σ PFC concentrations fluctuated from 3.3 to 14 ppb during the February 22 to June 22, 2010 period (Figure 4.10), with an average Σ PFC over this time period of 5.8 ppb. Like the cross-Canada landfill leachate samples (section 4.2.1), C4-C8 PFCAs were the dominant compounds, contributing on average of 64% to Σ PFC at a mean concentration of 3.7 ppb. As discussed in section 4.2.1, the dominance of the C4-C8 PFCs was expected (Figure 4.11), as they are degradation products of common precursors from commercial goods ultimately disposed in landfills (Lee et al., 2010, van Zelm et al., 2008, Russell et al., 2008, Prevedouros et al., 2006).

From March 16 to April 13, 2010, there was a large increase in Σ PFC, from 6.7 to 14 ppb. The increased PFC concentrations, particularly on April 13, appear to be caused by precursor degradation. Previous studies (Lee et al., 2010, Wang et al., 2009) have demonstrated the formation of PFCAs from the biodegradation of fluorotelomer-based precursors (e.g. fluorotelomer alcohols and polyfluorinated phosphonates) via fluorotelomer acid intermediates. These compounds are discussed in more detail in sections 4.4.2.3 and 4.4.2.5.

From March 16 to April 13, the proportion of C4-C8 PFCs was much lower (mean 41%). However, their combined concentration during this time period (mean concentration 4.0 ppb) was comparable to that in the other sampling periods. This indicates that direct sources of C4-C8 PFCs (e.g. from goods manufactured with PFCs) are more dominant than degradation of precursors. Aside from the March 16 to April 13 period, all other concentrations of compounds (C9-C14 PFCs, PFSA, FOSA, FTUA) were relatively constant.

As there were large temporal variations in PFC concentrations over the five-month sampling period, it appears that single grab samples may not be representative for monitoring PFCs in landfill leachate. The production and circulation of landfill leachate is a complex process that depends on factors which change with time, depending on such variables as temperature, rainfall, hydrology, local and bulk waste composition, and landfilling technology (Trankler et al., 2005, Khattabi et al., 2002, Blight et al., 1999). Therefore, sampling should be done over time, and possibly spatially arranged as well, to account for possible fluctuations in PFC levels and to obtain a representative range of PFC concentrations for a landfill.

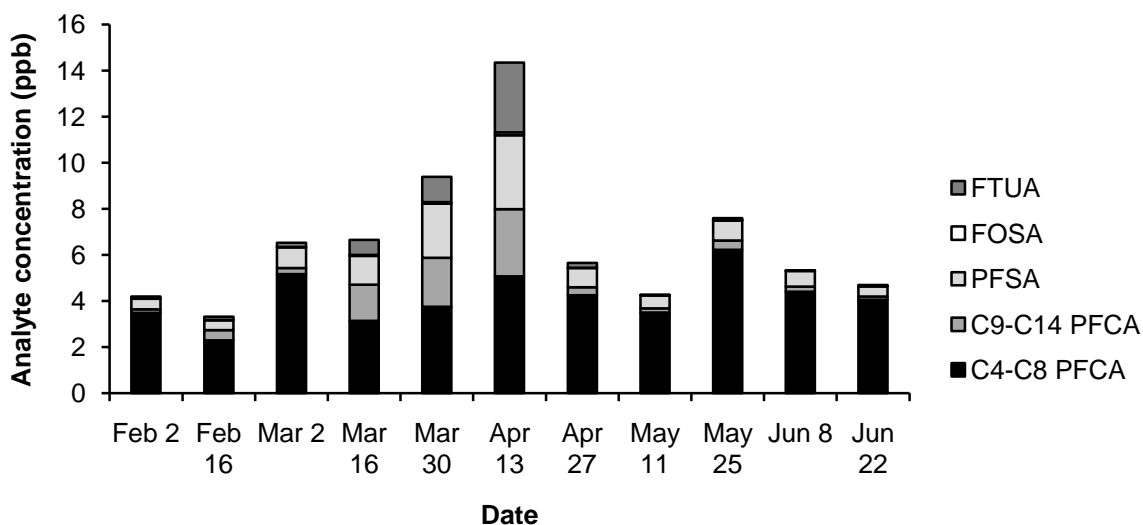


Figure 4.10: Σ PFC concentrations in landfill leachate samples from landfill B collected between February 2 and June 22, 2010. PFCs are grouped by class. PFCAs are further grouped by C4-C8 and C9-C14 compounds.

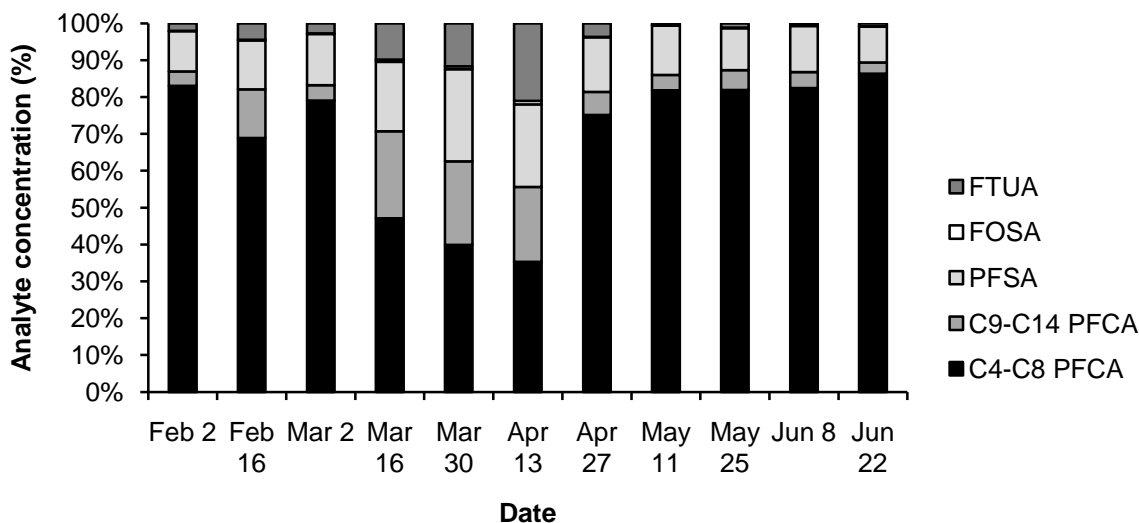


Figure 4.11: PFCs normalized as a percentage of Σ PFC in landfill leachate samples from landfill B collected between February 2 and June 22, 2010. PFCs are grouped by class. PFCAs are further grouped by C4-C8 and C9-C14 compounds.

4.4.2.1. Sampling method comparison

Samples on March 2, 2010 were collected in two different ways: bucket close to the surface and pump close to the bottom of the leachate well, described in section 3.1.3. The PFC concentrations from both collection methods are plotted in Figure 4.12. The mean percent difference between the two collection methods was 46%. Considering the heterogeneity of landfill leachate samples, variation in concentrations between sub-samples that are similar to the variation between the two sampling methods (i.e. spread of error bars similar to difference between mean concentrations), and that concentrations from one sampling method do not appear to be consistently greater or less than the other, it appears that the two sample collection methods produced results that are sufficiently accurate for the purposes of this study.

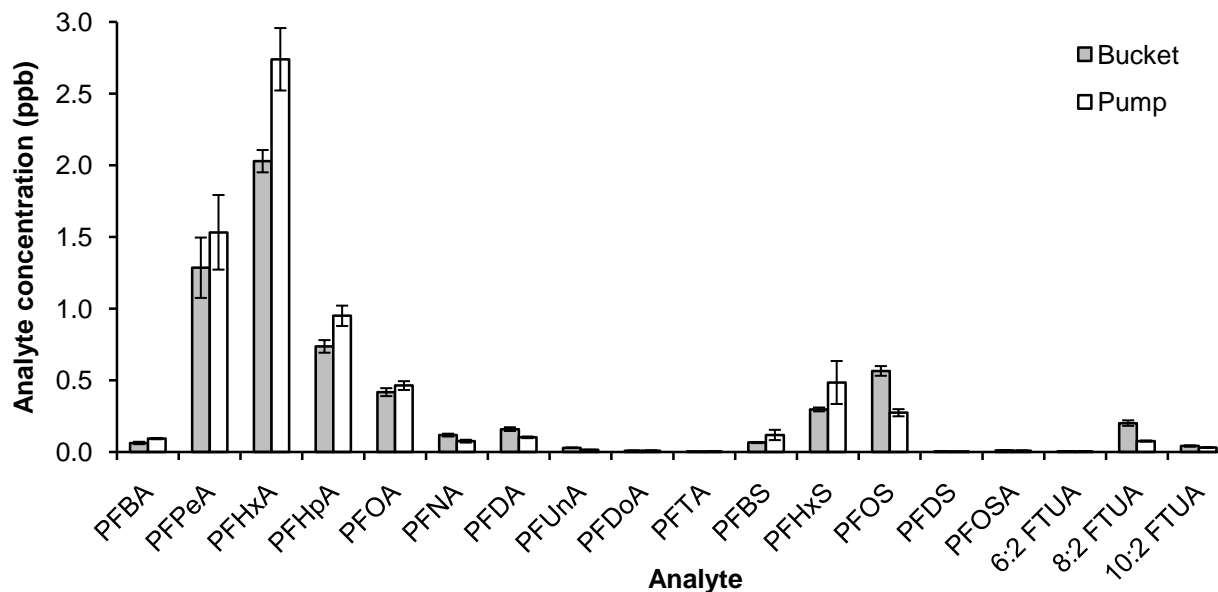


Figure 4.12: Comparison of PFC concentrations from landfill leachate collected by stainless steel bucket and pump at landfill B.

4.4.2.2. C4-C8 PFCA

The concentrations of the C4-C8 PFCAs are plotted in Figure 4.13. For all compounds except PFOA, the concentrations were reasonably constant. The PFBA, PFPeA, PFHxA, and PFHpA concentrations did not follow a clear pattern of change throughout the time period. There was a sharp increase of PFOA between March 16 and April 13; after this period, its concentration dropped back to levels similar to pre-March 16. The highest PFOA concentration was observed on April 13. The increased PFC concentrations, appear to be caused by precursor degradation as concentrations of 8:2 FTUA, a PFOA precursor, were highly correlated with PFOA. This is further discussed in section 4.4.2.9 below.

For all compounds, the lowest concentrations were found in the February 16 sample. It is interesting to note that the landfill leachate sample from February 16 also had the lowest electrical conductivity (EC), as well as lower than average TOC and particulates, as discussed in section 4.1.2. The influence of these parameters on PFC concentrations are discussed in more detail in sections 4.4.2.6 and 4.4.2.7 below.

PFHxA was at the highest concentration overall (mean concentration 2.1 ppb), with PFHpA and PFPeA next highest (mean concentrations 0.76 and 0.69 ppb, respectively), followed by PFOA (mean concentration 0.48 ppb) and PFBA (mean concentration 0.07 ppb). PFBA was the lowest, with no more than 0.1 ppb in any sample. This result differs from similar studies by Busch et al. (2010a) and Huset et al. (2011) where PFBA was the dominant compound.

Most of the spreads in error bars in Figure 4.13 are relatively small compared to the analyte concentrations. There were some analytes, however, where the standard error was larger (up to 50% of the analyte concentration), such as PFBA on April 13 and June 8. Overall, the relatively small variation between the sub-samples from different dates indicates good reproducibility of the extraction and analytical method. The analyte concentrations for PFPeA, PFHxA, PFHpA, and PFOA were well above the method detection limits (MDLs), by one to two orders of magnitude. Since PFBA concentrations were generally lower than other analytes and its MDL was about 10 times higher than for the other analytes, PFBA was relatively close to or below its MDL.

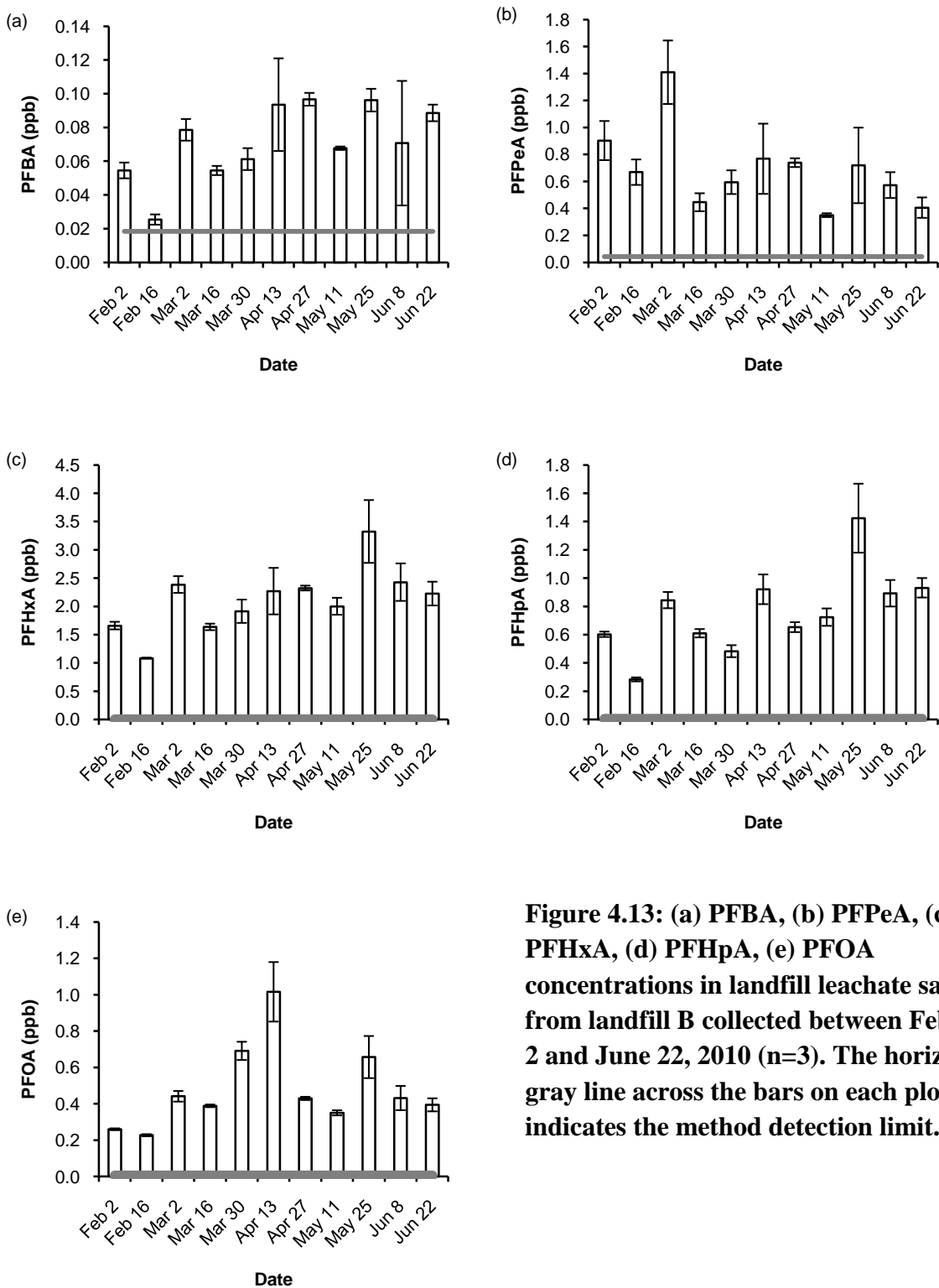


Figure 4.13: (a) PFBA, (b) PFPeA, (c) PFHxA, (d) PFHpA, (e) PFOA concentrations in landfill leachate samples from landfill B collected between February 2 and June 22, 2010 (n=3). The horizontal gray line across the bars on each plot indicates the method detection limit.

4.4.2.3. C9-C14 PFCA

The concentrations of the C9-C14 PFCAs are plotted in Figure 4.14. PFNA, PFDA, and PFDoA concentrations exhibited similar profiles to PFOA, increasing from March 16 to April 13. Again, this trend can be explained by precursor degradation, discussed below in section 4.4.2.9. PFUnA and PFTA did not increase from March 16 to April 13, but had similar profiles to each other. For both these compounds, the concentrations were highest on March 16, then were lower on March 30, and higher again on April 13. The reason is not known at this point, but there may be some precursor degradation pathways which differ from those of other compounds, leading to these compounds as end-products.

The concentrations of the C9-C14 compounds, except for the period from March 16 to April 13 were generally lower than for the C4-C8 compounds. PFDA had the highest concentration overall (mean concentration 0.43 ppb), followed by PFNA (mean concentration 0.24 ppb), PFUnA (mean concentration 0.11 ppb), PFDoA (mean concentration 0.02 ppb), and PFTA (mean concentration 0.002 ppb). Except for PFNA, which is produced in Japan for limited commercial applications, this group of compounds is not manufactured for commercial purposes (Prevedouros et al., 2006). Therefore, one would expect their concentrations in landfill leachate to be lower than the C4-C8 PFCAs.

Most of the spreads in error bars in Figure 4.14 are relatively small compared to the analyte concentrations. There was one sample (March 16) where the standard error was very large for PFNA, PFUnA, and PFTA (up to 87% of the analyte concentration), indicating either heterogeneity or inconsistency in the extraction method for those compounds in the sub-samples of that date. Overall, the relatively small variation among the sub-samples from different dates indicate good reproducibility of the extraction and analytical method. The analyte concentrations generally exceeded the method detection limits (MDLs) by one to two orders of magnitude. However, a few samples were found to have concentrations close to or below MDLs for PFUnA and PFTA.

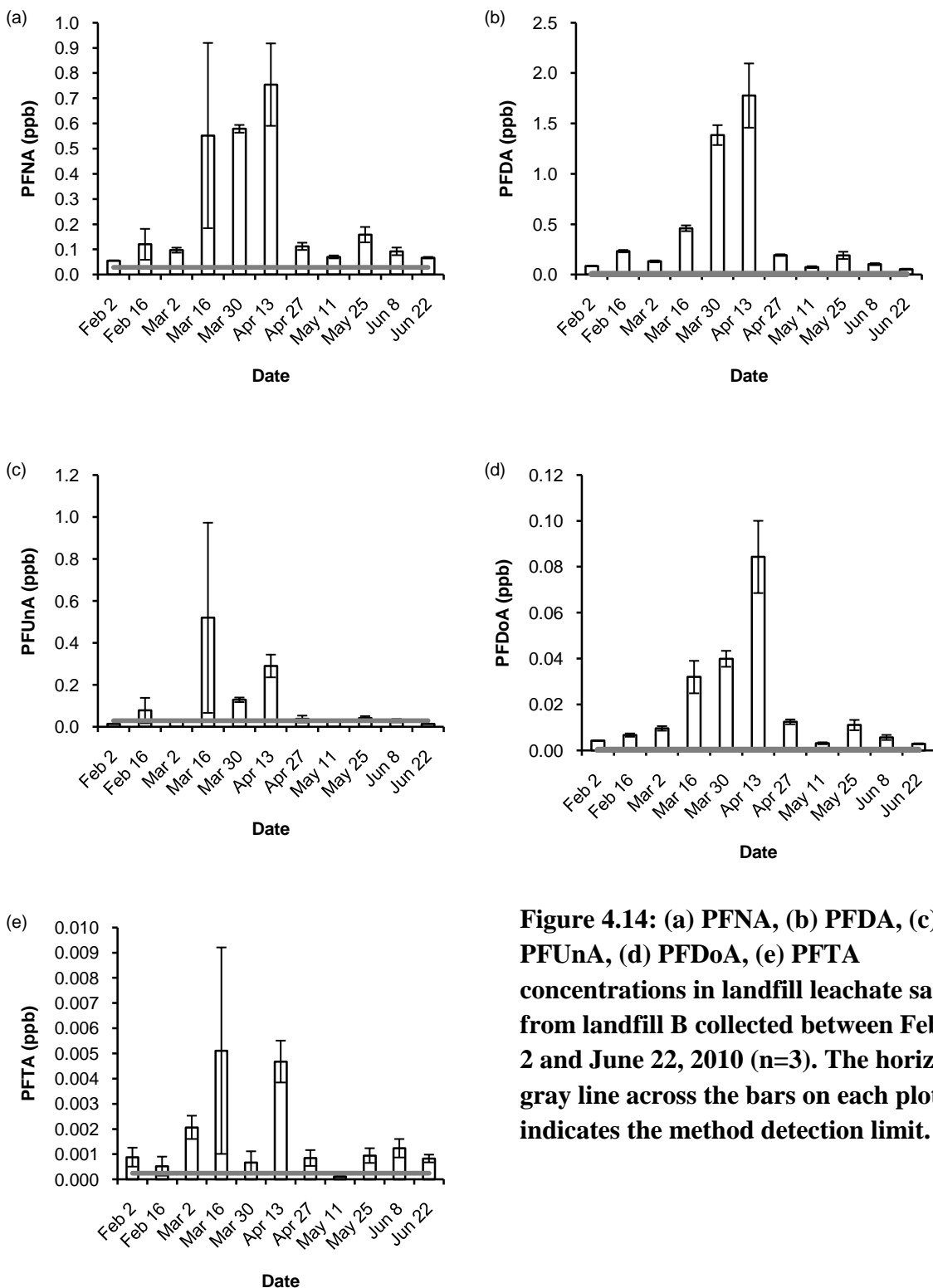


Figure 4.14: (a) PFNA, (b) PFDA, (c) PFUnA, (d) PFDoA, (e) PFTA concentrations in landfill leachate samples from landfill B collected between February 2 and June 22, 2010 (n=3). The horizontal gray line across the bars on each plot indicates the method detection limit.

4.4.2.4. PFSA

The concentrations of the PFSAAs are plotted in Figure 4.15. PFHxS and PFOS increased in a similar way to PFOA, PFNA, PFDA, and PFDoA from March 16 to April 13, again likely due to precursor degradation, as discussed in section 4.4.2.9. However, the concentrations of PFHxS for the same time period were not much higher than for the other sampling periods. PFBS exhibited a similar pattern to PFOS and PFHxS, but lagged by two weeks such that it increased substantially from March 30 to April 27. PFDS, on the other hand, was not detected from March 16 to April 27 when most of the other compounds were at their highest concentrations. The highest PFDS concentration was on February 16, the date where the lowest concentrations were present for most of the other compounds of interest. From these observations, it is clear that PFDS behaves very differently from the other PFSAAs. One would expect PFOS to be present in the highest concentrations as it is a degradation product of PFOSA (Prevedouros et al., 2006, D'eon & Mabury, 2011), and indeed PFOS was the dominant PFSA (mean concentration 0.72 ppb), followed by PFHxS (mean concentration 0.31 ppb), PFBS (mean concentration 0.06 ppb), and PFDS (mean concentration 0.001 ppb).

Most of the spreads in error bars in Figure 4.15 are relatively small compared to the analyte concentrations, indicating good reproducibility of the extraction and analytical method. For PFDS, the spreads in error bars were larger, sometimes exceeding 100% of the analyte concentration. Only about half of the samples were above MDLs for PFDS. It appears that the extraction and analytical method for PFDS was not as consistent as for the other analytes. The analyte concentrations for PFBS, PFHxS, and PFOS were well above the method detection limits (MDLs), by one to three orders of magnitude.

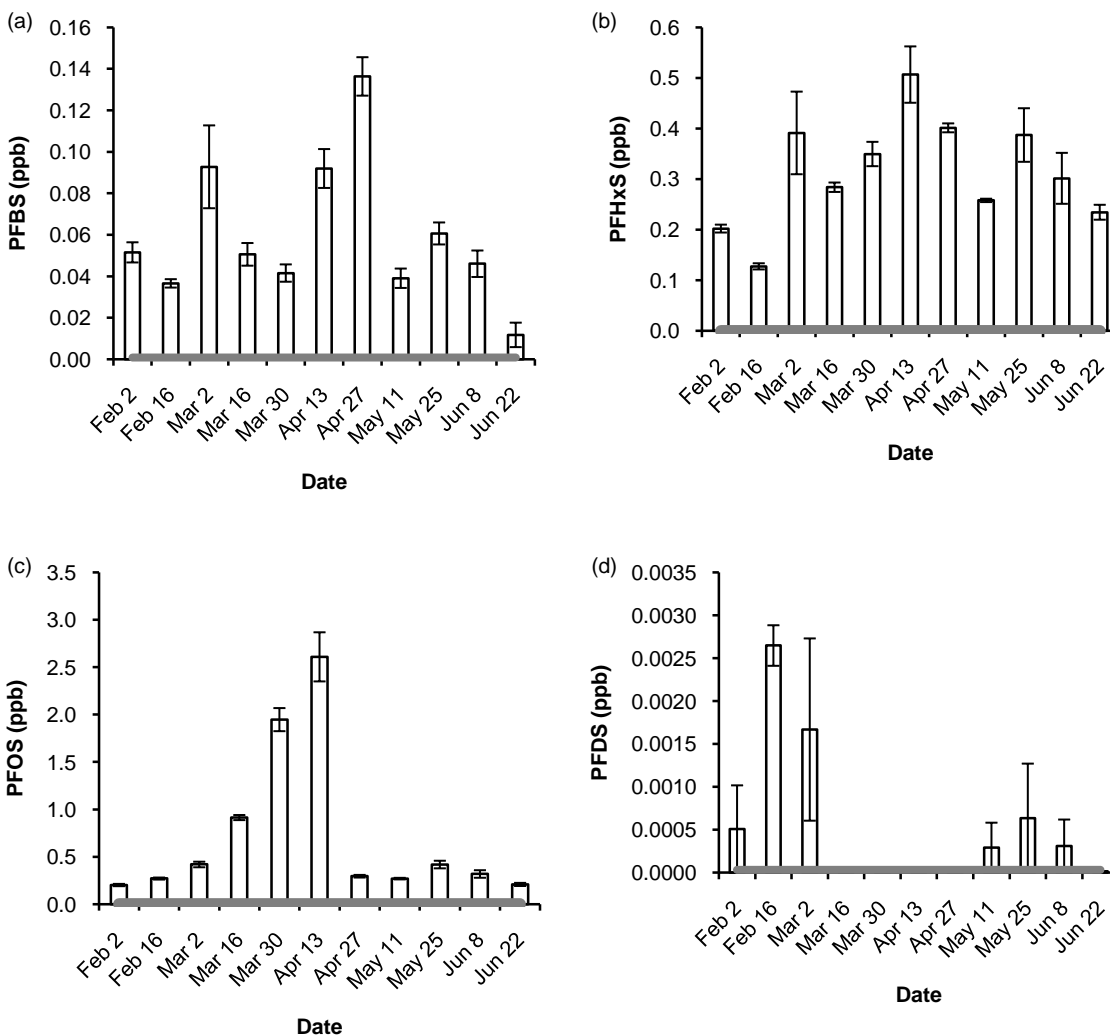


Figure 4.15: (a) PFBS, (b) PFHxS, (c) PFOS, (d) PFDS concentrations in landfill leachate samples from landfill B collected between February 2 and June 22, 2010 (n=3). The horizontal gray line across the bars on each plot indicates the method detection limit.

4.4.2.5. FOSA and FTUA

As only one FOSA was analyzed in these samples (PFOSA) and both FOSA and FTUA are precursors to the other analytes and with similar concentration profiles, these precursors are discussed together in this section.

The concentrations of the PFOSA and the FTUAs are plotted in Figure 4.16. 8:2 FTUA was the dominant precursor (mean concentration 0.33 ppb), especially for the sample drawn on April 13

where it was present at 2.5 ppb, almost ten times its mean concentration. 10:2 FTUA was the next highest precursor (mean concentration 0.17 ppb), followed by PFOSA (mean concentration 0.03 ppb), and 6:2 FTUA (mean concentration 0.008 ppb). All precursors increased by more than 200% from March 16 to April 13. These increased concentrations of PFOSA and FTUAs may have been caused by an abrupt change in landfill conditions during that time period. For example, sudden changes in precipitation may influence the transport and transformation of contaminants, as well as physical and chemical characteristics of leachate (Trankler et al., 2005, Wreford et al., 2000). Potential factors that might explain this increase, including rainfall, are discussed in sections 4.4.2.6 to 4.4.2.8. Correlations of PFOSA and FTUAs with leachate parameters monitored in this study were weak. Therefore, based on the data available, the exact cause of the increase of PFOSA and FTUAs from March 16 to April 13 is unknown. Aside from the March 16 to April 13 period, the precursor concentrations were relatively constant. To improve interpretation of PFC data in future studies, it is recommended that leachate samples be collected over a longer period of time, that they be analyzed for more parameters (e.g. other contaminants, biochemical oxygen demand), and that more landfill conditions (e.g. temperature, leachate flow rate) be monitored.

Most of the spreads in error bars in Figure 4.16 are relatively small compared to the analyte concentrations, indicating good reproducibility of the extraction and analytical method. Almost all analyte concentrations were well above method detection limits (MDLs), again by one to three orders of magnitude.

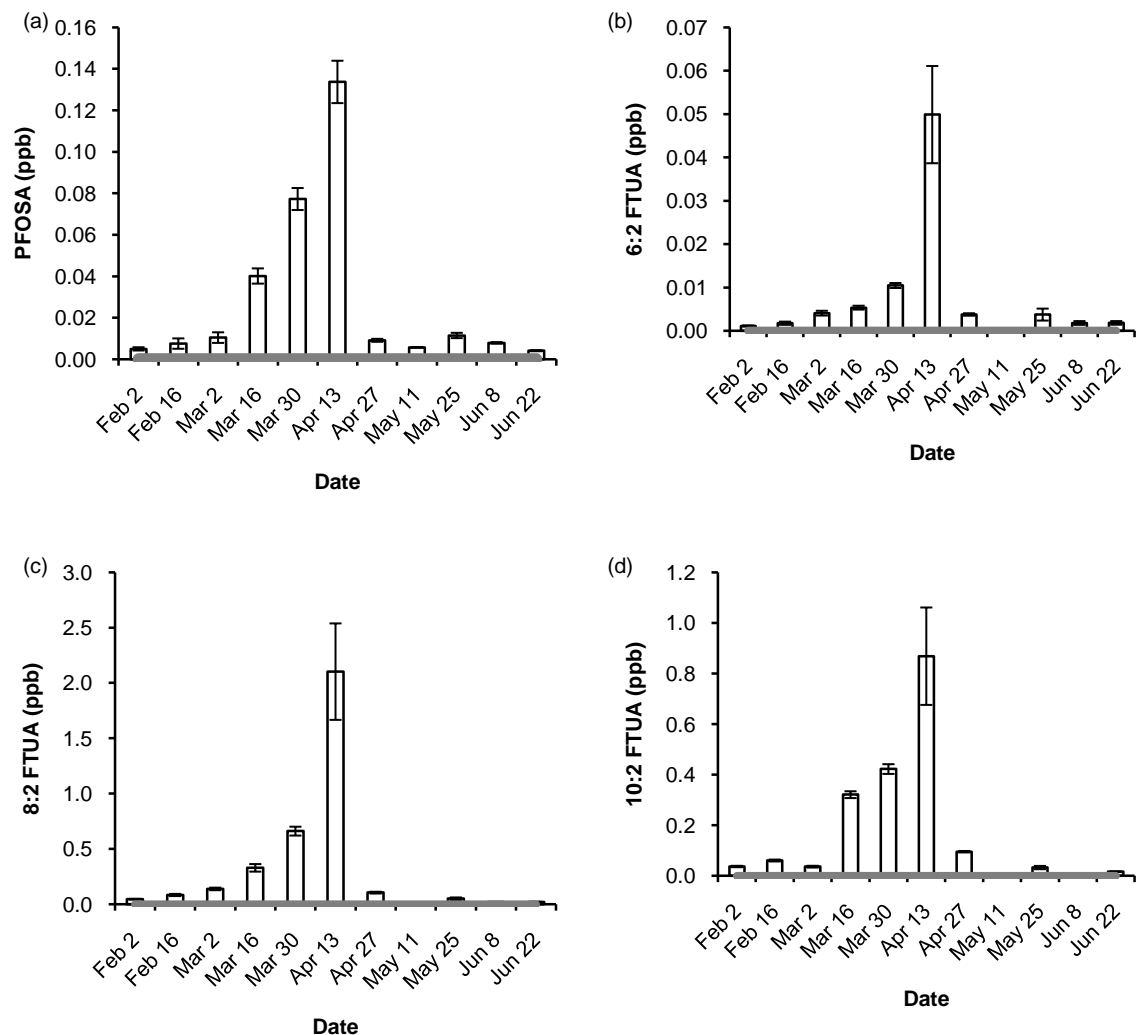


Figure 4.16: (a) PFOSA, (b) 6:2 FTUA, (c) 8:2 FTUA, (d) 10:2 FTUA concentrations in landfill leachate samples from landfill B collected between February 2 and June 22, 2010 (n=3). The horizontal gray line across the bars on each plot indicates the method detection limit.

4.4.2.6. Influence of total organic carbon

As discussed in section 4.2.4, PFCs are expected to have an affinity for organic carbon in landfill leachate. The correlation between the TOC and PFC concentrations was examined. The R^2 values between PFCs and TOC are listed in Appendix B, Table B.10. TOC data was unavailable for samples collected after April 27, so only data from February 2 to April 27 are plotted. Six of 18 compounds showed some correlation with total organic carbon (TOC) (Figure 4.17). These

were the shorter (<C7) chain PFCAs and PFSAs (PFBA, PFHxA, PFHpA, PFBS, and PFHxS). The correlations for these compounds were moderate to strong ($R^2 = 0.51$ to 0.78). PFBA had the highest correlation with TOC ($R^2 = 0.78$). Although PFPeA should also be in this group, it did not correlate with TOC (Figure 4.17 b). Its structure and properties are similar to PFBA and PFHxA, so it is unclear at this point why it does not behave like the other <C7 PFCAs and PFSAs. For all other PFCs, there were no clear correlations with TOC.

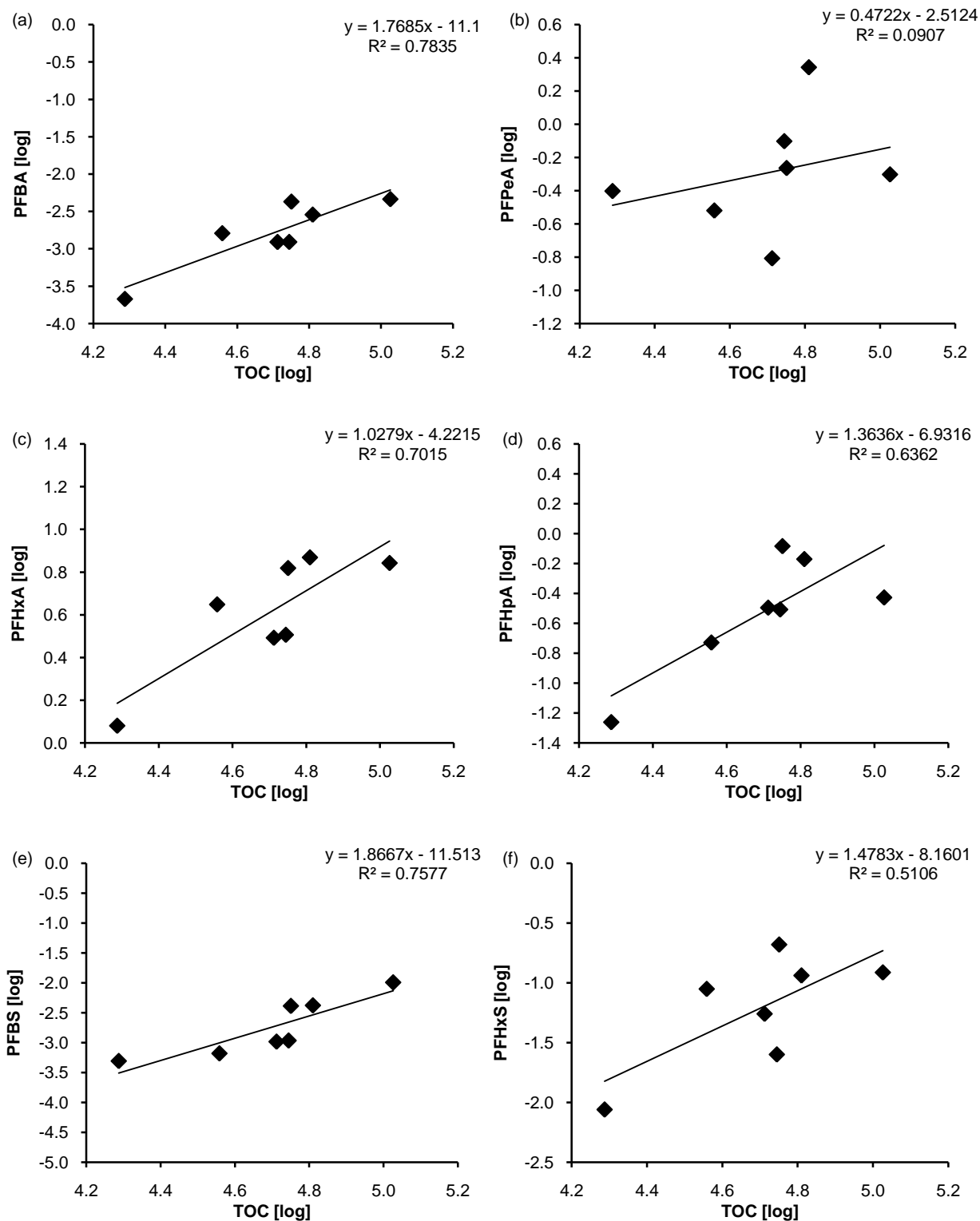


Figure 4.17: (a) PFBA, (b) PFPeA, (c) PFHxA, (d) PFHpA, (e) PFBS, (f) PFHxS versus total organic carbon in landfill leachate.

4.4.2.7. Influence of electrical conductivity

It was interesting that electrical conductivity (EC) and total organic carbon (TOC) are strongly correlated ($R^2 = 0.90$). The R^2 values between PFCs and EC are listed in Appendix B, Table B.10. Therefore, correlation of PFCs with EC was examined. Similar correlations were observed for EC with PFBA, PFHxA, and PFHpA (Figure 4.18 a, c, d). PFPeA did not correlate with EC (Figure 4.18 b). PFBS and PFHxS also did not correlate with EC (Figure 4.18 e, f), despite being moderately correlated with TOC. For all other PFCs, there were no obvious correlations with EC. EC is an indicator of salinity (APHA et al., 2005). Contrary to these results, other studies (Busch et al., 2010b, Sakurai et al., 2010) found that salinity was inversely correlated with PFCs in seawater. However, landfill leachate is a more complex matrix than seawater as it contains much more particulates and complex ions per unit volume which may affect the behaviour of PFCs.

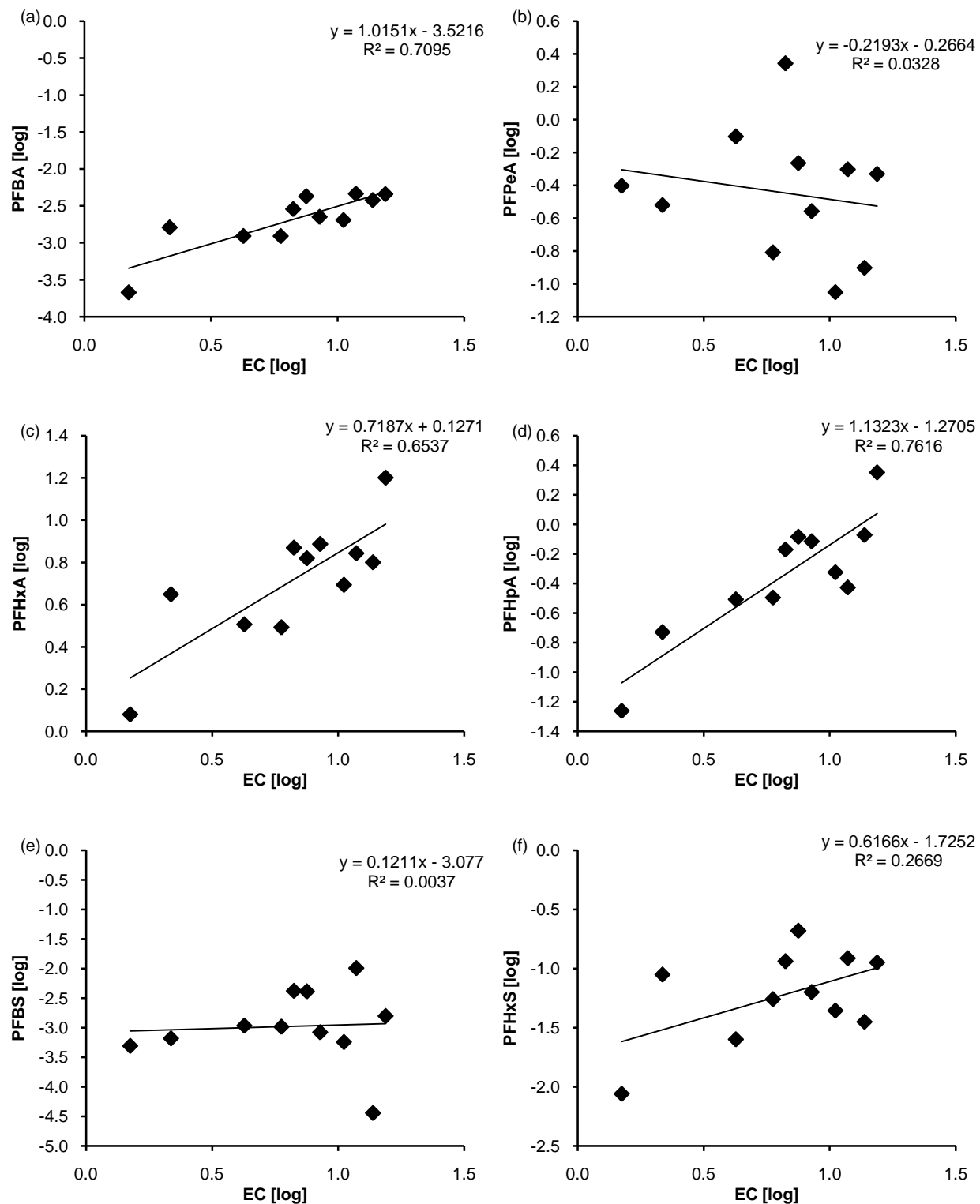


Figure 4.18: (a) PFBA, (b) PFPeA, (c) PFHxA, (d) PFHpA, (e) PFBS, (f) PFBS versus electrical conductivity in landfill leachate.

4.4.2.8. Influence of rainfall

Precipitation has a large effect on the quality of landfill leachate as it influences the transport and transformation of contaminants, as well as physical and chemical characteristics (Trankler et al., 2005, Wreford et al., 2000). For PFCs, precipitation could cause dilution in landfill leachate and hydrolysis of precursors, increasing PFC concentrations (Russell et al., 2008). Correlations between total rainfall 24 h prior to sampling and PFCs were examined. The R^2 values between PFCs and rainfall are listed in Appendix B, Table B.10. Log-log comparisons cannot be formed with data containing zeros (no rainfall within 24 h prior to sampling). As there was no rainfall in the 24 h period before some of the sampling trips, the data were compared without log transformations. There was little correlation between PFCs and rainfall ($R^2 < 0.25$). Correlations between total rainfall 14 days prior to sampling and PFCs were also examined as this allowed the data to be compared on log-log axes since there were no 14-day periods without rainfall. Again, there was little correlation between PFCs and rainfall ($R^2 < 0.26$). Since rainfall varies with seasons, the five-months of data obtained from this study may not be enough to determine the influence of rainfall on PFCs in landfill leachate. Long-term monitoring of PFCs in landfill leachate and rainfall (e.g. over at least one year) is recommended to capture seasonal variations in the data set.

4.4.2.9. Correlations with precursors

FTUAs are precursors to PFCAs, whereas FOSAs are precursors to PFSAAs (Prevedouros et al., 2006). Degradation pathways are complex as they can involve multiple steps, as discussed in 2.6. The major products of the degradation of precursor compounds are those with the same carbon length (e.g. 6:2 FTUA to PFHxA, 8:2 FTUA to PFOA, 10:2 FTUA to PFDA, and PFOSA to PFOS). The correlations between precursor compounds and their corresponding end-products were examined and are plotted in Figure 4.19. The R^2 values between precursors and their corresponding degradation products are listed in Table B.10 of Appendix B. PFOS and PFOSA were very strongly correlated ($R^2 = 0.98$), indicating that precursor degradation was the likely source of the large amount of PFOS in the samples from March 16 to April 13. PFDA and 10:2 FTUA were also strongly correlated ($R^2 = 0.86$). PFOA and 8:2 FTUA were moderately

correlated ($R^2 = 0.38$), whereas PFHxA and 6:2 FTUA were uncorrelated ($R^2 = 0.03$). These correlations provide some indication of the source of PFCs. As discussed in section 4.4.2.3, PFDA is not intentionally manufactured for commercial applications. This is also the case for PFOS, as only its precursors are used commercially (Prevedouros et al., 2006). Therefore, the likely primary source of PFDA and PFOS was precursor degradation. PFOA and PFHxA, on the other hand, are commercial products. PFOA and PFHxA could therefore originate from precursor degradation as well as from direct release from materials containing these compounds. As a result, PFOA and PFHxA were not as well correlated to their precursors as PFDA and PFOS. Since PFOA was moderately correlated with 8:2 FTUA, it appears that direct release and precursor degradation both played a role in its presence in landfill leachate. Direct release was likely the dominant contributor of PFHxA in landfill leachate, as it is uncorrelated with 6:2 FTUA. To improve elucidation of sources (direct versus degradation) of PFCs in landfill leachate, future work should examine PFC temporal trends over a longer time and include the analysis of other precursors and potential commercial products.

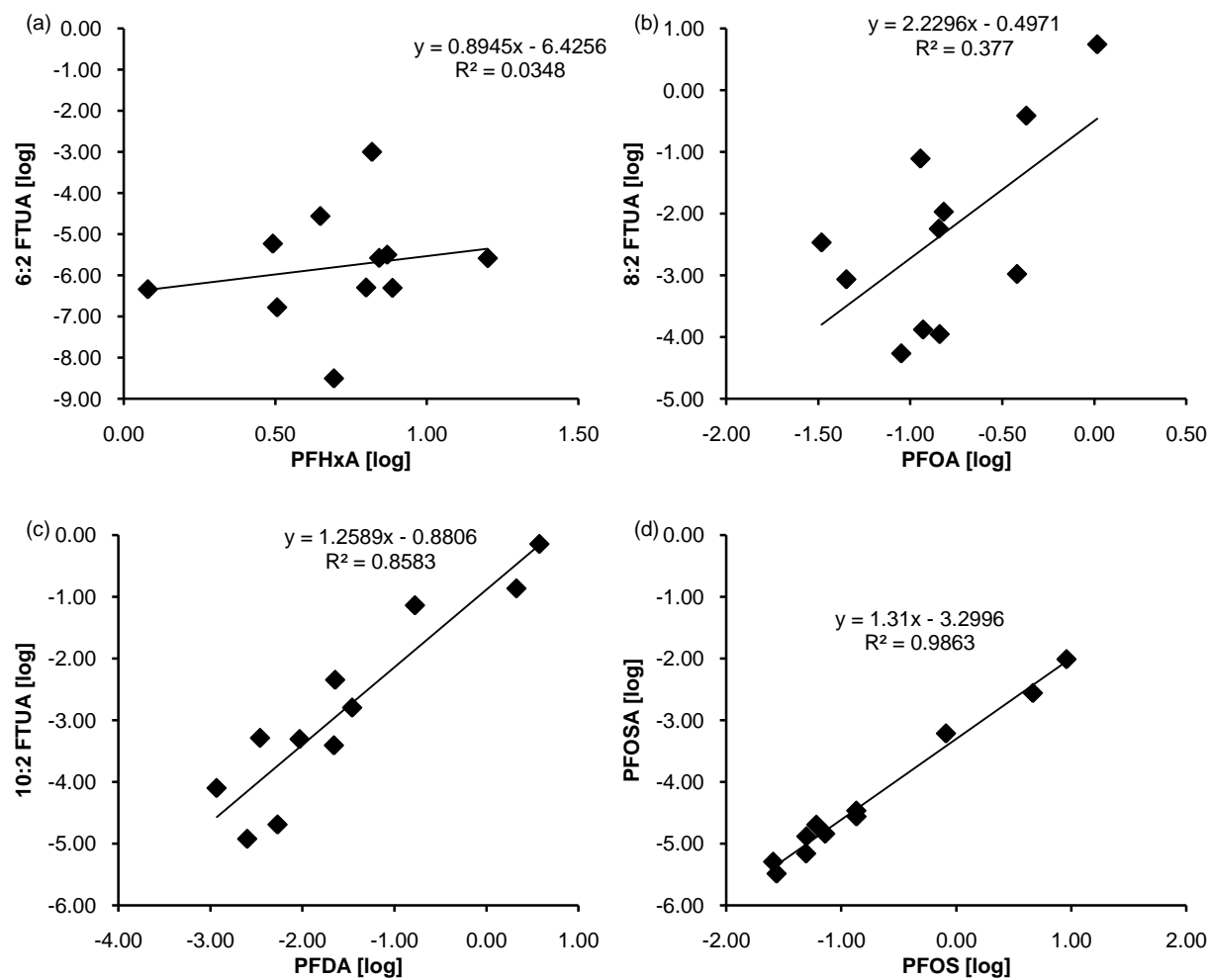


Figure 4.19: Precursor compounds versus major end-products for (a) 6:2 FTUA vs PFHxA, (b) 8:2 FTUA vs PFOA, (c) 10:2 FTUA vs PFDA, (d) PFOSA vs PFOS in landfill leachate.

Chapter 5: Batch adsorption test

5.1 Batch adsorption test results

The methodology for the batch adsorption tests discussed below is described in section 3.4. Data tables of PFC concentrations for this section are provided in Appendix D.

5.1.1 Group A results

There was little difference in the final concentrations (after 24 h of contacting) of PFCs in the control versus test experiments for Group A in experiments 1 (spiked leachate and bentonite) (Figure 5.1) and 2 (spiked water and bentonite) (Figure 5.2). The only statistically significant ($p < 0.05$) differences were observed for PFDA in both experiments. However, these differences were only 8% and 3% respectively. Overall, there was good agreement between replicates (mean relative standard deviation (RSD) 6%). From the negligible changes in PFC concentrations between the control (no bentonite) and test (with bentonite) experiments, PFCs in landfill leachate do not appear to bind to bentonite. The average spike recoveries (amount of PFC quantified through LC/MS/MS from the initial PFC spike) in the control experiments of landfill leachate and water were generally close (mean recovery 84%) to the expected concentration of 10 ppb. For PFHxA, PFOA, PFNA, and PFDA, the recovery was from 80 to 108%, indicating satisfactory accuracy. The recovery of PFOS was 65%, which is still acceptable for the LC/MS/MS method. PFBA had an unexpectedly low (26%) recovery, despite having good reproducibility (mean RSD 5%). This discrepancy may have been caused by an error in the concentration of the PFBA standard used to spike the leachate. Unfortunately, it was not possible to verify the concentration of the standard as it was no longer available for purchase.

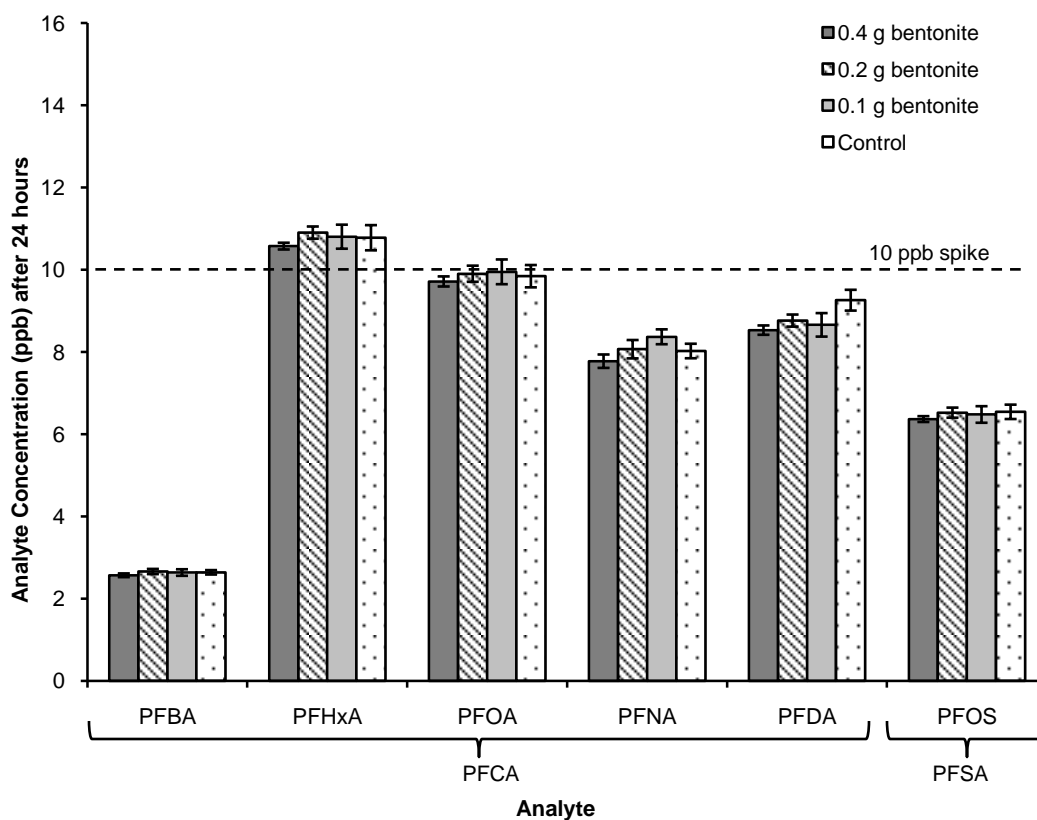


Figure 5.1: PFC concentrations in Group A after 24 h of contacting time in experiment 1 (spiked leachate and bentonite). Error bars denote standard error of the mean (n=4). Analytes are grouped by sub-class and arranged in order of increasing molecular weight.

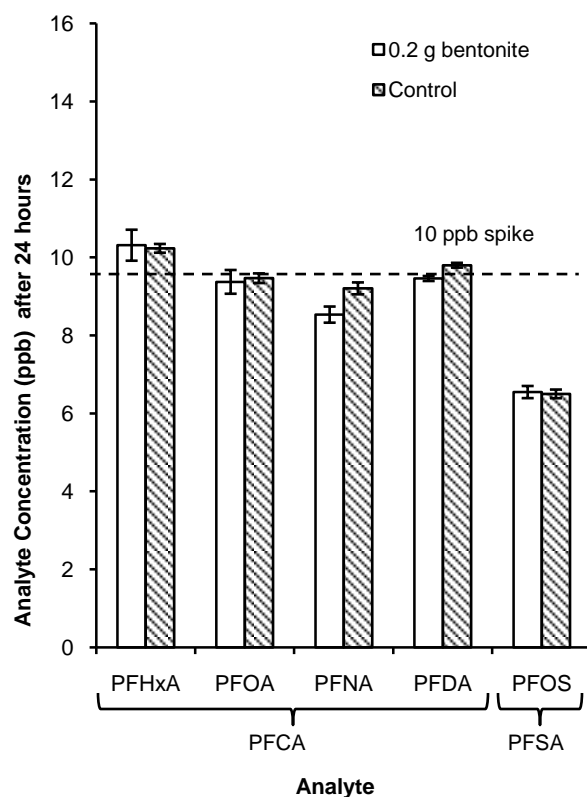


Figure 5.2: PFC concentrations in Group A after 24 h of contacting time in experiment 2 (spiked water and bentonite). Error bars denote standard error of the mean (n=3). Analytes are grouped by sub-class and arranged in order of increasing molecular weight.

5.1.2 Group B results

There were no statistically significant ($p < 0.05$) differences between control and test experiments for Group B in experiment 1 (spiked leachate and bentonite) (Figure 5.3) and experiment 2 (spiked water and bentonite) (Figure 5.4). There was more variation (mean RSD 22% vs. 6%) in the PFC concentrations overall for Group B than for Group A. However, this variation is still considered to be acceptable for a preliminary study. The spike recoveries were also lower (mean recovery 61%) in the control experiments. Even with these lower recoveries, it is clear that sodium bentonite does not appreciably remove PFCs from landfill leachate. One interesting observation was a clear trend of decreasing spike recoveries with larger analytes (by molecular weight) in the control experiments, particularly for the PFCAs. The mean spike

recovery dropped from 109% for PFPeA to 1% for PFTA. This is discussed further in section 5.3 below.

Matrix effects are a likely cause for the lower accuracy observed for Group B compared to Group A. Matrix effects, interferences caused by other components of a matrix on the quantification of an analyte, may decrease accuracy when quantifying PFCs in complex matrices (van Leeuwen et al., 2009, Li et al., 2009). Landfill leachate is a very complex matrix because it contains many organic and inorganic compounds which may enhance or suppress ionization during LC/MS/MS analysis. During sample processing, all samples were filtered with a 0.22 µm polypropylene filter. However, they were not cleaned up using a method such as solid phase extraction or Envi-Carb, which remove interfering compounds. Therefore, interferences from other landfill leachate compounds may still be present. Mass-labelled internal standards compensate for undesirable matrix effects as they behave in the same way as their corresponding compounds. Corresponding mass-labelled internal standards were not available for Group B analytes, so matrix effects were expected to have a larger effect on the results. Furthermore, van Leeuwen et al. (2009) noted that matrix effects are more pronounced at lower concentrations (e.g. 5 ppb), the relevant range for these experiments.

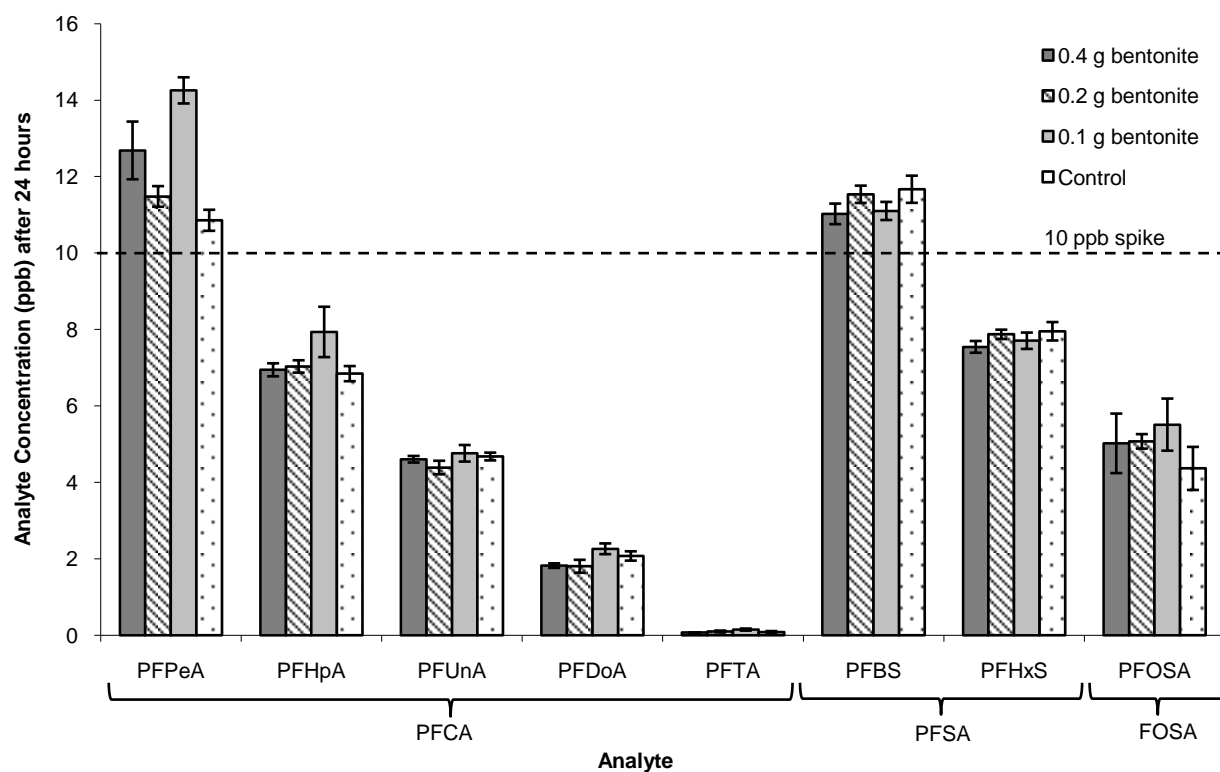


Figure 5.3: PFC concentrations in Group B after 24 h of contacting time in experiment 1 (spiked leachate and bentonite). Error bars denote standard error of the mean (n=4). Analytes are grouped by sub-class and arranged in order of increasing molecular weight.

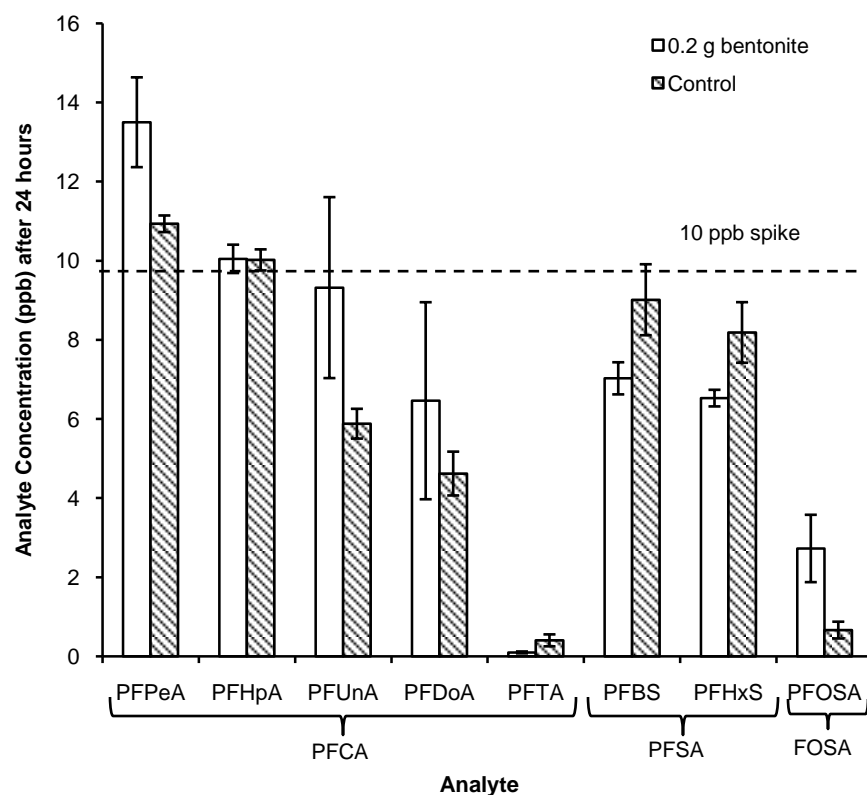


Figure 5.4: PFC concentrations in Group B after 24 h of contacting time in experiment 2 (spiked water and bentonite). Error bars denote the standard error of the mean (n=3). Analytes are grouped by sub-class and arranged in order of increasing molecular weight.

5.1.3 Single PFCs

There were no statistically significant ($p < 0.05$) differences between control and test experiments for experiment 3 (spiked leachate and bentonite) (Figure 5.5) and experiment 4 (spiked water and bentonite) (Figure 5.6). Overall, there was good agreement between replicates in both experiments (mean RSD 5%). PFCs in landfill leachate and water do not appear to bind to bentonite as the differences in PFC concentrations between the control (no bentonite) and test (with bentonite) experiments were negligible. The mean spike recoveries were generally higher than the expected concentration of 10 ppb for all PFCs except for PFBA. Mean spike recoveries for PFHxA, PFOA, and PFOS were from 106-132%. The mean spike recovery for PFBS in water was still satisfactory (138%), considering that PFBS does not have a corresponding mass-labelled quantification standard, so variations are expected to be higher. The mean spike

recovery for PFBS in landfill leachate was 215%, indicating potential matrix effects on the accuracy of the quantification method as discussed in section 5.1.2. Similar to experiment 1, PFBA had a low (27 to 29%) recovery, despite having good reproducibility (mean RSD 3%). Again, this may have been caused by an error in the concentration of the PFBA standard used to spike the leachate or water.

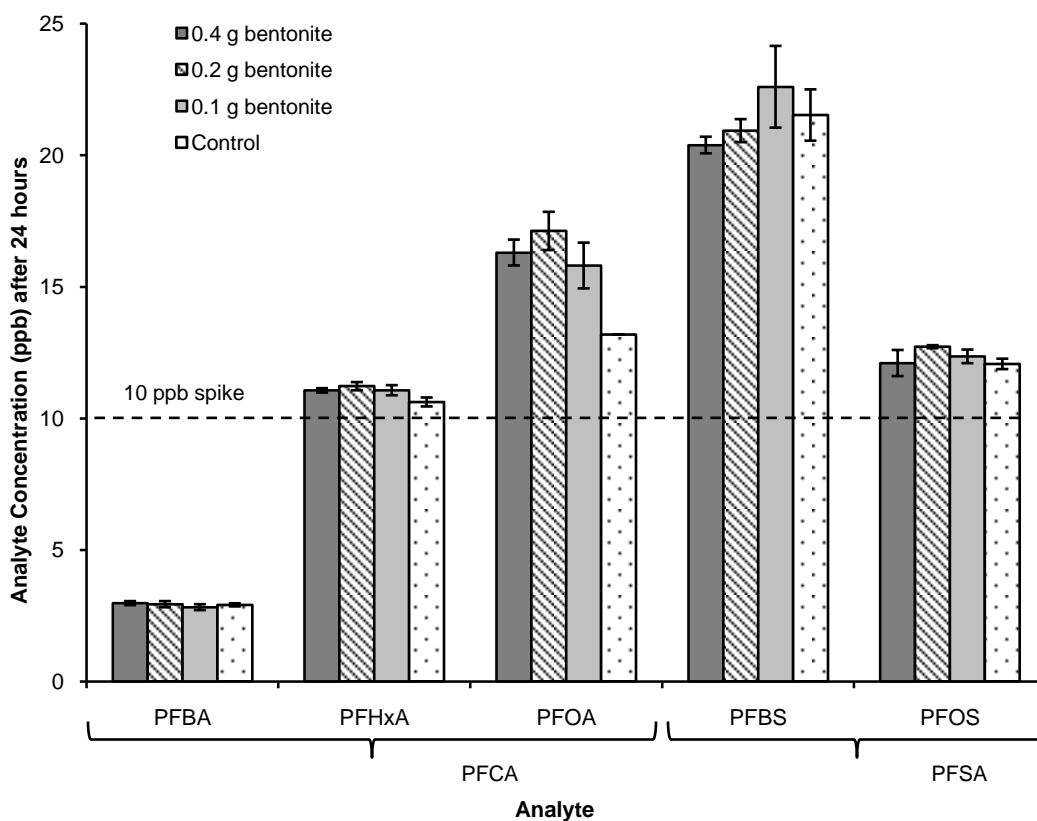


Figure 5.5: PFC concentrations after 24 h of contacting time in experiment 3 (spiked leachate and bentonite). Error bars denote the standard error of the mean (n=3). Analytes are grouped by sub-class and arranged in order of increasing molecular weight.

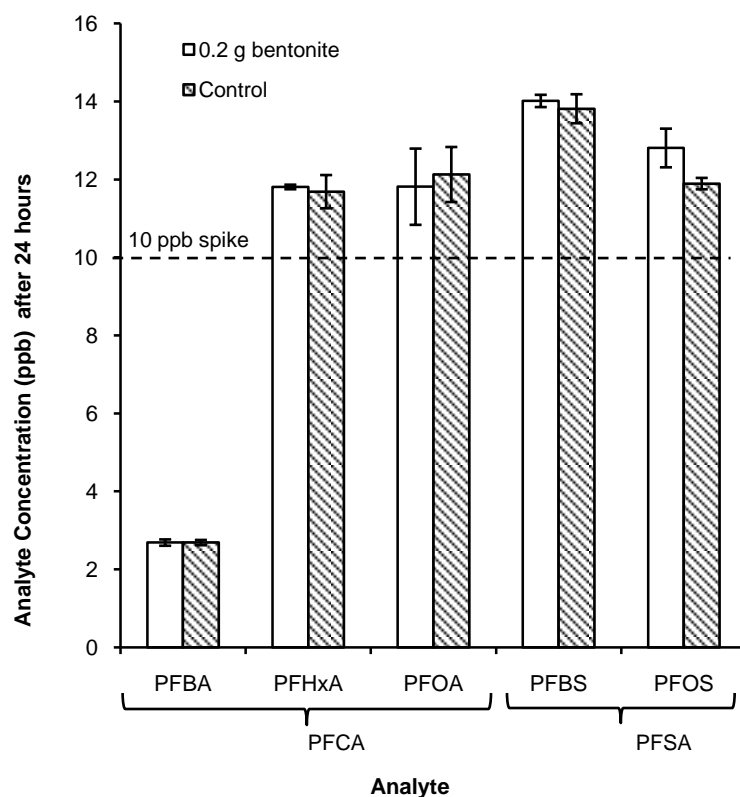


Figure 5.6: PFC concentrations after 24 h of contacting time in experiment 4 (spiked water and bentonite). Error bars denote the standard error of the mean (n=3). Analytes are grouped by sub-class and arranged in order of increasing molecular weight.

5.1.4 Mixture of PFCs versus single PFCs

The results from experiments 1 and 2 (mixture of PFCs) were compared with experiments 3 and 4 (single PFCs) to determine whether a mixture of PFCs would influence the sorption of PFCs on sodium bentonite. In a similar study (Li, 1999) on the sorption of metals on sodium bentonite, when a mixture of metals was used in the batch adsorption test solution, there was competition for sorption sites between the various metals species. In the case of PFCs in both landfill leachate and water, there does not appear to be competition between the analytes for sorption sites since the differences in concentrations between the control and test experiments were statistically insignificant ($p < 0.05$) in all cases.

There were variations in PFC concentrations when using a mixture of PFCs compared with single PFCs, depending on the analyte and matrix. The percent differences between the mixture of PFCs and single PFCs for landfill leachate (experiments 1 and 3) and water (experiments 2 and 4) are shown in Tables 5.1 and 5.2, respectively. The percent differences were calculated as the difference in PFC concentrations divided by the mean concentrations between the two experiments. In landfill leachate, the percent difference for PFBA and PFHxA were no more than 15% indicating good reproducibility. In water, PFHxA and PFOA were satisfactory in reproducibility, with percent differences less than 25%. PFBA could not be compared in water as it was added to the PFC solution in experiment 2. For the other compounds (PFBS and PFOS in both matrices, PFOA in landfill leachate), the concentrations differed substantially between the experiments, with the percent differences ranging from 41 to 68% and 37 to 66% in landfill leachate and water respectively for PFBS and PFOS. For PFOA in landfill leachate, the percent difference was 29 to 53%.

Despite these differences in the PFC concentrations between the experiments, as discussed in sections 5.1.1 to 5.1.3, the results still indicate that PFCs do not appear to bind to sodium bentonite, regardless of whether a mixture of PFCs or single PFCs were utilized in the batch adsorption tests.

Table 5.1: Comparison of PFC concentrations after 24 h of contacting time in experiments 1 and 3 (landfill leachate).

PFC		Condition			
		0.4 g bentonite	0.2 g bentonite	0.1 g bentonite	Control (no bentonite)
PFBA	Experiment 1 (ppb)	2.57	2.66	2.64	2.64
	Experiment 3 (ppb)	2.97	2.93	2.82	2.91
	% Difference	15%	10%	7%	10%
PFHxA	Experiment 1 (ppb)	10.58	10.90	10.81	10.78
	Experiment 3 (ppb)	11.06	11.22	11.07	10.62
	% Difference	4%	3%	2%	1%
PFOA	Experiment 1 (ppb)	9.72	9.90	9.95	9.84
	Experiment 3 (ppb)	16.30	17.12	15.81	13.18
	% Difference	51%	53%	45%	29%
PFBS	Experiment 1 (ppb)	11.02	11.54	11.10	11.67
	Experiment 3 (ppb)	20.39	20.93	22.60	21.53
	% Difference	60%	58%	68%	59%
PFOS	Experiment 1 (ppb)	7.54	7.87	7.71	7.95
	Experiment 3 (ppb)	12.10	12.72	12.35	12.07
	% Difference	46%	47%	46%	41%
Experiment 1: Mix of PFCs Experiment 3: Single PFCs					

Table 5.2: Comparison of PFC concentrations after 24 h of contacting time in experiments 2 and 4 (water).

PFC		Condition	
		0.2 g bentonite	Control (no bentonite)
PFBA	Experiment 2 (ppb)	N/A	N/A
	Experiment 4 (ppb)	2.69	2.69
	% Difference	N/A	N/A
PFHxA	Experiment 2 (ppb)	10.31	10.23
	Experiment 4 (ppb)	11.81	11.69
	% Difference	14%	13%
PFOA	Experiment 2 (ppb)	9.37	9.47
	Experiment 4 (ppb)	11.81	12.13
	% Difference	23%	25%
PFBS	Experiment 2 (ppb)	7.03	9.01
	Experiment 4 (ppb)	14.01	13.81
	% Difference	66%	42%
PFOS	Experiment 2 (ppb)	6.53	8.19
	Experiment 4 (ppb)	12.81	11.89
	% Difference	65%	37%
Experiment 2: Mix of PFCs Experiment 4: Single PFCs N/A: Not applicable			

5.2 Influence of surface charges

The results of BAT experiments in landfill leachate and water-spiked PFCs (mixture or single) led to no significant reduction in PFC concentrations after batch adsorption. The lack of PFCs sorption onto sodium bentonite was likely due to negative surface charges of PFCs. No published reports on the surface charge of perfluoroalkyl sulfonates could be found. However, as shown in structure diagrams (section 2.1, Figure 2.1), perfluoroalkyl sulfonates are negatively charged. Though perfluorocarboxylic acids and fluorotelomer unsaturated acids are used in acid form during manufacturing, once they are released to the environment, they are likely to be present in their anionic forms and thus negatively charged (i.e. to lose H and be left with O⁻ instead) (Goss, 2008). As indicated in section 3.4.2, the major component of sodium bentonite is montmorillonite, which has a negative surface charge. Like charges repel each other; therefore

the lack of sorption of PFCs onto sodium bentonite was likely due to negative surface charges of PFCs in the environment, preventing them from being sorbed onto the negatively-charged sodium bentonite liner.

5.3 PFCs in QA/QC rinse solutions

For the purpose of comparison, data from Groups A and B are combined in this section. PFC concentrations in all rinse solutions (landfill leachate for experiment 1, water for experiment 2) were below the 10 ppb PFC spike (Figures 5.7 and 5.8). PFC concentrations in the rinse solutions were generally lower in experiment 2 than in experiment 1. For experiment 2, HPLC water, which is expected to have no PFCs, was used as the rinsing solution; HPLC water is PFC-free as it is intended to make the mobile phase for the analytical instrument and calibration solutions. Landfill leachate, which was used as the rinsing solution for experiment 1 contains small amounts of PFCs, as shown in section 4.4.1. The amount of PFCs recovered in rinse landfill leachate and water is seen to have generally increased with increasing molecular weight of the analyte.

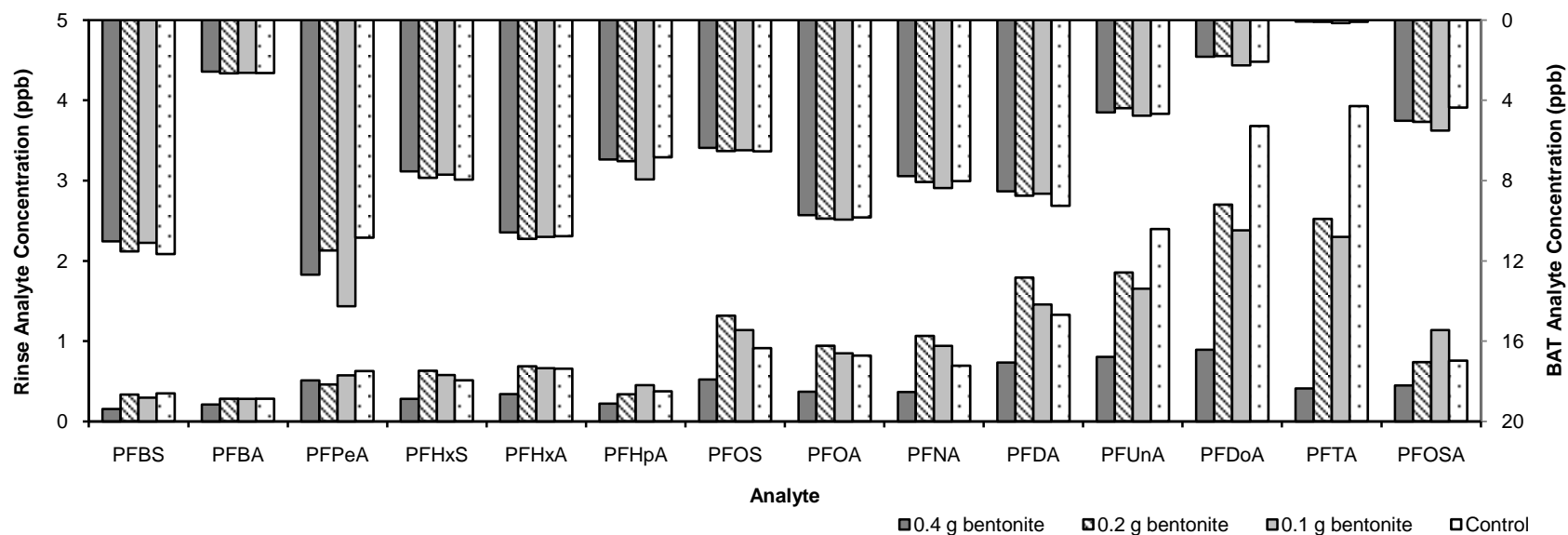


Figure 5.7: PFC concentrations in rinse solutions (bottom and left ordinate) compared to BATs (top and right ordinate) from experiment 1 (spiked leachate and bentonite). Analytes are ordered by increasing analyte molecular weight.

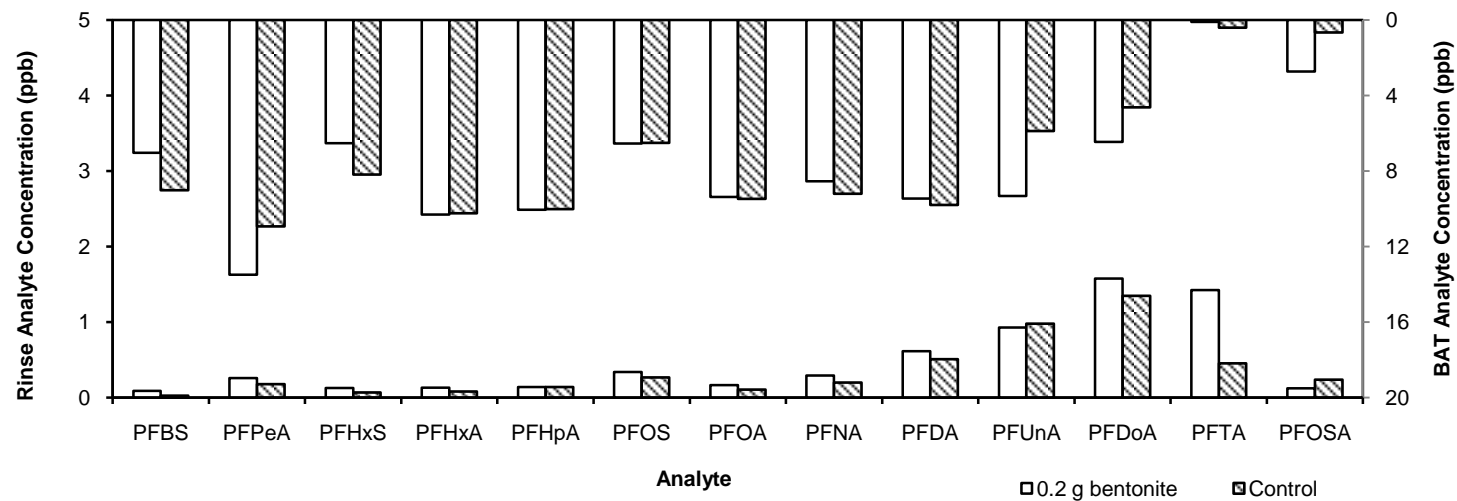


Figure 5.8: PFC concentrations in rinse solutions (bottom and left ordinate) compared to BATs (top and right ordinate) from experiment 2 (spiked water and bentonite). Analytes are arranged in order of increasing analyte molecular weight.

In the BAT results discussed in section 5.1, the spike recoveries of PFCs decreased as analyte molecular weight increased. It appears that some of the PFCs that were not recoverable in the BATs were found in the rinse solutions, generally in inverse amounts (i.e. if less was recovered in the BATs, more was recovered in the rinse solutions) (Figures 5.7 and 5.8). If the PFCs were binding to the polypropylene centrifuge tubes, then larger analytes were binding more than smaller analytes. Since polypropylene is a plastic and hydrocarbon-derived, PFCs with higher k_{oc} (measure of affinity to bind to organic carbon) would be expected to bind more to it. The organic carbon adsorption coefficients (k_{oc}) of PFCs generally increase with analyte molecular weight as discussed in 2.1. Overall, PFC concentrations in landfill leachate spiked recoveries (i.e. control experiments) are negatively correlated with k_{oc} (Figure 5.9). The two exceptions were PFBS, which had relatively low concentrations and low k_{oc} , and PFOSA, which has a much higher k_{oc} compared to similarly sized PFOS and PFOA analytes.

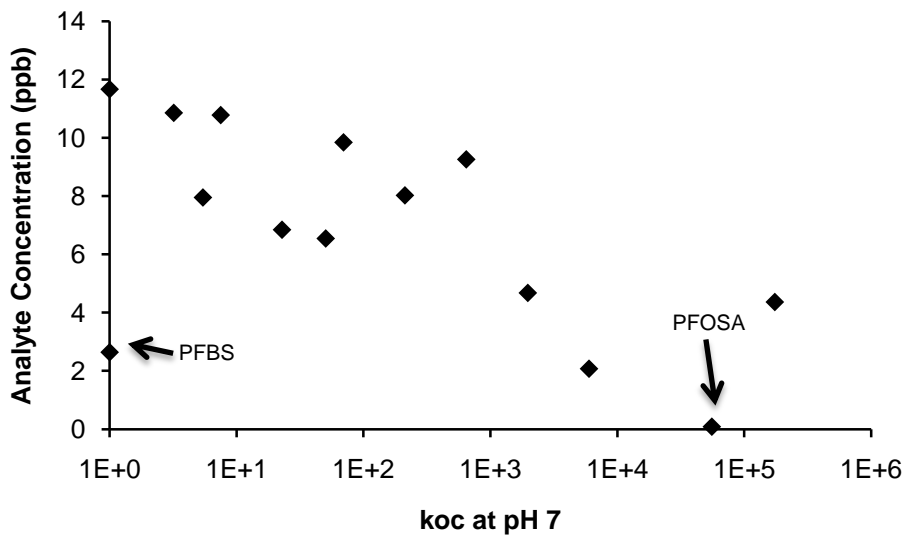


Figure 5.9: PFC concentration in landfill leachate (experiment 1 control) versus binding affinity (k_{oc}).

Chapter 6: Leaching cell test

6.1 Free swell test

The methodology for the free swell test is described in section 3.6.3. Sodium bentonite expanded by 30.5 mL/2 g in both unspiked and PFC spiked (10 ppb) distilled water. The swell indices were 26.5 mL/2 g and 27 mL/2 g for unspiked and PFC spiked (10 ppb) landfill leachate, respectively. The difference in swelling was negligible (< 2%) in landfill leachate and there was negligible difference in distilled water (Figure 6.1). There was more swelling in distilled water than in landfill leachate. This was due to the difference in dielectric constants between the two matrices, with the dielectric constant of distilled water being greater than that of landfill leachate (Lee et al., 2003). The swelling of clays decreases as the dielectric constant decreases (Green et al., 1983; Olgun & Yildiz, 2010). Since landfill leachate has a lower dielectric constant than distilled water, one would expect sodium bentonite to swell less in landfill leachate. The swelling potential of sodium bentonite is an indicator of hydraulic conductivity as more swelling leads to lower hydraulic conductivity. Since PFCs do not appear to change the swelling capacity of sodium bentonite, one would expect that its hydraulic conductivity would not be affected by the presence of PFCs.

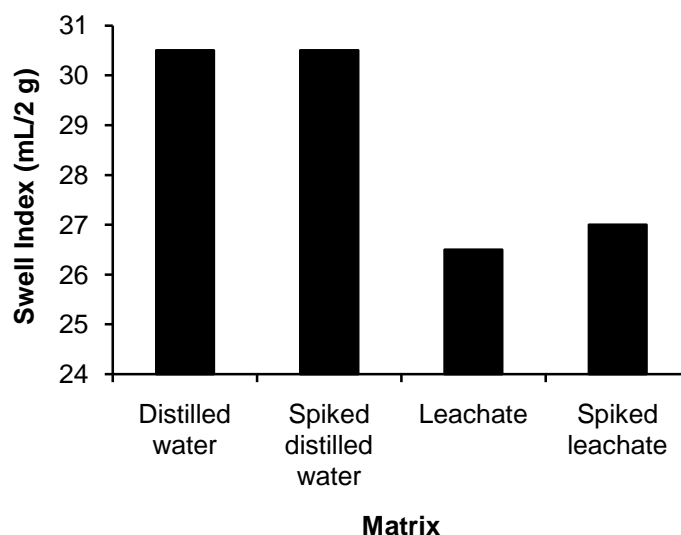


Figure 6.1: Comparison of swell indices of sodium bentonite in distilled water and landfill leachate with and without the addition of PFCs (10 ppb).

6.2 Flow rate and hydraulic conductivity in leaching cell tests

The methodology for the leaching cell tests discussed below is described in section 3.6. Data tables with the effluent volume and calculated hydraulic conductivities are in 0.

6.2.1 Tap water permeation through sand-bentonite admix

Over 72 days, 61 mL of effluent were collected from the leaching cell test. As illustrated in Figure 6.2, the flow rate was constant throughout the experiment, with a mean flow rate of 0.8 mL/d. After the acclimatization period, the pressure was held constant at 45 kPa, with the exception of day 22 where the pressure rose to 47 kPa and was subsequently adjusted back to 45 kPa. The constant flow rate indicates steady hydraulic conductivity (k); k only fluctuated between 7×10^{-10} and 2×10^{-9} cm/s (Figure 6.3), a minor difference, as hydraulic conductivities are typically compared on the scale of orders of magnitude. The mean k was 1×10^{-9} cm/s.

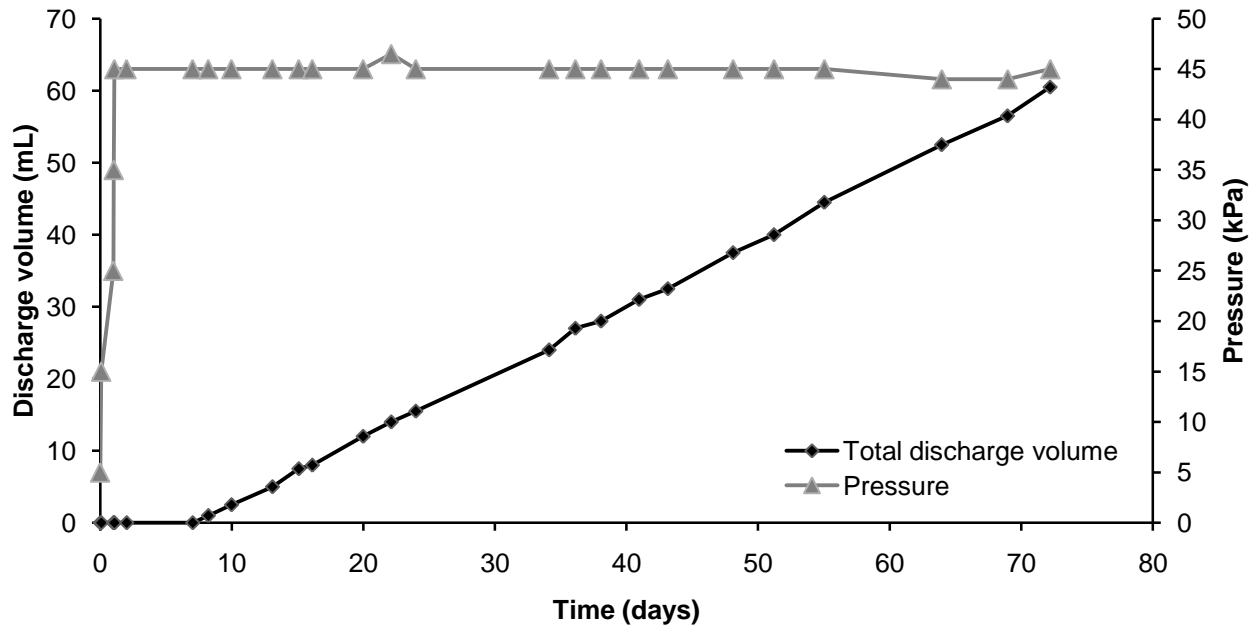


Figure 6.2: Total discharge volume and pressure for a leaching cell test with water permeating through sand-bentonite admix.

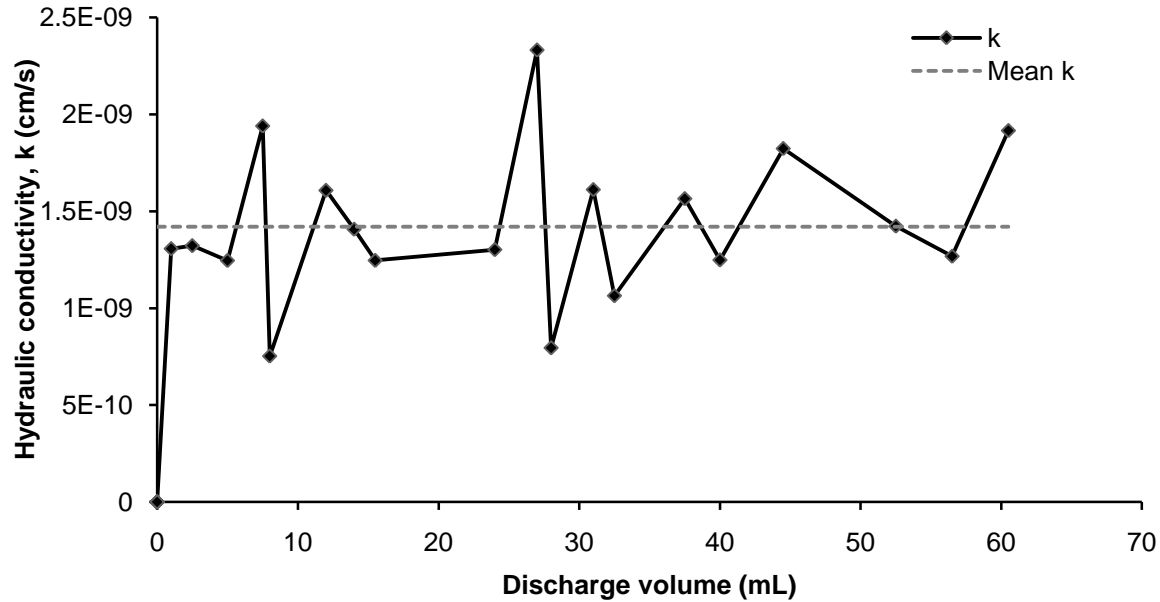


Figure 6.3: Hydraulic conductivity as a function of discharge volume for a leaching cell test, with water permeating through sand-bentonite admix.

6.2.2 Landfill leachate permeation through sand-bentonite admix

Over 84 days, 107 and 130 mL of effluent were collected from the replicate leaching cell tests. The flow rate was constant throughout the experiment until day ~68, when it began to increase (Figure 6.4). From day 0 to 68, the mean flow rate was 0.8 mL/d. From day 68 to 84, the mean flow rate increased to 4 mL/d. Due to the increase in flow rate, k also increased. k was initially nearly steady with minor fluctuations between 4×10^{-10} and 2×10^{-9} cm/s (Figure 6.5) until the discharge volume reached around 60 to 70 mL. After this, k increased and peaked at 2×10^{-8} to 3×10^{-8} cm/s at a discharge volume of 100 to 120 mL. k then decreased again, back to $\sim 1 \times 10^{-8}$ cm/s by the end of the experiment. The mean k for the entire experiment was 3×10^{-9} cm/s. As seen in Figures 6.4 and 6.5, there was good agreement between the two replicate experiments, indicating satisfactory reproducibility.

A possible reason for the sudden increase in k in the leaching cell tests is a sudden change in pressure. Although it appeared that the pressure was constant at 35 kPa after the acclimatization period, it is possible that during the experiment, the compressor which provided the air for the system may have turned off momentarily (e.g. due to a power interruption) and then restarted.

This would not have been tracked as pressure readings were only taken every few days. Such a sudden change in pressure may have caused the particles in the sand-bentonite admix to be rearranged, creating preferential flow paths. It is also possible for preferential flow paths to be created on their own, without a sudden pressure change. However, both leaching cells experienced a similar increase in k at around the same time. Therefore, an external factor that affects both leaching cells, such as a sudden pressure change, is likely to have caused the increase in hydraulic conductivity. The decrease in k at the end of the experiment may then have been due to blockage of the preferential flow paths created during the sudden rearrangement of particles in the sand-bentonite admix.

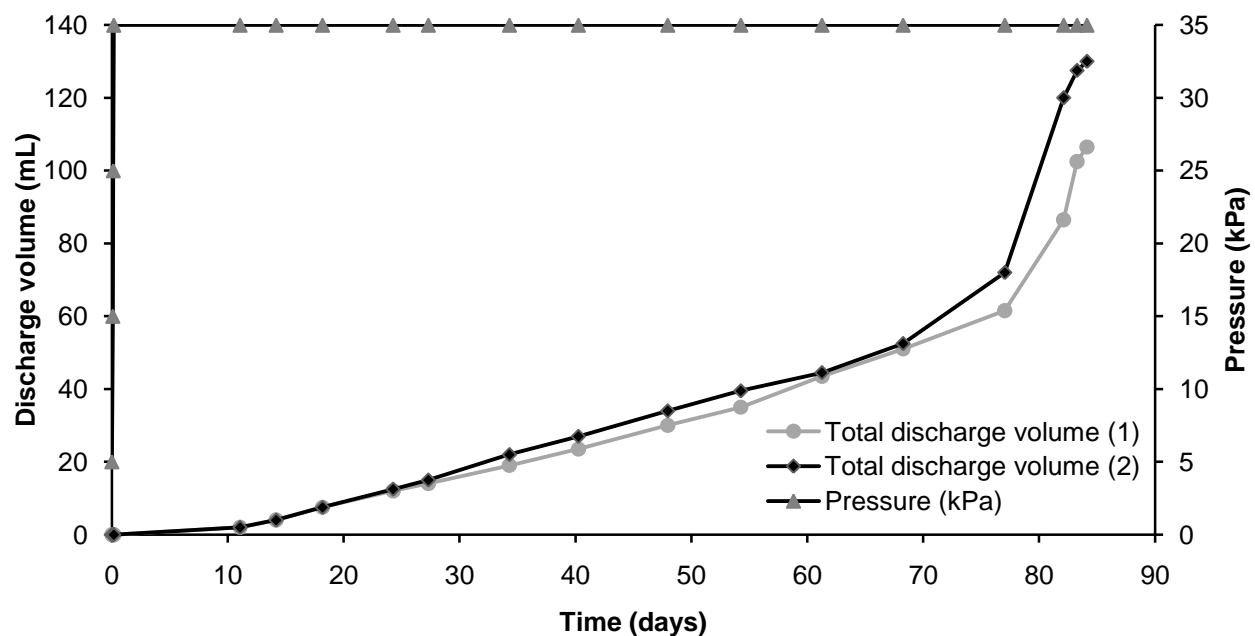


Figure 6.4: Total discharge volume and pressure for a leaching cell test with landfill leachate permeating through sand-bentonite admix.

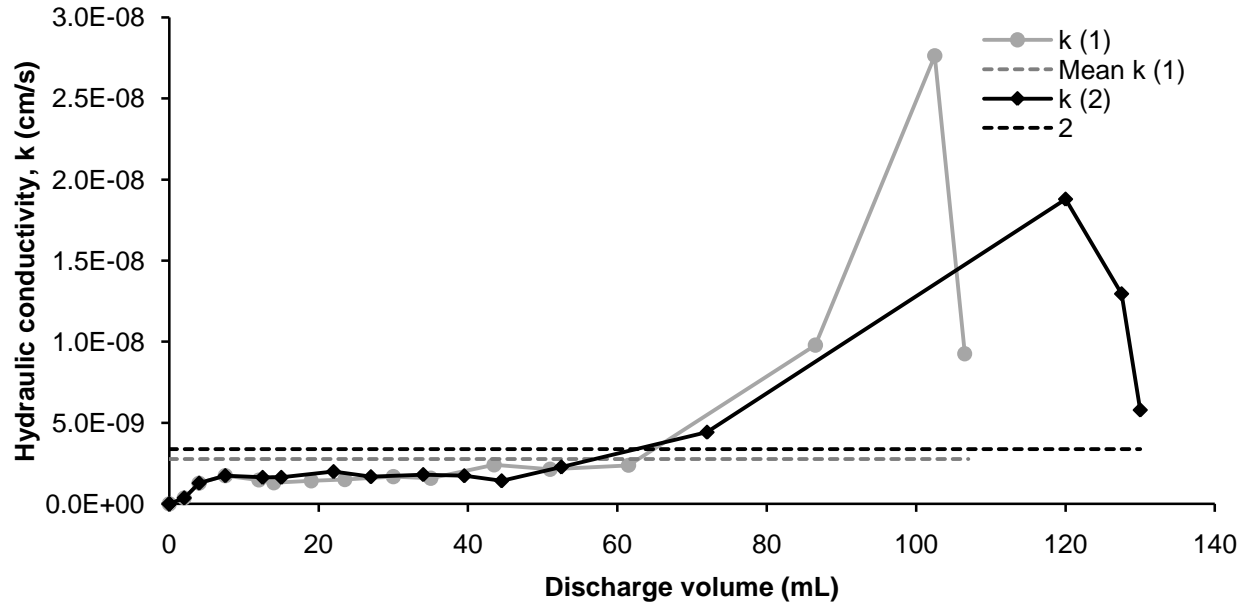


Figure 6.5: Hydraulic conductivity as a function of discharge volume for a leaching cell test, with landfill leachate permeating through sand-bentonite admix.

6.2.3 PFC-spiked landfill leachate permeation through sand-bentonite admix

Over 76 days, 40 and 38 mL of effluent were collected from the replicate leaching cell tests. The flow rates were constant throughout the experiment until around day 61, when the flow rates began to slowly decrease (Figure 6.6). From day 0 to 61, the mean flow rate was 0.5 mL/d, whereas from day 61 to 76, the mean flow rate decreased to 0.4 mL/d. Due to the failure of the air compressor on day 15, the pressure fluctuated greatly until day 23 when the compressor was repaired. While it was broken, compressed air cylinders provided pressure for the system. However, these did not contain enough air to last more than one or two days and had to be replaced when they became empty, leading to the multiple drops in pressure from days 15 to 23. Despite these changes in pressure from days 15 to 23 and small change in flow rate at the end of the experiment, k did not fluctuate much more than for the earlier leaching cell tests described above. k fluctuated between 2×10^{-10} and 2×10^{-9} cm/s (Figure 6.7), with a mean of 1×10^{-9} cm/s. As seen in Figures 6.6 and 6.7, there was good agreement between the two replicate experiments, indicating satisfactory reproducibility. Due to soil heterogeneities, hydraulic

conductivity is typically an order of magnitude estimation and usually presented with no more than one or two significant figures (Scalia & Benson, 2011, Eleftheriou & Costopoulos, 1997).

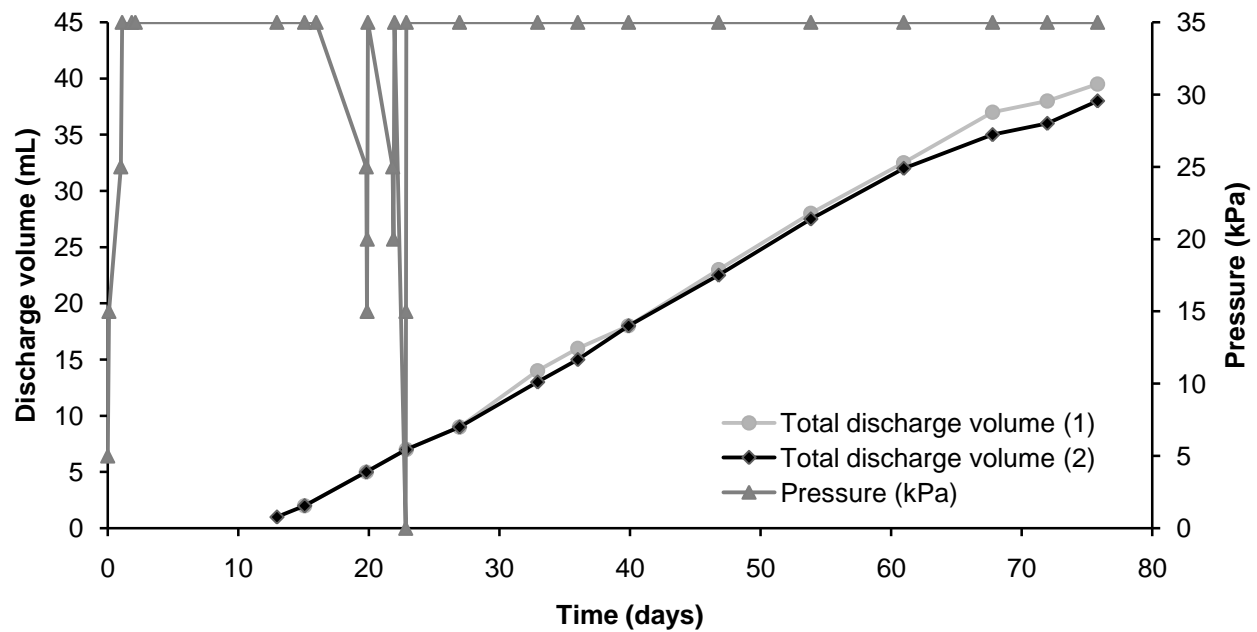


Figure 6.6: Total discharge volume and pressure for a leaching cell test with PFC-spiked landfill leachate permeating through sand-bentonite admix.

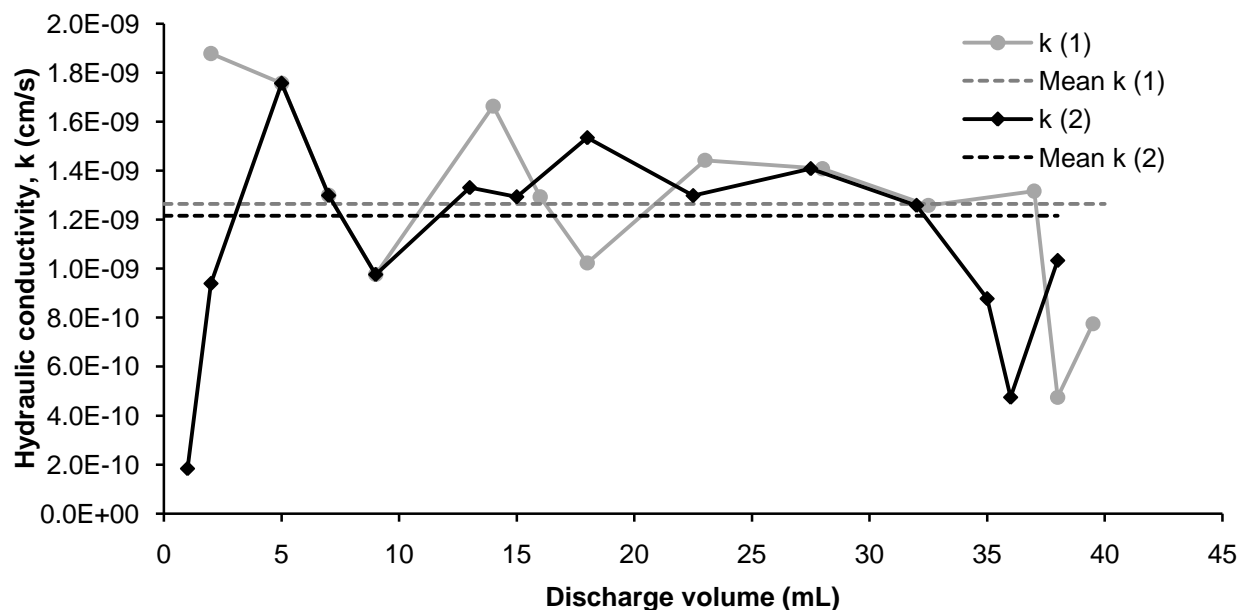


Figure 6.7: Hydraulic conductivity as a function of discharge volume for a leaching cell test, with PFC-spiked landfill leachate permeating through sand-bentonite admix.

6.2.4 Influence of PFCs on hydraulic conductivity

The mean and range of k from leaching cell tests for the three different conditions are summarized in Table 6.1. All k values were in the range of 10^{-10} to 10^{-9} cm/s, except for the peak k from the landfill leachate leaching cell test. With similar means and ranges of k between tap water, landfill leachate, and PFC-spiked landfill leachate, it appears that PFCs do not negatively affect the hydraulic conductivity of sodium bentonite landfill liners. This is consistent with the results from the free swell tests (section 6.1), which showed that the swelling index of sodium bentonite was not affected by the presence of PFCs.

Table 6.1: Mean and range of hydraulic conductivity (k) from leaching cell tests.

Leaching cell test	Mean k (cm/s)	Range of k (cm/s)
Tap water permeated through sand-bentonite admix	1×10^{-9}	7×10^{-10} to 2×10^{-9}
Landfill leachate permeated through sand-bentonite admix	3×10^{-9}	4×10^{-10} to 3×10^{-8}
PFC-spiked landfill leachate permeated through sand-bentonite admix	1×10^{-9}	2×10^{-10} to 2×10^{-9}

6.3 PFC concentrations in leaching cell test effluents

PFCs were extracted from leaching cell test effluents by liquid-liquid and solid phase extraction, described in sections 3.3.1.2 and 3.3.1.3, respectively. The detection limits from liquid-liquid extraction were not low enough for these samples, whereas those from solid phase extraction were satisfactory. Therefore, only the results from solid phase extraction are included below. Data tables from the solid phase extraction results are in 0. As the vast majority of results from liquid-liquid extraction were below or close to method detection limits, the corresponding results are not reported.

6.3.1 Tap water

The concentration profile of PFCs in the effluent from the sand-bentonite admix test permeated with tap water is illustrated in Figure 6.8. PFBA was the dominant compound, with a concentration of 0.18 ppb. The other compounds ranged in concentration from below method detection limits to 0.06 ppb. The PFC concentrations in tap water are generally lower by nearly an order of magnitude than the PFC concentrations in landfill leachate and PFC-spiked landfill leachate discussed below. PFBA was the only compound with a concentration comparable to landfill leachate, indicating that there may have been some contamination of the tap water with PFBA during sample extraction as its concentration was much higher than for all the other compounds. Overall, other than PFBA, it appears that PFC contamination in the lab for the leaching cell tests was minimal.

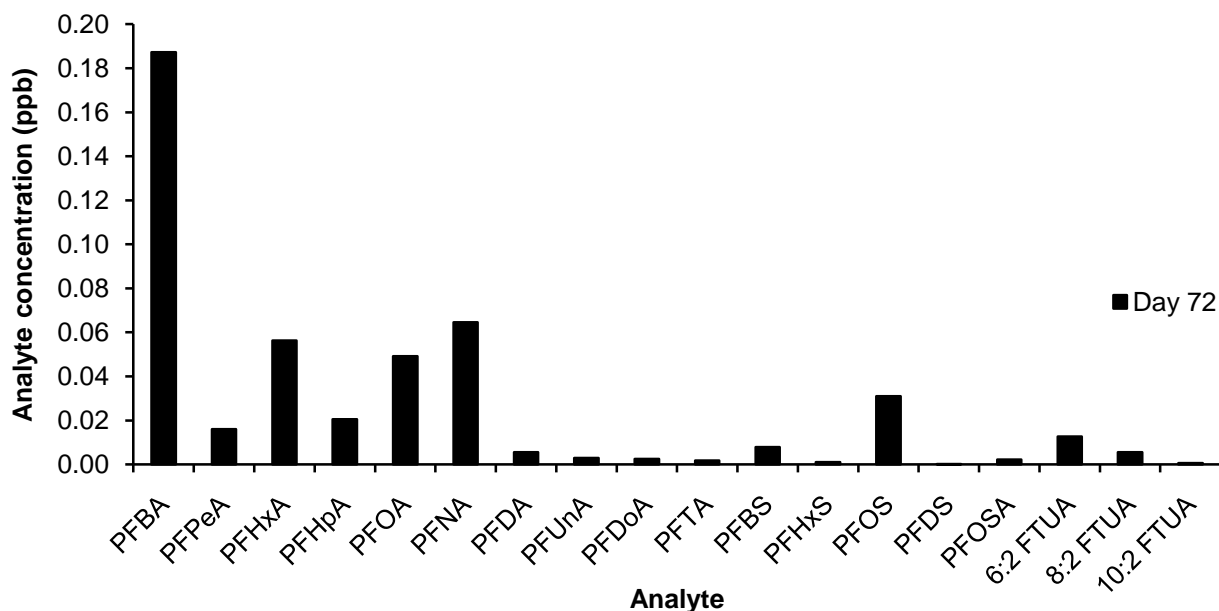


Figure 6.8: PFC concentrations in effluent from a leaching cell test with tap water permeated through sand-bentonite admix. Analytes are ordered by class. Within each class, analytes are arranged in order of increasing molecular weight.

6.3.2 Landfill leachate

The concentration profiles of PFCs in the effluent and from the reservoir in the sand-bentonite admix test involving permeation of landfill leachate are illustrated in Figures 6.9 to 6.11. The compounds are plotted in three figures for ease of reading. Dominant compounds in the reservoir landfill leachate were PFNA and PFUnA. This was unexpected, since these compounds are typically present at much lower concentrations than other compounds in landfill leachate, as discussed in Chapter 4. Overall, PFCAs were the dominant compounds, followed by PFSAs, and precursors (FOSA and FTUA). The C4 to C8 PFCAs were present at the highest concentrations, reflecting the relative concentrations of PFCs in landfill leachate (section 4.4.2.1). The PFC concentrations in landfill leachate from the reservoir were generally higher than in the effluent. For most PFCAs and PFSAs, the concentration increased with time. This was expected, since the number of binding sites on the sand-bentonite admix decreased as they became occupied, so that more PFCs penetrated through the leaching cell. Precursors, on the other hand, decreased over time, except for 6:2 FTUA, which was not detected in the reservoir landfill leachate. Since the

experiment ran at room temperature over an 84 day period, these precursors may have degraded, causing their concentrations to decrease over time, adding an additional potential source of increase in PFCAs and PFSA's over time.

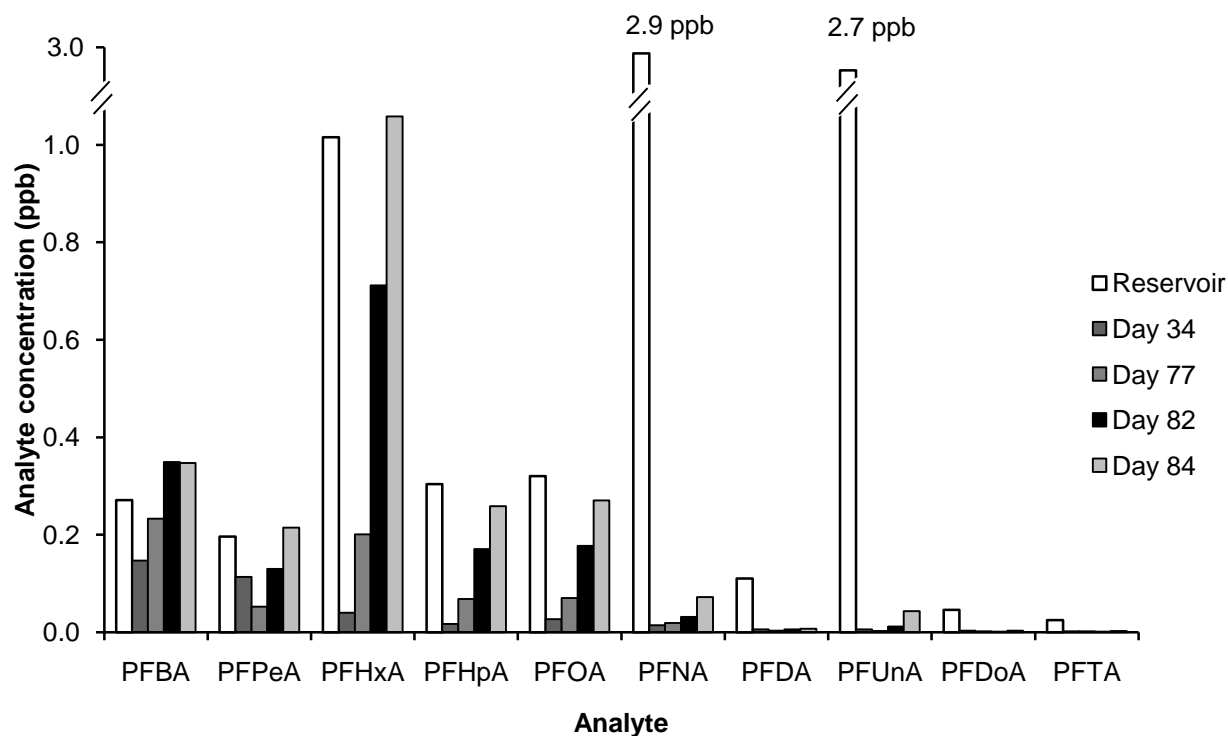


Figure 6.9: PFCA concentrations in effluent and from the reservoir from a leaching cell test with landfill leachate permeating through sand-bentonite admix. Analytes are arranged in order of increasing molecular weight.

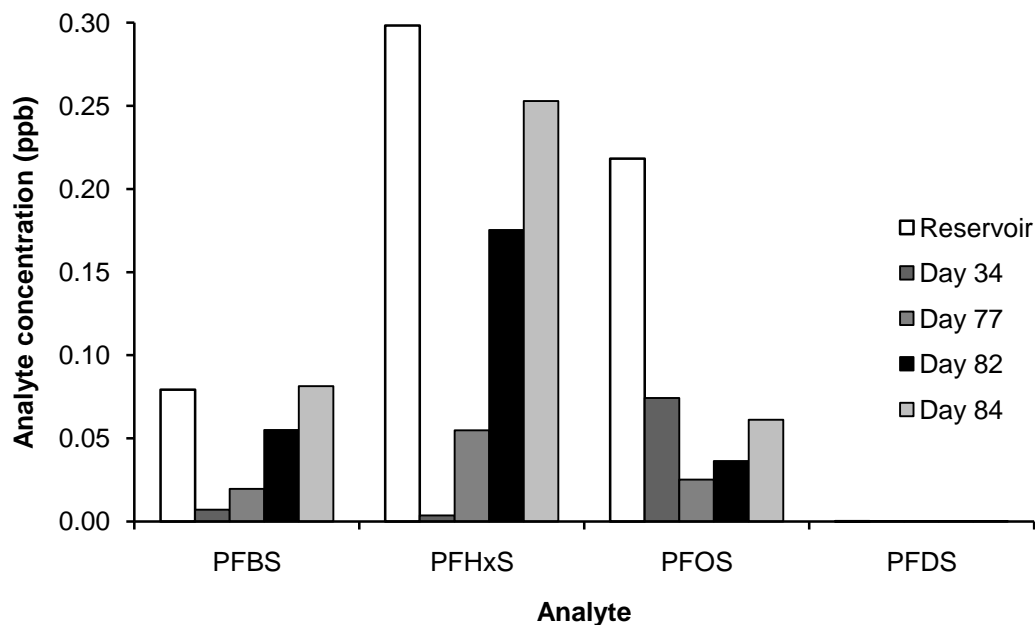


Figure 6.10: PFSA concentrations in effluent and from the reservoir from a leaching cell test with landfill leachate permeating through sand-bentonite admix. Analytes are arranged in order of increasing molecular weight.

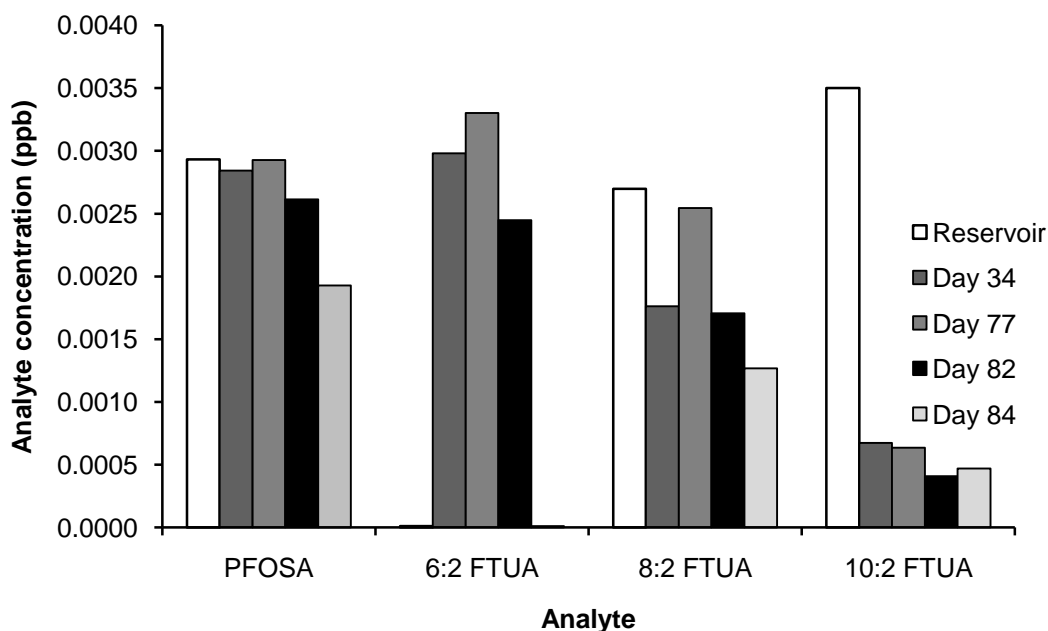


Figure 6.11: FOSA and FTUA concentrations in effluent and from the reservoir from a leaching cell test with landfill leachate permeating through sand-bentonite admix. Analytes are arranged in order of increasing molecular weight.

6.3.3 PFC-spiked landfill leachate

The concentration profiles of PFCs in the reservoir and effluent from the sand-bentonite admix test permeated with PFC-spiked landfill leachate are plotted in Figures 6.12 to 6.13. The results are split between two figures for ease of reading due to the large spread in scale. Most of the PFCs in the PFC-spiked landfill leachate from the reservoir were not detected at the expected concentration of 10 ppb. Instead, PFPeA, PFHxA, PFHpA, and PFNA were twice to three times the spiked concentration, whereas other compounds such as PFOA and PFBS were detected at about half the spiked concentration. Only PFDA, PFUnA, and PFTA were within about 20% of the expected 10 ppb PFC spike. As the PFC-spiked landfill leachate in the reservoir sat at room temperature for 76 days while the experiment was running, the characteristics of the landfill leachate could have varied, causing the PFC concentrations to also change. Possible transformations that could have occurred in the reservoir include degradation of PFC precursors to yield more PFC degradation products (e.g. PFCAs and PFSAs), sorption of PFCs to the walls of the reservoir, and sorption of PFCs on particulates in the leachate. Due to the small discharge volume from the leaching cells (~50 mL over 76 days), these changes could not be monitored over time as the entire sample of effluent was required for one sample extraction.

The dominant compounds in the effluent were the shorter-chain PFCAs (PFPeA, PFHxA, PFHpA, PFOA) and PFSAs (PFBS, PFHxS). This was also observed in the batch adsorption tests (section 5.1). All other PFCs were present at much lower concentrations (< 0.2 ppb) or were below the method detection limits. PFHxA had the highest concentration, 2.4 ppb. The high concentrations of PFHxA and PFHpA compared to other PFCs reflect their high concentrations in the influent. However, PFPeA, which had the highest concentration in the influent, did not have a similarly high concentration in the effluent. Overall, the observations from this leaching cell test are consistent with the expected sorption behavior of PFCs onto soils. As discussed in section 2.1, the distribution coefficients (k_d) of PFCs increased with the size (molecular weight) of the compound. Therefore, the larger PFCs are expected to be retained more in the sand-bentonite admix.

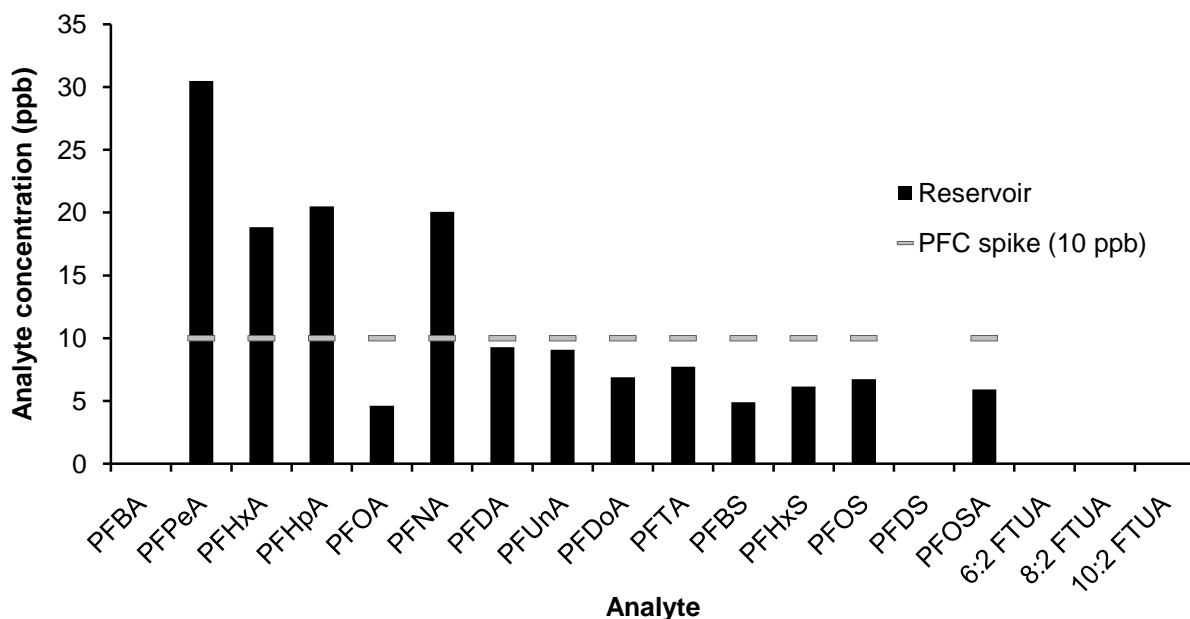


Figure 6.12: PFC concentrations in PFC-spiked landfill leachate from the reservoir supplying a leaching cell test with PFC-spiked landfill leachate permeating through sand-bentonite admix. Analytes are ordered by class. Within each class, analytes are arranged in order of increasing molecular weight.

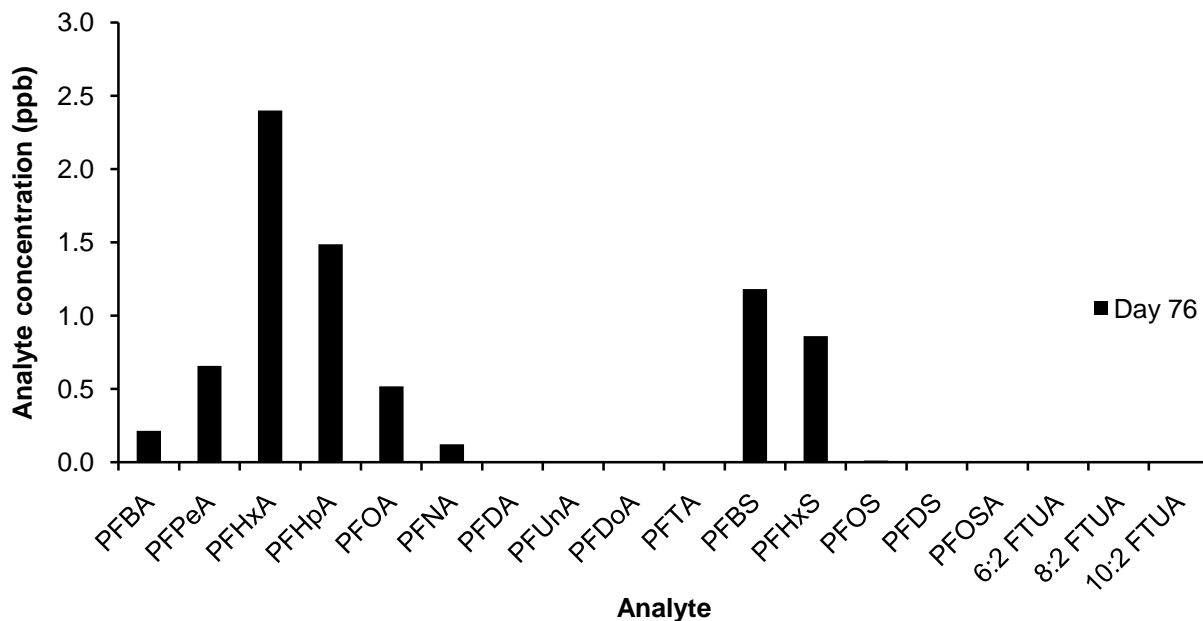


Figure 6.13: PFC concentrations in effluent from a leaching cell test with PFC-spiked landfill leachate permeating through sand-bentonite admix. Analytes are ordered by class. Within each class, analytes are arranged in order of increasing molecular weight.

6.4 PFC concentrations in sand-bentonite admixes

PFCs were extracted from samples of sand-bentonite admix from the leaching cell tests by Method B, described in section 3.3.2.2. Data tables with PFC concentrations of sand-bentonite admix processed by Method B are in 0. The sand-bentonite admix columns were sliced into four layers and sub-sampled by the method described in section 3.6.5.

6.4.1 Permeation test with tap water

Due to the low concentrations in the effluent, the sand-bentonite admix from this leaching cell test was not analyzed for PFCs.

6.4.2 Permeation test with landfill leachate

The concentrations of PFCs in sodium-bentonite admix permeated with landfill leachate are plotted in Figure 6.14. The PFC concentrations were generally the same in all layers, except for the large amount of PFOS retained in layer b. The overall consistency of PFC concentrations between layers indicates that PFCs were not being retained preferentially in one part of the leaching cell. Analyte concentrations varied greatly in the admix, from close to or below method detection limits to 0.72 ng/g. Dominant compounds were PFPeA and PFOS. For the PFCAs, the concentrations in the admix generally decreased with increasing size (molecular weight) of the compound, a trend that was also noted in the batch adsorption tests (section 5.1). All PFSA's except for PFOS, as well as PFUnA and PFDoA, were below method detection limits in all layers.

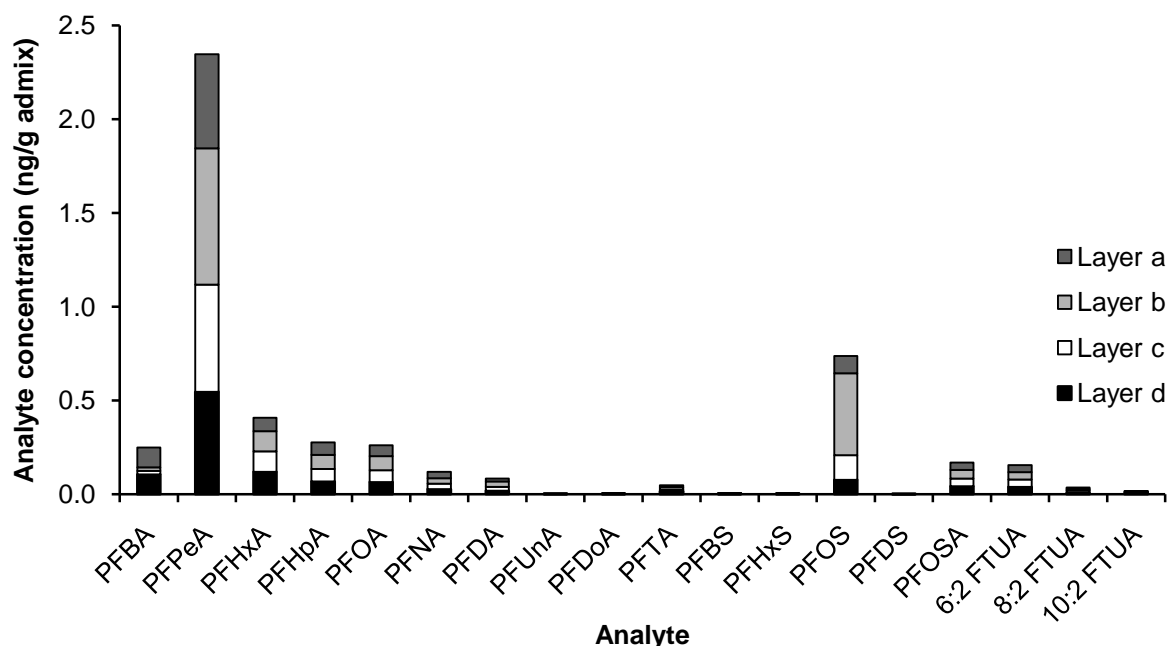


Figure 6.14: PFC concentrations in sand-bentonite admix layers from a leaching cell test with landfill leachate permeating through sand-bentonite admix. Analytes are ordered by class. Within each class, analytes are arranged in order of increasing molecular weight. Layers are ordered such that leachate flows from layer d to layer a.

6.4.3 Permeation test with PFC-spiked landfill leachate

The concentration of PFCs in sodium-bentonite admix permeated with PFC-spiked landfill leachate are plotted in Figure 6.15. The PFC concentrations were generally similar for different layers, particularly for PFPeA, PFHxA, and PFHpA. These were also the dominant compounds in the admix. PFDA and PFOSA did not appear to be retained in layer a, whereas there was slightly more retention of PFOS in layer b. Overall, the similar PFC concentrations for different layers indicates that most PFCs were not retained preferentially in one part of the leaching cell. Analyte concentrations were almost all greater than those from the leaching cell tests with unspiked landfill leachate. One would expect that admix permeated by PFC-spiked landfill leachate would contain more PFCs than admix permeated with unspiked landfill leachate. The analyte concentrations ranged from close to or below method detection limits to 1.0 ng/g. For the PFCAs, the concentrations in the admix generally decreased with compound size (molecular

weight). PFUnA and PFDoA were below method detection limits in all layers, while PFTA was close to the method detection limits.

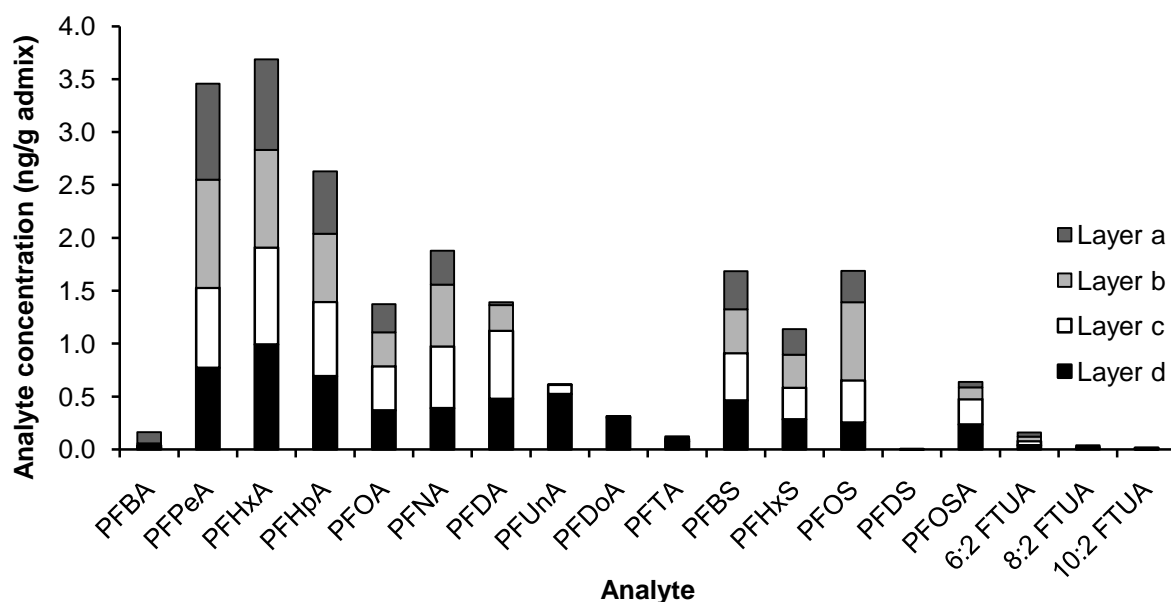


Figure 6.15: PFC concentrations in sand-bentonite admix layers from a leaching cell test with PFC-spiked landfill leachate permeating through sand-bentonite admix. Analytes are ordered by class. Within each class, analytes are arranged in order of increasing molecular weight. Layers are ordered such that leachate flows from layer d to layer a.

6.5 Mass balance of PFCs in leaching cell tests

A schematic of the leaching cell test is illustrated in Figure 3.1 in section 3.6 where the method for the leaching cell tests is described. Mass balances were calculated for PFCs in leaching cell tests assuming that the only source of PFCs into the system is from the leachate or water in the reservoir and that these PFCs would either be retained in the sand-bentonite admix or pass through the leaching cell into the collected effluent. Therefore, the amount of PFCs in the leachate or water before the LCT should equal the amount of PFCs in the effluent plus that in the sand-bentonite admix.

6.5.1 Tap water permeating through sand-bentonite admix

The sand-bentonite admix from this leaching cell test was not analyzed for PFCs. As a result, a mass balance could not be determined.

6.5.2 Landfill leachate permeating through sand-bentonite admix

The total masses of PFCs in the leachate entering the leaching, in the effluent and in the sand-bentonite admix are plotted in Figure 6.16. The results are greatly scattered as there were large imbalances in the mass of PFCs in the feed leachate stream compared to the sum of the effluent and sand-bentonite admix, as seen in the percent differences listed in Table 6.2. The percent differences were calculated as the difference in the mass of PFCs in the feed leachate and the combined total in the effluent and sand-bentonite admix, divided by the mean of the above-mentioned masses. PFHxA was the only analyte with a percent difference less than 10%. For other compounds, the percent difference ranged from 20 to 200%, with a mean percent difference of 121%.

In a similar study conducted by Gorgy (2011) on polybrominated diphenyl ethers (PBDEs) in water permeating through a sand-bentonite column, the total mass of PBDEs retained in the sand-bentonite and in the effluent was much less than the initial leachate before LCT. This mass imbalance was attributed to sorption of PBDEs on colloidal and suspended solids that were not captured in the sample extraction procedure. This may also be a viable explanation in this study for the mass imbalances where the mass in the effluent and sand-bentonite admix was less than in leachate before LCT. However, of the PFCs analyzed, the majority (14 of 18) were greater in the effluent and sand-bentonite admix than in entering leachate. Overall, there were no clear patterns observed in the relative proportions of PFCs in the three matrices, making it difficult to elucidate the source of the additional PFCs in the sand-bentonite admix and effluent. As discussed in section 6.3.1, there did not appear to be PFC contamination in the control (tap water) experiment. Hence it was unlikely that the additional PFCs came from the experimental facility itself, the water used to prepare the sand-bentonite admix, or the sand-bentonite admix itself.

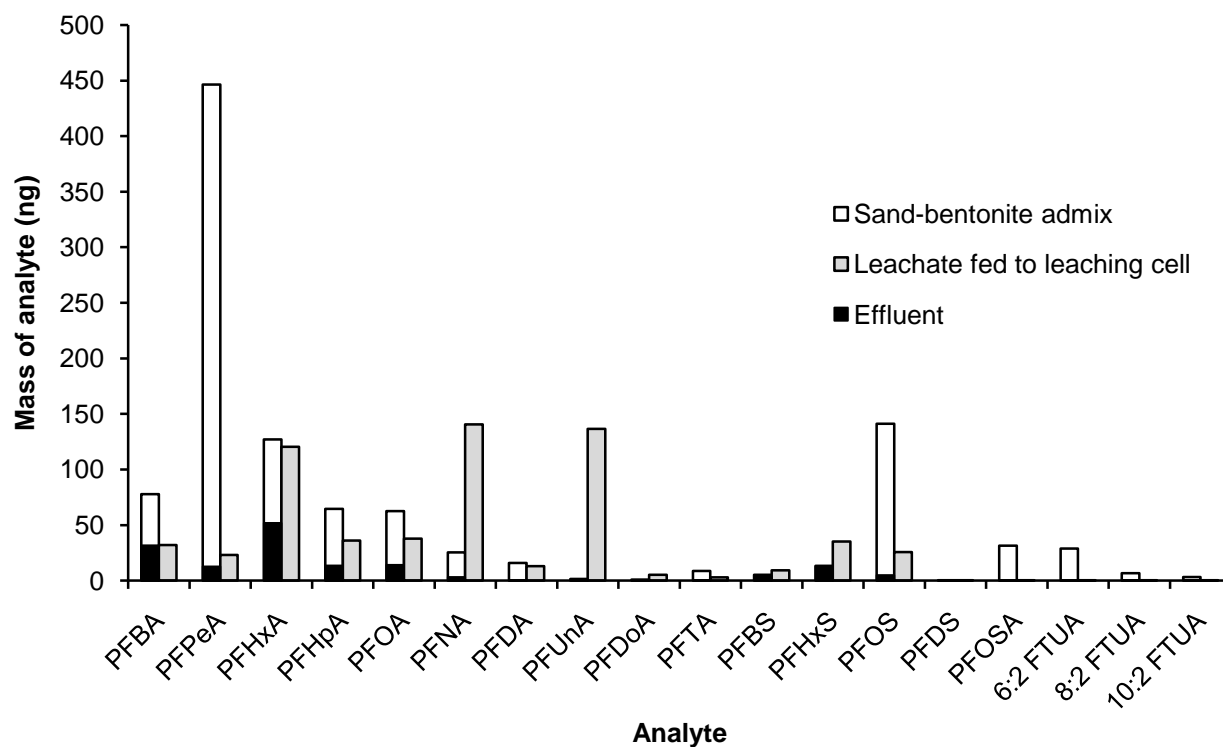


Figure 6.16: Mass of PFCs in influent, effluent, and sand-bentonite admixes from a leaching cell test with landfill leachate permeating through sand-bentonite admix. Analytes are ordered by class. Within each class, analytes are arranged in order of increasing molecular weight.

Table 6.2: Percent differences between PFCs in leachate fed to leaching cell and the sum of those in effluent and sand-bentonite admix from a leaching cell test with landfill leachate permeating through sand-bentonite admix.

Analyte	Percent Difference	+/- ^a
PFBA	83%	+
PFPeA	180%	+
PFHxA	6%	+
PFHpA	57%	+
PFOA	49%	+
PFNA	139%	-
PFDA	20%	+
PFUnA	195%	-
PFDoA	138%	-
PFTA	102%	+
PFBS	57%	-
PFHxS	89%	-
PFOS	138%	+
PFDS	195%	+
PFOSA	196%	+
6:2 FTUA	200%	+
8:2 FTUA	182%	+
10:2 FTUA	155%	+
Mean % difference	121%	
^a +: PFCs in effluent and sand-bentonite admix greater than in leachate before LCT -: PFCs in effluent and sand-bentonite admix less than in leachate before LCT		

6.5.3 PFC-spiked landfill leachate permeating through sand-bentonite admix

The total masses of PFCs in the influent from the reservoir, effluent, and sand-bentonite admixes are plotted in Figure 6.17. The results were less scattered than the LCTs with unspiked landfill leachate. However, there were still imbalances in the mass of PFCs in the leachate before LCT compared to the effluent and sand-bentonite admix, as seen in the percent differences listed in Table 6.3. The percent differences were calculated in the same way as in section 6.5.2. The analytes with the lowest percent differences were PFHxS (2%) and PFHxA (6%). For other compounds, the percent difference ranged from 18 to 192%. It is interesting to note that PFHxA also had a low percent difference in the unspiked LCTs. The mass balances in the PFC-spiked

LCTs were generally more consistent than for the unspiked LCTs. The mean percent difference was 86%, lower than for the unspiked LCTs. The largest percent differences were observed in the compounds found at the lowest amounts, which were also the compounds not included in the PFC spike (PFBA, PFDS, 6:2 FTUA, 8:2 FTUA and 10:2 FTUA). Since the PFC spike was intended to counteract the heterogeneities in landfill leachate, larger variations in the unspiked compounds are therefore expected. Similarly, this would also explain the larger variations in the unspiked LCTs.

Based on the relatively high proportions of PFCs in the sand-bentonite admix versus those in the effluent illustrated in Figure 6.17, it appears that PFCs were retained in the sand-bentonite admix. The mass balances from these LCTs were also similar to the mass balances from Gorgy's (2011) experiments, discussed in section 6.5.2, since most of the spiked compounds were greater in the leachate upstream of the leaching cell than in the combined effluent and sand-bentonite admix. The percent difference in the mass balances generally increased with molecular weight. This was especially apparent for PFNA, PFDA, PFUnA, PFDA, and PFTA. This pattern was also observed in the Batch Adsorption Tests (BATs), discussed in section 5.1. As mentioned in section 5.1, a potential reason for this pattern is that larger molecules have a greater binding affinity (k_{oc}) and as a result, may stick to polypropylene centrifuge tubes used in the extraction procedure.

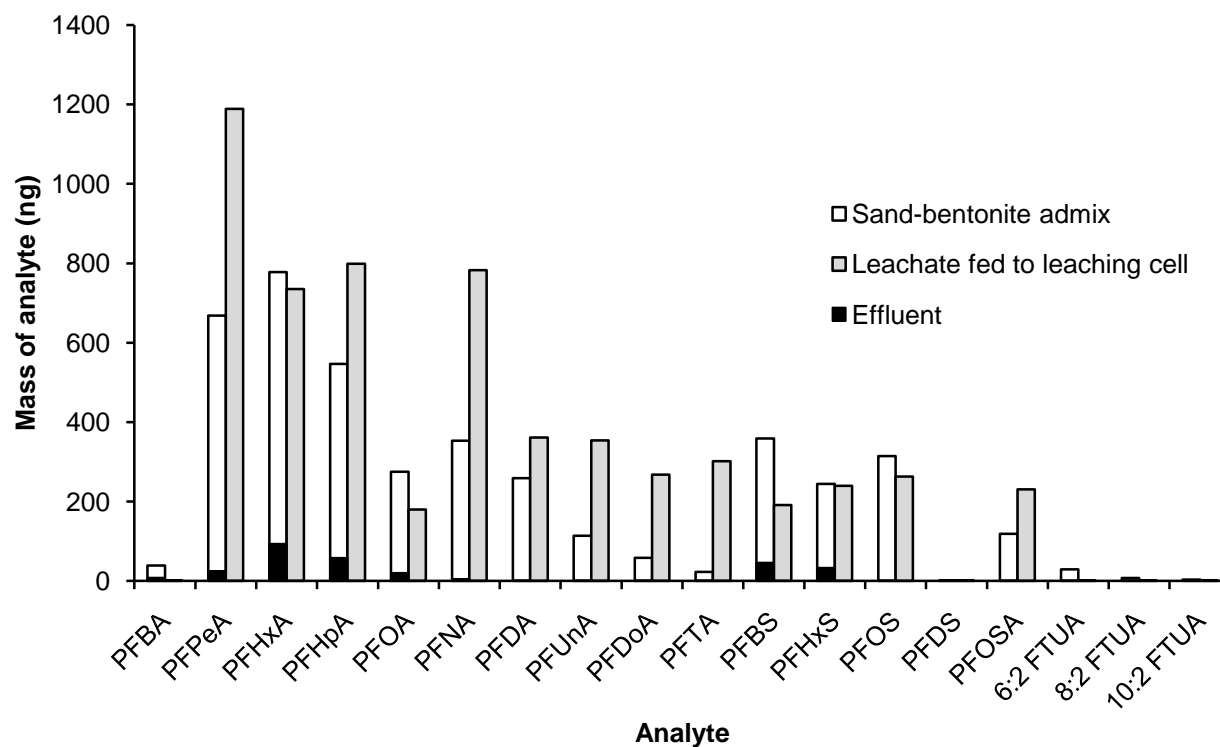


Figure 6.17: Mass of PFCs in influent, effluent, and sand-bentonite admixes from a leaching cell test with PFC-spiked landfill leachate permeating through sand-bentonite admix. Analytes are ordered by class. Within each class, analytes are arranged in order of increasing molecular weight.

Table 6.3: Percent differences between PFCs fed to leaching cell and the sum of those in effluent and sand-bentonite admix from a leaching cell test with landfill leachate permeating through sand-bentonite admix.

Analyte	Percent Difference	+/- ^a
PFBA	188%	+
PFPeA	56%	-
PFHxA	6%	+
PFHpA	38%	-
PFOA	42%	+
PFNA	76%	-
PFDA	33%	-
PFUnA	103%	-
PFDoA	129%	-
PFTA	172%	-
PFBS	61%	+
PFHxS	2%	+
PFOS	18%	+
PFDS	154%	-
PFOSA	64%	-
6:2 FTUA	192%	+
8:2 FTUA	149%	+
10:2 FTUA	71%	+
Mean % difference	86%	
^a +: PFCs in effluent and sand-bentonite admix greater than in leachate before LCT -: PFCs in effluent and sand-bentonite admix less than in leachate before LCT		

Chapter 7: Conclusions and recommendations

7.1 Conclusions

7.1.1 Perfluorinated compounds in landfill leachate samples

The key findings from the analysis of perfluorinated compounds in landfill leachate samples are summarized as follows:

- Cross-Canada samples:
 - Perfluorinated compounds (PFCs) are ubiquitous in landfill leachates from across Canada and vary considerably with concentrations, generally being lower in the North than in the South, likely due to the presence of fewer PFC manufacturing industries and lower economic ability to purchase consumer goods in the North.
 - There was little correlation between PFCs and population, total organic carbon, geography, landfill size, or precipitation. This is likely due to the complex matrix and heterogeneity of landfill leachate.
 - The relative distributions and concentrations of PFCs in Canada are similar to those in the United States and Germany.
- Landfill A samples:
 - PFCs concentrations were higher in landfill leachate than both landfill gas condensate and river water.
 - The distributions of PFCs were similar between landfill leachate and river water, with PFCAs being dominant. However, PFCAs were not dominant in landfill gas condensate. As condensate is more acidic than leachate and water, PFCAs have become volatile and are therefore not captured during sampling.
 - Detection limits for the extraction method used in this study were not low enough for soil samples. However, based on peaks in the LC/MS/MS chromatograms, it appears that landfill leaching field soil contained greater amounts of PFCs than borrow pit soil (background sample).

- Landfill B samples:
 - PFC concentrations increased from mid-March to mid-April for some compounds (PFOA, PFNA, PFDA, PFDoA, PFOS, 6:2 FTUA, 8:2 FTUA, 10:2 FTUA and PFOSA), whereas others were relatively constant. The increases can be attributed to increased amounts of precursors, particularly for PFOA, PFDA and PFOS. The concentrations of precursors and corresponding major degradation end-products were strongly correlated.
 - There is evidence that some compounds have more mixed sources (direct and degradation) than others. Almost all PFDA appears to come from degradation, whereas some PFOA is from degradation, and PFHxA mostly originates from direct sources.
 - Total organic carbon (TOC) and electrical conductivity (EC) were correlated with PFCs with fewer than 7 fluorinated carbons, except for PFPeA. PFCs are expected to have an affinity for organic carbon and are thus correlated to TOC. The correlation with EC was not expected, as other studies have observed inverse correlations. However, landfill leachate is a complex matrix. so the particulates and complex ions likely have an effect on the behaviour of PFCs.
 - Within the five-month monitoring period, rainfall did not appear to correlate with PFCs, although data were sparse. The five months of data obtained from this study may be insufficient to determine the influence of rainfall on PFCs in landfill leachate.
 - As there were large temporal variations in some PFC concentrations over the five-month sampling period, single grab samples may not be representative for monitoring PFCs in landfill leachate.
- The dominant PFC (highest concentrations overall) was PFHxA. PFOA and PFOS were also detected in the vast majority of samples, but at concentrations lower than for PFHxA. PFOS was generally detected at lower concentrations than PFOA.
- PFCs of similar size were well correlated with each other, likely due to similar physical and chemical properties leading to similar behaviour in the environment.
- PFCAs, particularly those with fewer than eight fluorinated carbons, were generally found at the greatest concentrations in landfill leachate samples. These PFCAs are

degradation products of the most widely manufactured fluorotelomer-based and perfluoroalkyl sulfonyl products that are ultimately disposed of in landfills. This is a substantial source of precursors that may degrade into PFCAs in landfill leachate.

- PFHxS was found at concentrations similar to, or higher than, PFOS in landfills A and B. Though PFOS is typically dominant PFSA in the environment, significant use of PFHxS in various surface treatments has been reported. Products with these surface treatments (e.g. carpets) may contribute to larger PFHxS loadings in landfill leachate.

7.1.2 Batch adsorption test

The key findings of the batch adsorption tests are as follows:

- Differences in concentrations after batch adsorption tests (BATs) between the control experiments and test experiments were mostly statistically insignificant ($p < 0.05$). Hence it appears that PFCs in landfill leachate do not readily bind to sodium bentonite.
- Using a mixture of PFCs versus single PFCs does not appear to have had an impact on the sorption of PFCs on sodium bentonite.
- The lack of sorption of PFCs onto sodium bentonite was likely due to negative surface charges of PFCs in the environment, preventing them from being sorbed onto the negatively-charged sodium bentonite liner.
- Matrix effects were the most likely cause of inaccuracy for compounds quantified by non-corresponding mass-labelled internal standards.
- Low spike recoveries observed for some PFCs (e.g. PFUnA, PFDoA, PFOSA) are likely caused by these compounds adhering to the sides of containers due to their affinity for carbon (high k_{oc} values).

7.1.3 Leaching cell test

The key findings of the leaching cell tests are as follows:

- Leaching cell tests on sand-bentonite admix columns permeated with water, landfill leachate and 10 ppb spiked landfill leachate led to similar hydraulic conductivity values, indicating that PFCs do not compromise the performance of bentonite landfill liners.
- The sand-bentonite admix appears to retain some PFCs under the leaching cell test conditions, despite the results of the batch adsorption tests showing that bentonite itself does not appear to bind to PFCs.
- For most PFCAs and PFSAs in the effluent, the concentration increased with time. The number of binding sites on the sand-bentonite admix likely decreased as they became occupied and allowed more PFCs to penetrate the leaching cell. Precursors generally decreased over time, likely due to degradation, adding an additional potential source of increase in PFCAs and PFSAs over time.
- There did not appear to be retention of PFCs in a particular layer of the sand-bentonite admix, as the concentrations of PFCs for different sand-bentonite admix layers were similar.
- The mass balance data were scattered, likely due to a combination of losses or gains from PFCs adhering to walls or colloids, and degradation of precursors.

7.2 Recommendations

Key recommendations for future work based on the results of this study are as follows:

- Include more PFCs in the chemical analyses to provide a broader understanding of the sources of these compounds in the environment. In particular, it would be useful to include more precursors and commercial standards.
- To improve data interpretation in future studies and assist in the analysis of factors that may influence PFC, leachate samples should be analyzed for additional leachate parameters (e.g. other contaminants, biochemical oxygen demand), and additional landfill conditions (e.g. temperature, leachate flow rate, waste composition) should be monitored.

- Analysis of samples of soil and solid waste from these landfills for PFCs would help to understand how these compounds behave in landfills and identify sources of PFCs in landfill leachate.
- Due to the complex nature of landfill systems, use multi-regression and multivariate data analyses to determine factors that may affect the presence of PFCs in landfill leachate.
- Landfill leachate should be sampled regularly over longer periods of time (e.g. at least one year) and possibly spatially arranged as well, to account for possible fluctuations in PFC levels and to obtain a representative range of PFC concentrations for a landfill.
- Conduct batch adsorption tests and leaching cell tests with other commonly-used landfill liner materials, such as compacted natural soil, to improve knowledge on how PFCs may behave in landfills under various conditions. It would also be beneficial to conduct these experiments at controlled temperatures similar to the temperatures within a landfill, and to monitor concentrations of PFCs in the control throughout the experiment to track potential precursor degradation.
- Conduct leaching cell tests with larger diameter cells and more replicates to allow for greater generation of effluent volumes for chemical analyses and contingency, in case there is unexpected early breakthrough due to side-wall leakage or formation of preferential flow paths.
- Further develop clean-up and extraction methodologies to improve the recovery of PFCs from landfill leachate and environmental samples and to reduce potential matrix interferences, thereby improving overall quality assurance/quality control (QA/QC).

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Appendix A: Supplementary information for materials and methods

Table A.1: Sampling methods for cross-Canada landfill leachate (Danon-Schaffer, 2010)

#	Type of Waste	Collection Method	Date of Sampling
1	Municipal	Waterra®	Fall 2005
2	Municipal + Industrial	Grab sample - jar attached to rod	Spring 2006
3	Municipal	Grab sample - jar attached to rod	Spring 2006
4	Residential + Commercial	Unavailable	Fall 2006
5	Unavailable	Unavailable	Spring 2006
6	Municipal + C&D	Spigot during tanker truck loading	Spring 2006
7	Municipal + ICI	Unavailable	Spring 2006
8	Municipal	Waterra®	Fall 2006
9	Municipal + ICI	Active/inactive portion	Summer 2006
10	Municipal	Active/inactive portion	Summer 2006
11	Municipal	Bucket from leachate pumping station	Spring 2005
12	Municipal + 60% ICI	Bailers	Winter 2006
13	Municipal + 60% ICI	Bailers	Winter 2006
14	Municipal + ICI	Bailer	Spring 2006
15	Municipal	Dedicated sampling rope	Summer 2006
16	Municipal	Active/inactive area, half pre/post-2002	Summer 2006
17	Municipal + Industrial	Small bucket on rope approx 10 m down	Spring 2006
18	Municipal + Industrial	Bailer	Fall 2006
19	Municipal	Bailer	Fall 2006
20	Municipal	Waterra®	Summer 2006
21	Municipal	Bottle submerge	Summer 2006
22	Municipal	Bottle submerge	Summer 2006
23	Municipal	Bottle submerge	Summer 2006
24	Municipal	Bottle submerge	Summer 2006
25	Municipal	Bottle submerge	Summer 2006
26	Municipal	Bottle submerge	Summer 2006
27	Municipal	Bottle submerge	Summer 2006
ICI: Institutional, Commercial, and Industrial C&D: Construction and Demolition			

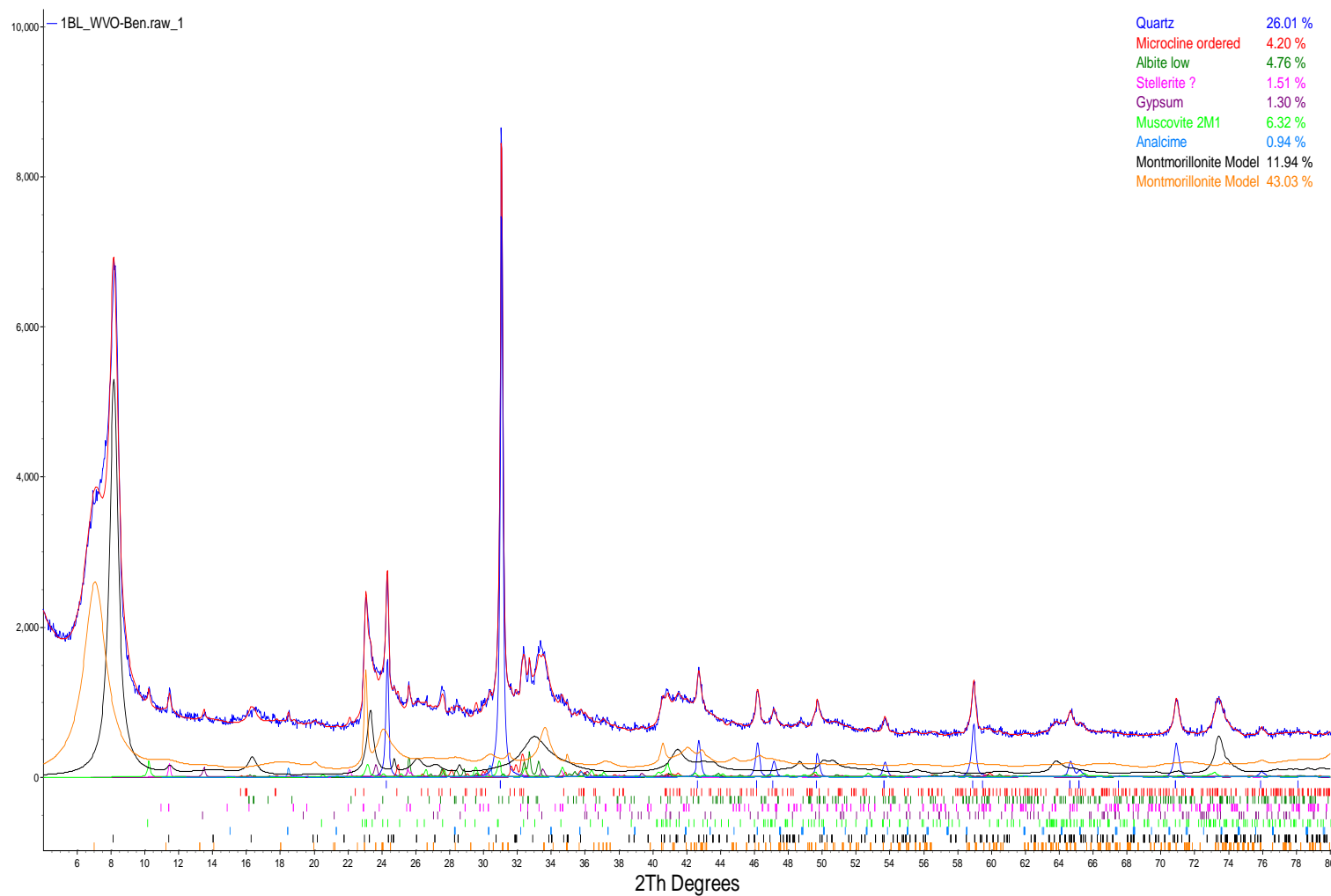


Figure A.1: Rietveld refinement plot of Envirogel® MSW 10 (blue line - observed intensity at each step; red line - calculated pattern; solid grey line below – difference between observed and calculated intensities; vertical bars, positions of all Bragg reflections). Coloured lines are individual diffraction patterns of all phases.

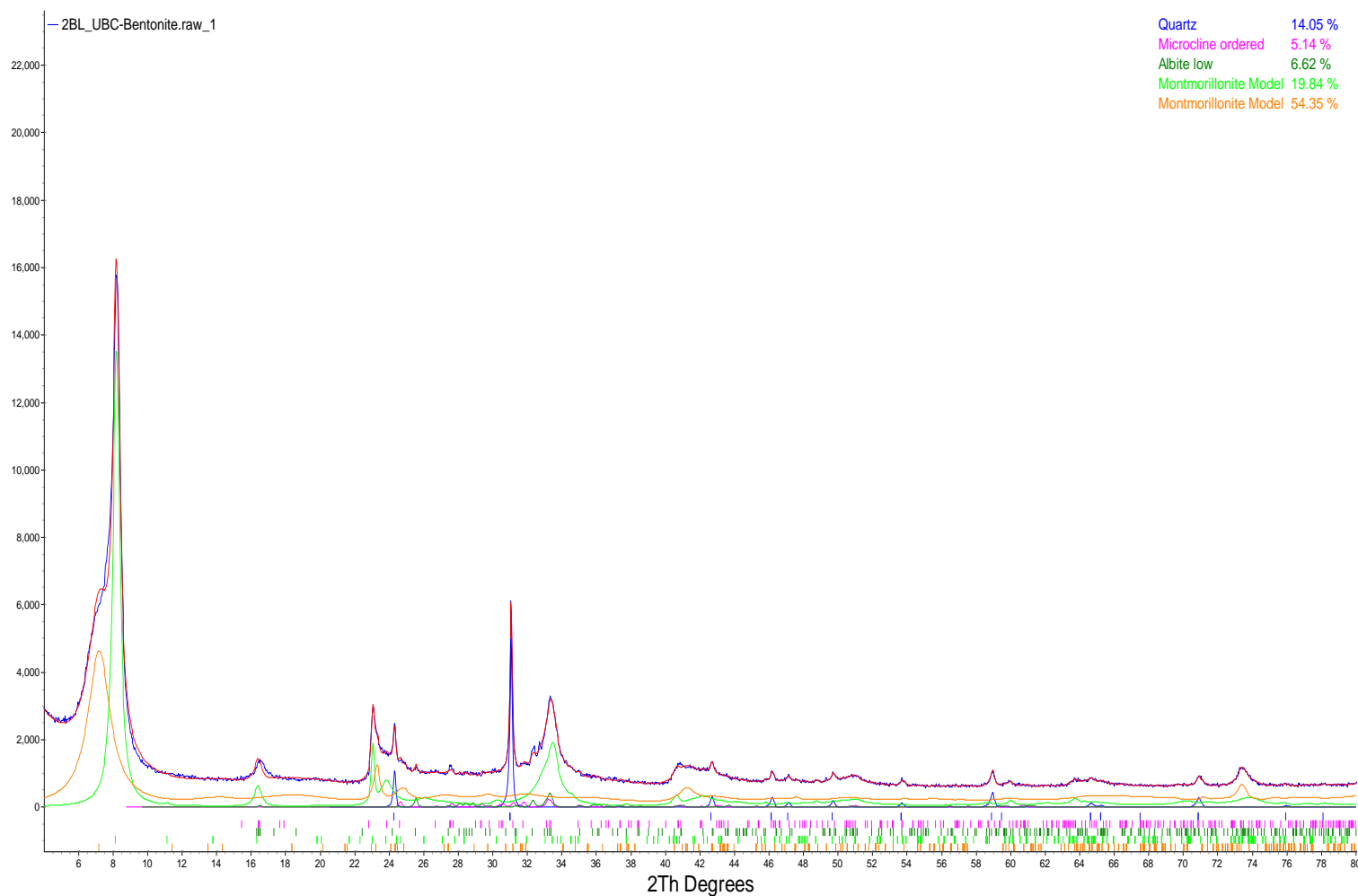


Figure A.2: Rietveld refinement plot of sodium bentonite from Canadian Clay Products (blue line - observed intensity at each step; red line - calculated pattern; solid grey line below – difference between observed and calculated intensities; vertical bars, positions of all Bragg reflections). Coloured lines are individual diffraction patterns of all phases.

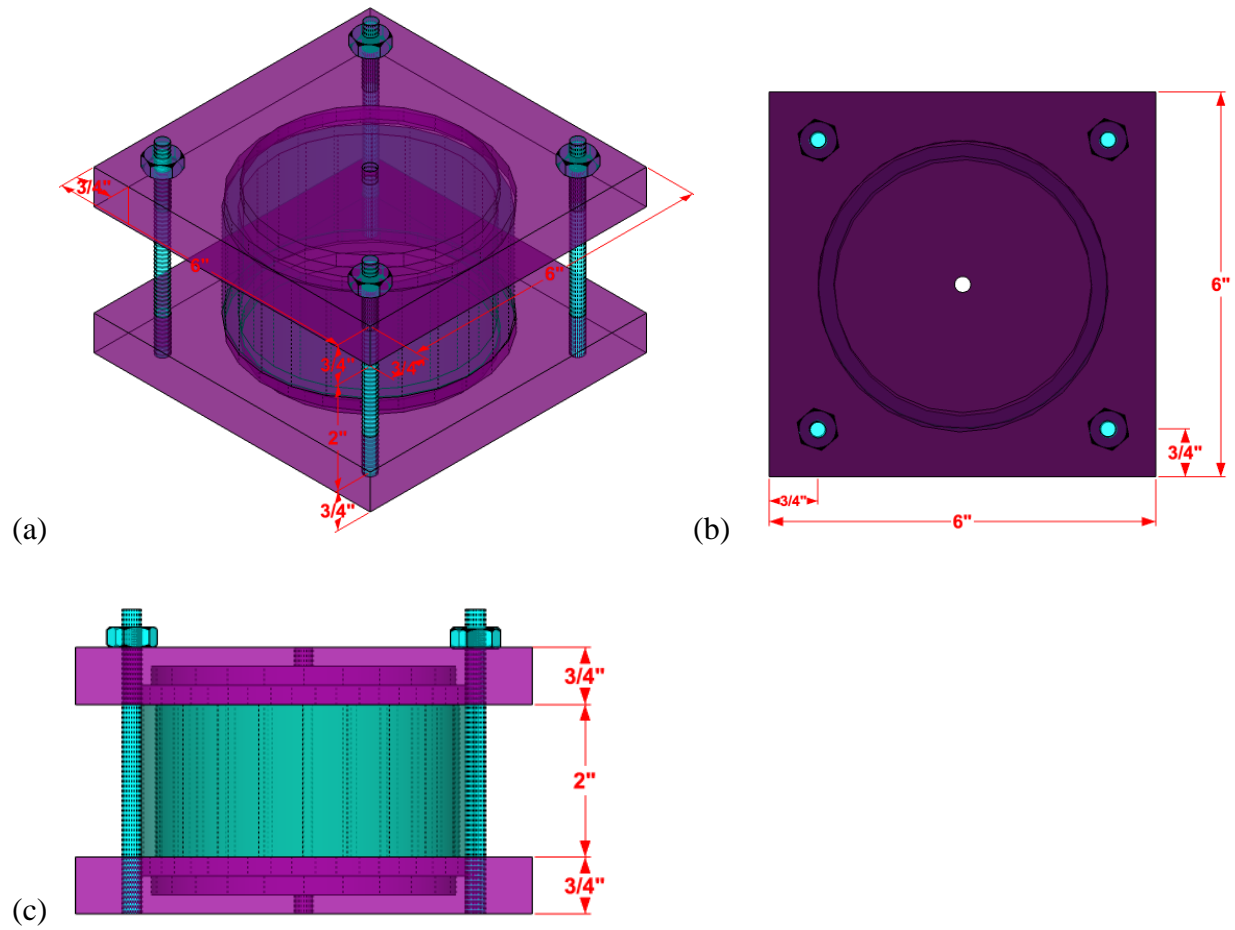


Figure A.3: Schematic of leaching cell test apparatus in (a) in isometric view, (b) top view, and (c) side view.

Appendix B: Data tables for landfill leachate characterization

Table B.1: Metals in landfill A samples

Metal	Blank (mg/L)	Leachate (mg/L)	Standard Deviation (mg/L)	Range (mg/L)
Aluminum (Al)	0.17	0.37	0.030	0.34-0.40
Arsenic (As)	0.012	0.018	0.006	0.011-0.022
Barium (Ba)	ND	0.026	0.006	0.020-0.032
Beryllium (Be)	ND	ND	ND	ND
Boron (B)	ND	0.090	0.037	0.064-0.13
Cadmium (Cd)	ND	ND	ND	ND
Calcium (Ca)	ND	24.8	1.24	23.7-26.1
Cobalt (Co)	0.004	ND	ND	ND
Copper (Cu)	0.090	0.062	0.010	0.053-0.073
Iron (Fe)	0.17	2.94	0.68	2.53-3.73
Magnesium (Mg)	ND	12.6	0.78	12.0-13.5
Manganese (Mn)	ND	0.15	0.010	0.14-0.16
Molybdenum (Mo)	0.001	ND	ND	ND
Nickel (Ni)	ND	ND	ND	ND
Lead (Pb)	ND	ND	ND	ND
Selenium (Se)	0.021	ND	ND	ND
Thallim (Tl)	ND	ND	ND	ND
Zince (Zn)	ND	ND	ND	ND

Table B.2: Metals in landfill B samples

Metal	Blank (mg/L)	Leachate (mg/L)	Standard Deviation (mg/L)	Range (mg/L)
Aluminum (Al)	0.14	0.80	0.042	0.75-0.82
Arsenic (As)	ND	ND	ND	ND
Boron (B)	0.028	0.82	0.12	0.69-0.91
Barium (Ba)	0.002	0.19	0.007	0.19-0.20
Calcium (Ca)	0.34	47.7	1.66	46.5-49.6
Cadmium (Cd)	ND	ND	ND	ND
Chromium (Cr)	0.004	0.03	0.020	0.008-0.043
Copper (Cu)	0.29	0.08	0.021	0.066-0.105
Iron (Fe)	10.5	145	5.26	140-151
Potassium (K)	0.016	32.4	0.88	31.6-33.3
Magnesium (Mg)	0.64	142	5.51	138-148
Manganese (Mn)	ND	0.30	0.013	0.29-0.31
Nickel (Ni)	ND	ND	ND	ND
Lead (Pb)	ND	0.003	0.002	0.002-0.006
Silicon (Si)	0.21	5.09	0.18	4.91-5.27
Sodium (Na)	0.092	24.3	1.22	23.1-25.5
Zinc (Zn)	0.031	0.05	0.005	0.045-0.055

Table B.3: Cross-Canada PFCs

Sample #	Geo	PFBA (ppb)	PFPeA (ppb)	PFHxA (ppb)	PFHpA (ppb)	PFOA (ppb)	PFNA (ppb)	PFDA (ppb)	PFUnA (ppb)	PFDoA (ppb)	PFBS (ppb)	PFHxS (ppb)	PFOS (ppb)	PFOSA (ppb)	Total (ppb)	Population (2006 census)	Annual Tonnage of Waste (tonnes)	Annual Precipitation (mm)	Total Organic Carbon (mg/L)	Particulates (mg/L)
1	S	0.002	0.005	0.001	0.001	0.434	0.022	0.004	0.001	0.001	0.009	0.128	0.128	0.004	0.74	120,000	100,000	380.5	367.5	2428
2	S	0.299	0.447	0.519	0.173	0.468	0.008	0.003	0.003	0.003	0.031	0.056	0.006	0.003	2.02	4,500	12,700	487.7	N/A	N/A
3	S	0.150	0.163	0.579	0.236	0.327	0.007	0.002	0.001	0.001	0.098	0.518	1.020	0.003	3.11	56,000	38,000	484.4	134.7	108
4	S	0.002	0.314	1.120	0.384	0.382	0.015	0.005	0.001	0.001	0.042	0.327	0.035	0.003	2.63	900,000	740,000	412.6	317.4	1162
5	S	0.031	0.004	0.009	0.006	0.023	0.002	0.003	0.001	0.001	0.002	0.006	0.031	0.003	0.12	200,000	478,474	388.1	220.2	546
6	S	0.301	0.458	1.040	0.419	0.491	0.022	0.026	0.001	0.001	0.272	0.450	0.045	0.005	3.53	375,000	156,000	943.5	180.6	270
7	S	0.267	0.219	0.343	0.102	0.202	0.001	0.001	0.001	0.001	0.001	0.041	0.012	0.001	1.19	375,000	N/A	943.5	58.6	320
8	S	3.260	3.920	7.090	2.310	3.450	0.117	0.011	0.011	0.011	0.338	0.798	0.023	0.025	21.36	276,000	160,000	1452.2	456.5	308
9	S	0.134	0.132	0.301	0.217	0.418	0.021	0.006	0.002	0.002	0.141	0.258	0.060	0.004	1.70	210,000	80,000	991.3	104.1	291
10	S	0.276	0.244	0.882	0.232	0.322	0.013	0.003	0.003	0.003	0.041	0.122	0.006	0.003	2.15	107,000	40,000	1036.9	187.7	473
11	S	0.002	0.780	1.190	0.630	0.694	0.059	0.023	0.011	0.003	1.370	0.360	0.006	0.003	5.13	2,500,000	900,000	792.7	333.4	242
12	S	0.002	0.225	0.821	0.401	0.684	0.050	0.098	0.005	0.002	0.058	0.358	0.156	0.023	2.89	124,000	250,000	907.9	129.1	153
13	S	0.292	0.367	1.430	0.987	1.450	0.078	0.190	0.006	0.032	0.310	3.010	4.840	0.063	13.05	500,000	165,000	912.9	389.1	118
14	S	0.111	0.194	0.305	0.103	0.131	0.003	0.003	0.003	0.003	0.012	0.060	0.006	0.003	0.94	600,000	67,000	1223.2	239.0	1100
15	S	0.007	0.005	0.004	0.004	0.008	0.001	0.001	0.001	0.001	0.002	0.002	0.002	0.001	0.04	64,400	162,796	910.1	8.1	68
16	S	0.489	0.424	0.592	0.211	0.350	0.014	0.005	0.001	0.001	0.062	0.204	0.063	0.005	2.42	60,000	160,000	910.1	40.1	61
17	S	0.131	0.112	0.298	0.123	0.302	0.011	0.006	0.001	0.001	0.049	0.180	0.036	0.001	1.25	46,000	47,000	1002	91.0	173
18	S	0.073	0.142	0.362	0.209	0.437	0.016	0.006	0.001	0.001	0.041	0.185	0.107	0.015	1.59	47,000	26,000	1232.9	61.8	256
19	S	0.002	0.392	0.890	0.429	0.859	0.030	0.011	0.001	0.001	0.076	0.423	0.275	0.010	3.40	32,000	40,000	1173.3	131.4	175
20	N	0.031	0.080	0.050	0.041	0.068	0.003	0.001	0.001	0.001	0.003	0.011	0.017	0.001	0.31	20,461	25,000	267.4	63.1	413
21	N	0.088	0.179	0.420	0.151	0.190	0.096	0.004	0.001	0.001	0.088	0.469	0.360	0.007	2.05	930	N/A	167.8	22.7	33
22	N	0.005	0.009	0.019	0.011	0.018	0.002	0.001	0.001	0.001	0.001	0.003	0.001	0.001	0.07	20,000	10,000	280.7	257.9	1316
23	N	0.018	0.011	0.015	0.009	0.006	0.001	0.001	0.001	0.001	0.002	0.002	0.004	0.001	0.07	3,484	N/A	248.4	77.7	64
24	N	0.088	0.622	0.314	0.077	0.048	0.001	0.001	0.001	0.001	0.007	0.013	0.010	0.001	1.18	8,000	10,000	412	20.8	123
25	N	0.008	0.027	0.063	0.020	0.042	0.005	0.002	0.001	0.001	0.001	0.036	0.046	0.009	0.26	1,477	N/A	138.8	102.5	52
26	N	0.042	0.199	0.090	0.022	0.027	0.006	0.001	0.001	0.001	0.018	0.078	0.242	0.013	0.74	654	N/A	216.7	35.3	215
27	N	0.005	0.009	0.014	0.006	0.018	0.004	0.001	0.001	0.001	0.005	0.001	0.007	0.002	0.07	1,236	N/A	403	9.5	50
S = South; N = North																				

Table B.4: Cross-Canada PFCs procedural blanks

#	PFBA (ppb)	PFPeA (ppb)	PFHxA (ppb)	PFHpA (ppb)	PFOA (ppb)	PFNA (ppb)	PFDA (ppb)	PFUnA (ppb)	PFDoA (ppb)	PFBS (ppb)	PFHxS (ppb)	PFOS (ppb)	PFOSA (ppb)
1	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.002	<0.002	<0.002	<0.001
2	<0.0025	<0.0025	<0.0025	<0.0025	<0.0025	<0.0025	<0.0025	<0.0025	<0.0025	<0.005	<0.005	<0.005	<0.0025
3	<0.00167	<0.00167	<0.00167	<0.00167	<0.00167	<0.00167	<0.00167	<0.00167	<0.00167	<0.00333	<0.00333	<0.00333	<0.00167
4	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.002	<0.002	<0.002	<0.001
5	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.002	<0.002	<0.002	<0.001

Table B.5: Cross-Canada PFCs R² values

	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFBS	PFHxS	PFOS	PFOSA
PFBA		0.27	0.25	0.22	0.12	0.02	0.01	0.08	0.11	0.02	0.03
PFPeA	0.27		0.89	0.84	0.54	0.29	0.22	0.53	0.52	0.07	0.19
PFHxA	0.25	0.89		0.97	0.56	0.34	0.32	0.54	0.56	0.10	0.23
PFHpA	0.22	0.84	0.97		0.63	0.41	0.43	0.62	0.62	0.13	0.26
PFOA	0.12	0.54	0.56	0.63		0.68	0.60	0.65	0.82	0.25	0.38
PFNA	0.02	0.29	0.34	0.41	0.68		0.60	0.71	0.71	0.33	0.57
PFDA	0.01	0.22	0.32	0.43	0.60	0.60		0.54	0.61	0.30	0.49
PFBS	0.08	0.53	0.54	0.62	0.65	0.71	0.54		0.71	0.23	0.33
PFHxS	0.11	0.52	0.56	0.62	0.82	0.71	0.61	0.71		0.51	0.51
PFOS	0.02	0.07	0.10	0.13	0.25	0.33	0.30	0.23	0.51		0.54
PFOSA	0.03	0.19	0.23	0.26	0.38	0.57	0.49	0.33	0.51	0.54	
Population	0.01	0.08	0.12	0.18	0.29	0.08	0.33	0.18	0.19	0.00	0.01
Annual Waste	0.06	0.00	0.00	0.00	0.00	0.07	0.11	0.04	0.03	0.03	0.10
Precipitation	0.12	0.21	0.24	0.30	0.35	0.10	0.27	0.26	0.18	0.00	0.05
TOC	0.00	0.06	0.11	0.14	0.32	0.19	0.28	0.13	0.25	0.02	0.09

PFUnA and PFDoA were excluded from this table because more than 85% of the data points for these compounds were below method detection limits.

Table B.6: PFCs in landfill A samples

Sample	Concentration (ppb)																	
	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTA	PFBS	PFHxS	PFOS	PFDS	PFOSA	6:2 FTUA	8:2 FTUA	10:2 FTUA
Condensate	1.50E -3	4.52E -3	4.34E -3	1.32E -3	2.98E -3	1.23E -3	2.98E -3	9.28E -4	1.32E -3	3.74E -4	1.04E -2	1.47E -3	5.90E -3	1.51E -4	6.53E -3	4.00E -7	2.65E -7	8.18E -5
MDL Condensate	2.60E -4	2.05E -4	1.47E -4	5.76E -5	2.53E -5	5.13E -5	2.74E -5	2.10E -5	2.31E -5	3.25E -5	1.02E -5	5.76E -6	7.11E -6	4.66E -6	6.68E -6	4.00E -6	2.65E -6	4.06E -6
River water 1	4.38E -4	nd	1.71E -3	1.17E -3	4.46E -3	5.28E -4	6.28E -4	3.29E -4	1.71E -4	1.60E -4	1.40E -4	3.18E -5	2.53E -4	3.35E -6	2.62E -5	5.75E -7	3.82E -7	9.05E -5
MDL River water 1	3.74E -4	nd	2.11E -4	8.28E -5	3.63E -5	7.38E -5	3.94E -5	3.02E -5	3.32E -5	4.67E -5	1.46E -5	8.29E -6	1.02E -5	6.70E -6	9.61E -6	5.75E -6	3.82E -6	5.85E -6
River water 2	3.22E -4	nd	1.14E -3	1.27E -4	4.17E -4	3.36E -4	3.22E -4	1.72E -4	5.69E -5	3.37E -6	3.08E -4	5.99E -7	1.59E -4	1.50E -5	1.16E -5	4.15E -7	2.76E -7	5.79E -5
MDL River water 2	2.70E -4	nd	1.53E -4	5.98E -5	2.62E -5	5.33E -5	2.84E -5	2.18E -5	2.39E -5	3.37E -5	1.06E -5	5.99E -6	7.38E -6	4.84E -6	6.94E -6	4.15E -6	2.76E -6	4.22E -6
Landfill leachate	2.02E -2	4.02E -1	4.73E -1	3.37E -1	1.87E -1	2.84E -2	1.44E -2	1.49E -2	1.80E -4	2.44E -5	1.28E -2	1.98E -1	6.31E -2	1.75E -5	2.70E -3	3.00E -6	1.99E -6	5.00E -4
MDL Leachate	1.83E -2	4.21E -2	1.66E -2	6.07E -3	5.55E -3	2.84E -2	5.03E -3	2.98E -2	1.73E -4	2.44E -4	8.44E -4	4.33E -5	1.54E -3	3.50E -5	5.02E -5	3.00E -5	1.99E -5	3.05E -5
nd: non-detect, signal peak was too small compared to noise																		

Table B.7: PFC concentrations in soil samples from landfill A

Sample	Concentration (ppb)																	
	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTA	PFBS	PFHxS	PFOS	PFDS	PFOSA	6:2 FTUA	8:2 FTUA	10:2 FTUA
Borrow pit soil 1	< 0	< 0	No Peak	No Peak	< 0	< 0	5.6	33.6	3140	No Peak	< 0	< 0	< 0	< 0	< 0	< 0	< 0	< 0
Borrow pit soil 2	< 0	< 0	No Peak	< 0	< 0	< 0	10.2	No Peak	223	< 0	< 0	< 0	< 0	No Peak	< 0	< 0	No Peak	< 0
Borrow pit soil 3	< 0	< 0	< 0	No Peak	< 0	< 0	9.49	22.7	244	< 0	< 0	< 0	< 0	No Peak	< 0	< 0	< 0	< 0
Borrow pit soil spike 1	1.86	< 0	2.09	1.89	1.97	1.94	2260	3820	15400	< 0	1.69	1.64	2.01	7.28	5.88	0.616	0.659	1.95
Borrow pit soil spike 2	2.25	0.117	2.55	2.2	2.42	2.31	2600	4060	12100	< 0	1.69	1.64	2.34	7.57	8.25	0.884	1	2.29
Borrow pit soil spike 3	2.19	< 0	2.51	2.35	2.29	2.21	1740	3090	7830	< 0	1.42	1.34	2.32	7.64	10.1	0.893	1.03	2.29
Average	2.1	0.1	2.4	2.1	2.2	2.2	2200.0	3656.7	11776.7	-	1.6	1.5	2.2	7.5	8.1	0.8	0.9	2.2
RSD (%)	10.0	-	10.7	10.9	10.4	8.9	19.7	13.8	32.2	-	9.7	11.2	8.3	2.5	26.2	19.7	23.0	9.0
Recovery (%)	105.0	5.9	119.2	107.3	111.3	107.7	11000.0	18283.3	58883.3	-	80.0	77.0	111.2	374.8	403.8	39.9	44.8	108.8
Leaching field soil 1	< 0	< 0	< 0	< 0	< 0	< 0	16.3	75.6	400	< 0	< 0	< 0	< 0	< 0	< 0	< 0	< 0	< 0
Leaching field soil 2	< 0	< 0	< 0	< 0	< 0	< 0	28.4	60	343	< 0	< 0	< 0	< 0	< 0	< 0	< 0	< 0	< 0
Leaching field soil 3	< 0	< 0	< 0	< 0	< 0	< 0	31.4	90.5	538	< 0	< 0	< 0	< 0	< 0	< 0	No Peak	< 0	< 0
Leaching field soil spike 1	1.92	< 0	2.05	1.8	1.84	2.01	1450	2180	5530	< 0	1.43	1.37	1.97	6.57	7.74	0.876	0.769	1.69
Leaching field soil spike 2	2.19	< 0	2.39	1.97	2.23	2.35	1590	3180	5390	< 0	1.56	1.46	2.3	10.1	11.7	0.963	0.931	2.09
Leaching field soil spike 3	2.15	< 0	2.29	2	2.59	2.31	1330	2030	3990	< 0	1.92	1.76	2.35	7.09	8.24	1.67	1.15	2.28
Average	2.1	-	2.2	1.9	2.2	2.2	1456.7	2463.3	4970.0	-	1.6	1.5	2.2	7.9	9.2	1.2	1.0	2.0
RSD (%)	7.0	-	7.8	5.6	16.9	8.4	8.9	25.4	17.1	-	15.5	13.3	9.4	24.1	23.4	37.2	20.1	14.9
Recovery (%)	104.3	-	112.2	96.2	111.0	111.2	72833.3	12316.7	24850.0	-	81.8	76.5	110.3	396.0	461.3	58.5	47.5	101.0
PFC spike = 2 ppb for each analyte																		

Table B.8: PFCs in landfill B samples

Sample	Concentration (ppb)															6:2 FTUA	8:2 FTUA	10:2 FTUA
	PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTA	PFBS	PFHxS	PFOS	PFDS	FOSA			
BLANK	0.014	0.012	0.009	0.003	0.003	0.010	0.003	0.009	0.000	0.000	0.001	0.000	0.002	0.0000	0.000	0.000	0.000	0.000
Dec 2	0.052	0.873	1.499	0.507	0.282	0.050	0.094	0.015	0.006	0.000	0.054	0.202	0.176	0.002	0.003	0.000	0.000	0.005
Feb 2	0.055	0.903	1.659	0.602	0.260	0.056	0.085	0.015	0.004	0.001	0.052	0.202	0.204	0.0005	0.005	0.001	0.047	0.037
Feb 16	0.025	0.669	1.083	0.283	0.227	0.120	0.233	0.078	0.007	0.001	0.037	0.128	0.272	0.0026	0.008	0.002	0.085	0.061
Mar 2	0.079	1.410	2.385	0.844	0.441	0.097	0.131	0.030	0.010	0.002	0.093	0.391	0.420	0.002	0.010	0.004	0.139	0.037
Mar 16	0.054	0.446	1.636	0.609	0.389	0.552	0.460	0.520	0.032	0.005	0.051	0.284	0.915	0.0000	0.040	0.005	0.330	0.321
Mar 30	0.061	0.595	1.913	0.483	0.691	0.579	1.384	0.129	0.040	0.001	0.042	0.350	1.948	0.0000	0.077	0.010	0.662	0.423
Apr 13	0.094	0.768	2.268	0.920	1.016	0.754	1.777	0.290	0.084	0.005	0.092	0.507	2.609	0.0000	0.134	0.050	2.103	0.869
Apr 27	0.097	0.739	2.323	0.653	0.429	0.112	0.193	0.038	0.012	0.001	0.136	0.401	0.296	0.0000	0.009	0.004	0.106	0.096
May 11	0.068	0.350	2.001	0.723	0.350	0.070	0.074	0.030	0.003	0.000	0.039	0.258	0.271	0.0003	0.006	0.0002	0.014	0.007
May 25	0.096	0.719	3.323	1.423	0.657	0.159	0.191	0.042	0.011	0.001	0.061	0.387	0.420	0.0006	0.011	0.004	0.051	0.033
June 8	0.071	0.573	2.427	0.892	0.431	0.092	0.103	0.030	0.006	0.001	0.046	0.302	0.320	0.0003	0.008	0.002	0.019	0.009
June 22	0.089	0.406	2.225	0.931	0.394	0.067	0.053	0.015	0.003	0.001	0.012	0.234	0.210	0.0000	0.004	0.002	0.021	0.017
Mar 2: Average of samples collected by pump and bucket																		

Table B.9: PFCs in landfill B samples (raw data)

Sample	Concentration (ppb)																	
	PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTA	PFBS	PFHxS	PFOS	PFDS	PFOSA	6:2 FTUA	8:2 FTUA	10:2 FTUA
Blank 1	0.0141	0.0214	0.0071	0.0027	0.0031	0.0024	0.0018	0.0009	No peak	No peak	0.0011	0.0001	0.0019	0.0001	No peak	No peak	0.0017	0.0013
Blank2	0.0133	0.0134	0.0081	0.0022	0.0042	0.0140	0.0026	0.0139	No peak	No peak	No peak	No peak	0.0017	0.0002	No peak	No peak	0.0020	0.0004
Blank3	0.0158	0.0016	0.0118	0.0042	0.0029	0.0123	0.0034	0.0118	0.0001	0.0008	No peak	No peak	0.0015	No peak	0.0001	No peak	0.0013	0.0015
AVG BLANK	0.0140	0.0120	0.0090	0.0030	0.0030	0.0100	0.0030	0.0090	-	-	-	-	0.0020	-	-	-	0.0017	0.0011
STDEV	0.0010	0.0100	0.0030	0.0010	0.0010	0.0060	0.0010	0.0070	-	-	-	-	0.0000	-	-	-	0.0000	0.0010
5 ppb std	1.0320	3.3950	4.7290	4.1840	4.2380	4.7140	5.0590	5.3060	4.5030	4.8710	3.6630	3.9890	4.3900	4.2390	4.9680	3.0360	4.1470	4.3750
5 ppb std	1.5310	3.4040	4.1600	3.9970	4.2370	4.2740	4.3060	4.4820	4.9190	5.3050	3.9820	3.9960	4.1650	4.4760	5.8170	2.9190	4.5860	4.1870
1 ppb std	0.3470	1.0290	1.1180	1.0620	1.1000	1.3280	1.0510	1.1490	0.9790	1.0410	0.8250	1.0280	1.1810	1.0810	1.1280	1.0080	1.4410	1.3590
Dec2-1	0.0513	0.7430	1.3242	0.6567	0.2498	0.0511	0.0302	0.0057	0.0018	0.0000	0.0667	0.2353	0.1491	0.0005	0.0029	- 0.0008	0.0341	0.0220
Dec2-2	0.0573	1.1574	1.5770	0.4691	0.3146	0.0526	0.1281	0.0066	0.0074	0.0002	0.0761	0.2406	0.1651	0.0004	0.0049	- 0.0008	0.0045	- 0.0007
Dec2-3	0.0475 49	0.7193 71	1.5964 39	0.3944 21	0.2828 14	0.0472 33	0.1251 64	0.0060 44	0.0092 34	0.0008 72	0.0457 17	0.1873 65	0.1320 92	0.0005 36	0.0011 05	0.0012 55	0.0071 92	- 0.0007 59
AVG Dec 2	0.0520 8	0.8732 8	1.4992 2	0.5067 4	0.2823 9	0.0503 2	0.0944 6	0.0061 0	0.0061 4	0.0003 4	0.0535 5	0.2023 1	0.1760 2	0.0016 8	0.0029 6			0.0052 7
STDEV	0.0049 4	0.2463 6	0.1519 1	0.1351 3	0.0324 1	0.0027 7	0.0556 9	0.0004 7	0.0039 0	0.0004 7	0.0182 2	0.0278 4	0.0172 0	0.0019 0	0.0018 9	0.0024 1	0.0147 5	0.0069 0
Feb 2-1	0.064	1.068	1.738	0.632	0.266	0.057	0.089	0.011	0.004	0.001	0.056	0.213	0.173	0.001	0.005	0.009	0.076	0.045
Feb 2-2	0.048	0.614	1.713	0.609	0.250	0.054	0.086	0.009	0.004	0.001	0.057	0.198	0.169	0.001	0.004	0.003	0.045	0.034
Feb 2-3	0.051	1.027	1.526	0.566	0.263	0.056	0.082	0.010	0.005	0.000	0.072	0.233	0.200	0.001	0.006	0.000	0.047	0.036
AVG Feb 2	0.055	0.903	1.659	0.602	0.260	0.056	0.085	0.010	0.004	0.001	0.062	0.215	0.181	0.001	0.005	0.004	0.056	0.038
STDEV	0.008	0.251	0.116	0.033	0.009	0.001	0.004	0.001	0.000	0.001	0.009	0.018	0.017	0.000	0.001	0.005	0.017	0.006

Table B.9 continued

Sample	Concentration (ppb)																	
	PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTA	PFBS	PFHxS	PFOS	PFDS	PFOSA	6:2 FTUA	8:2 FTUA	10:2 FTUA
Feb 16-1	0.025	0.649	1.088	0.285	0.220	0.051	0.212	0.015	0.006	0.000	0.042	0.139	0.233	0.001	0.005	0.002	0.076	0.054
Feb 16-2	0.031	0.841	1.096	0.306	0.239	0.243	0.233	0.199	0.008	0.001	0.040	0.147	0.265	0.000	0.013	0.004	0.102	0.058
Feb 16-3	0.021	0.516	1.066	0.258	0.222	0.067	0.253	0.020	0.006	0.000	0.039	0.125	0.258	0.001	0.005	0.000	0.083	0.074
AVG Feb 16	0.025	0.669	1.083	0.283	0.227	0.120	0.233	0.078	0.007	0.001	0.040	0.137	0.252	0.001	0.008	0.002	0.087	0.062
STDEV	0.005	0.163	0.016	0.024	0.010	0.106	0.020	0.105	0.001	0.001	0.001	0.011	0.017	0.000	0.004	0.002	0.013	0.011
Mar 2B-1	0.051	0.995	1.879	0.651	0.367	0.099	0.134	0.019	0.007	0.001	0.064	0.294	0.467	0.001	0.007	0.004	0.167	0.034
Mar 2B-2	0.060	1.695	2.140	0.796	0.462	0.131	0.173	0.025	0.010	0.002	0.075	0.348	0.564	0.002	0.012	0.013	0.215	0.050
Mar 2B-3	0.079	1.168	2.070	0.765	0.426	0.126	0.173	0.025	0.011	0.001	0.069	0.337	0.567	0.002	0.016	0.009	0.237	0.052
AVG Mar 2B	0.063	1.286	2.029	0.737	0.418	0.118	0.160	0.023	0.009	0.001	0.069	0.327	0.533	0.001	0.012	0.008	0.206	0.045
STDEV	0.014	0.365	0.135	0.076	0.048	0.017	0.023	0.003	0.002	0.001	0.006	0.029	0.057	0.001	0.005	0.004	0.036	0.010
Mar 2P-1	0.093	1.379	2.825	1.088	0.512	0.095	0.108	0.014	0.011	0.004	0.106	0.430	0.286	0.002	0.007	0.008	0.101	0.040
Mar 2P-2	0.102	2.041	3.068	0.913	0.473	0.069	0.109	0.015	0.011	0.004	0.215	0.801	0.209	0.002	0.014	0.003	0.071	0.030
Mar 2P-3	0.086	1.179	2.328	0.851	0.407	0.064	0.091	0.012	0.008	0.002	0.082	0.299	0.202	0.001	0.007	0.009	0.082	0.022
AVG. Mar 2P	0.094	1.533	2.740	0.951	0.464	0.076	0.103	0.014	0.010	0.003	0.134	0.510	0.233	0.001	0.009	0.007	0.085	0.031
STDEV	0.008	0.451	0.377	0.123	0.053	0.017	0.010	0.002	0.001	0.001	0.071	0.261	0.047	0.000	0.004	0.003	0.015	0.009
Mar16-1	0.058	0.401	1.538	0.578	0.382	0.180	0.406	0.064	0.024	0.001	0.049	0.309	0.911	0.009	0.041	0.011	0.277	0.292
Mar16-2	0.056	0.359	1.632	0.668	0.380	0.188	0.468	0.070	0.025	0.001	0.041	0.279	0.873	0.006	0.034	0.028	0.382	0.332
Mar16-3	0.049	0.577	1.737	0.582	0.403	1.287	0.505	1.426	0.046	0.013	0.052	0.305	0.975	0.008	0.046	0.006	0.347	0.345
AVG Mar16	0.054	0.446	1.636	0.609	0.389	0.552	0.460	0.520	0.032	0.005	0.047	0.298	0.920	0.008	0.040	0.015	0.335	0.323
STDEV	0.005	0.115	0.100	0.051	0.013	0.637	0.050	0.785	0.012	0.007	0.006	0.017	0.052	0.001	0.006	0.012	0.053	0.028

Table B.9 continued

Sample	Concentration (ppb)																	
	PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTA	PFBS	PFHxS	PFOS	PFDS	PFOSA	6:2 FTUA	8:2 FTUA	10:2 FTUA
Mar30-1	0.063	0.425	1.783	0.514	0.734	0.572	1.416	0.127	0.041	0.000	0.037	0.400	2.425	0.015	0.084	0.024	0.742	0.412
Mar 30-2	0.072	0.719	2.317	0.535	0.748	0.608	1.538	0.149	0.045	0.002	0.040	0.366	2.403	0.013	0.081	0.029	0.686	0.465
Mar30-3	0.049	0.640	1.639	0.398	0.591	0.556	1.200	0.112	0.033	0.000	0.032	0.311	2.079	0.011	0.067	0.006	0.585	0.458
AVG Mar 30	0.061	0.595	1.913	0.483	0.691	0.579	1.384	0.129	0.040	0.001	0.036	0.359	2.302	0.013	0.077	0.020	0.671	0.445
STDEV	0.011	0.152	0.357	0.074	0.087	0.027	0.171	0.019	0.006	0.001	0.004	0.045	0.194	0.002	0.009	0.012	0.079	0.029
Apr13-1	0.065	0.469	1.950	0.864	0.874	0.617	1.525	0.241	0.072	0.005	0.067	0.468	3.069	0.025	0.126	0.066	1.899	0.700
Apr13-2	0.067	0.548	1.771	0.773	0.831	0.566	1.395	0.232	0.066	0.003	0.067	0.449	2.761	0.023	0.121	0.058	1.843	0.636
Apr13-3	0.148	1.287	3.084	1.124	1.342	1.080	2.410	0.399	0.116	0.006	0.085	0.616	3.847	0.032	0.154	0.101	3.342	1.267
AVG Apr 13	0.094	0.768	2.268	0.920	1.016	0.754	1.777	0.290	0.084	0.005	0.073	0.511	3.226	0.026	0.134	0.075	2.361	0.868
STDEV	0.048	0.451	0.712	0.182	0.284	0.283	0.552	0.094	0.027	0.001	0.010	0.092	0.560	0.005	0.018	0.023	0.850	0.348
Apr27-1	0.093	0.761	2.368	0.595	0.412	0.103	0.190	0.021	0.012	0.001	0.128	0.392	0.239	0.000	0.008	0.008	0.107	0.088
Apr27-2	0.093	0.782	2.237	0.716	0.442	0.141	0.181	0.070	0.015	0.001	0.178	0.421	0.291	0.002	0.011	0.023	0.083	0.095
Apr27-3	0.104	0.675	2.364	0.646	0.433	0.093	0.209	0.022	0.011	0.000	0.133	0.407	0.273	0.000	0.009	0.017	0.114	0.096
Avg. Apr 27	0.097	0.739	2.323	0.653	0.429	0.112	0.193	0.038	0.012	0.001	0.146	0.407	0.268	0.001	0.009	0.016	0.102	0.093
STDEV	0.007	0.056	0.075	0.061	0.015	0.025	0.014	0.028	0.002	0.001	0.027	0.015	0.026	0.001	0.001	0.008	0.016	0.004
May11-1	0.069	0.362	1.753	0.602	0.324	0.067	0.059	0.017	0.003	0.000	0.041	0.285	0.235	0.000	0.005	0.011	0.029	-0.001
May11-2	0.066	0.322	1.978	0.802	0.354	0.062	0.074	0.022	0.003	0.000	0.039	0.272	0.250	0.001	0.006	0.002	0.023	-0.001
May11-3	0.068	0.366	2.271	0.766	0.372	0.081	0.090	0.014	0.004	0.000	0.036	0.277	0.259	0.000	0.006	-0.001	0.020	-0.001
Avg May11	0.068	0.350	2.001	0.723	0.350	0.070	0.074	0.018	0.003	0.000	0.039	0.278	0.248	0.000	0.006	0.004	0.024	-0.001
STDEV	0.002	0.024	0.260	0.106	0.024	0.010	0.016	0.004	0.001	0.000	0.002	0.007	0.012	0.000	0.000	0.006	0.005	0.000

Table B.9 continued

Sample	Concentration (ppb)																	
	PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTA	PFBS	PFHxS	PFOS	PFDS	PFOSA	6:2 FTUA	8:2 FTUA	10:2 FTUA
May25-1	0.109	1.279	4.306	1.903	0.872	0.213	0.251	0.060	0.015	0.002	0.074	0.485	0.427	0.001	0.013	-0.001	0.092	0.053
May25-2	0.092	0.433	2.384	1.107	0.476	0.107	0.126	0.027	0.007	0.001	0.052	0.320	0.317	0.001	0.009	-0.001	0.045	0.018
May25-3	0.087	0.444	3.279	1.260	0.622	0.156	0.195	0.038	0.011	0.001	0.069	0.429	0.418	0.001	0.012	0.007	0.061	0.023
Avg. May 25	0.096	0.719	3.323	1.423	0.657	0.159	0.191	0.042	0.011	0.001	0.065	0.411	0.387	0.001	0.011	0.002	0.066	0.031
STDEV	0.012	0.485	0.962	0.422	0.201	0.053	0.062	0.017	0.004	0.001	0.012	0.084	0.061	0.000	0.002	0.005	0.024	0.018
June8-1	0.127	0.761	3.035	1.078	0.565	0.121	0.123	0.037	0.008	0.002	0.057	0.393	0.367	0.001	0.009	-0.001	0.020	-0.001
June8-2	0.001	0.451	2.351	0.824	0.369	0.068	0.092	0.013	0.005	0.001	0.038	0.287	0.257	0.001	0.007	-0.001	0.035	0.004
June8-3	0.085	0.506	1.894	0.775	0.360	0.088	0.096	0.014	0.005	0.002	0.038	0.253	0.255	0.001	0.008	-0.001	0.018	-0.001
Avg. June 8	0.071	0.573	2.427	0.892	0.431	0.092	0.103	0.021	0.006	0.001	0.044	0.311	0.293	0.001	0.008	-0.001	0.024	0.001
STDEV	0.064	0.166	0.574	0.162	0.116	0.026	0.017	0.014	0.002	0.001	0.011	0.073	0.064	0.000	0.001	0.000	0.009	0.002
June22-1	0.079	0.304	1.847	0.796	0.322	0.062	0.043	0.008	0.003	0.001	0.014	0.226	0.163	0.000	0.004	0.002	0.020	0.012
June22-2	0.094	0.360	2.253	1.022	0.433	0.068	0.055	0.009	0.003	0.001	0.020	0.266	0.194	0.000	0.004	-0.001	0.031	0.019
June22-3	0.093	0.553	2.574	0.975	0.427	0.072	0.062	0.009	0.003	0.001	0.020	0.299	0.216	0.001	0.004	-0.001	0.046	0.013
Avg. June 22	0.089	0.406	2.225	0.931	0.394	0.067	0.053	0.009	0.003	0.001	0.018	0.264	0.191	0.000	0.004	0.000	0.032	0.015
STDEV	0.009	0.131	0.365	0.119	0.062	0.005	0.009	0.001	0.000	0.000	0.004	0.037	0.026	0.000	0.000	0.002	0.013	0.004

Table B.10: R² values for temporal series

	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDaA	PFTA	PFBS	PFHxS	PFOS	PFDS	PFOSA	6:2FTUA	8:2FTUA	10:2FTUA	TotPFC	pH	EC	TSS	Temp	Rain-2wk	TOC	Rain-24h		
PFBA	1.00	0.01	0.84	0.75	0.44	0.00	0.00	0.03	0.02	0.04	0.07	0.70	0.02	0.20	0.01	0.07	0.00	0.00	0.30	0.31	0.71	0.00	0.24	0.10	0.78	0.04		
PFPeA	0.01	1.00	0.02	0.00	0.01	0.00	0.02	0.01	0.04	0.14	0.40	0.08	0.00	0.18	0.01	0.15	0.11	0.04	0.05	0.00	0.03	0.30	0.27	0.04	0.09	0.01		
PFHxA	0.84	0.02	1.00	0.87	0.42	0.00	0.01	0.06	0.00	0.02	0.06	0.61	0.01	0.03	0.00	0.03	0.01	0.03	0.23	0.56	0.65	0.02	0.34	0.22	0.70	0.07		
PFHpA	0.75	0.00	0.87	1.00	0.31	0.01	0.04	0.05	0.00	0.05	0.01	0.43	0.00	0.02	0.00	0.01	0.03	0.06	0.17	0.49	0.76	0.00	0.38	0.26	0.64	0.25		
PFOA	0.44	0.01	0.42	0.31	1.00	0.46	0.45	0.18	0.53	0.18	0.10	0.75	0.62	0.24	0.56	0.57	0.38	0.28	0.91	0.04	0.09	0.07	0.02	0.01	0.09	0.01		
PFNA	0.00	0.00	0.00	0.01	0.46	1.00	0.91	0.86	0.92	0.34	0.07	0.22	0.92	0.30	0.95	0.66	0.80	0.80	0.65	0.16	0.07	0.09	0.07	0.10	0.02	0.14		
PFDA	0.00	0.02	0.01	0.04	0.45	0.91	1.00	0.72	0.93	0.24	0.15	0.19	0.90	0.20	0.94	0.70	0.89	0.86	0.63	0.17	0.16	0.17	0.18	0.11	0.04	0.17		
PFUnA	0.03	0.01	0.06	0.05	0.18	0.86	0.72	1.00	0.74	0.33	0.07	0.07	0.67	0.18	0.74	0.42	0.64	0.68	0.35	0.28	0.10	0.10	0.06	0.16	0.05	0.01		
PFDaA	0.02	0.04	0.00	0.00	0.53	0.92	0.93	0.74	1.00	0.44	0.25	0.36	0.89	0.25	0.94	0.81	0.91	0.87	0.75	0.14	0.05	0.21	0.12	0.12	0.01	0.04		
PFTA	0.04	0.14	0.02	0.05	0.18	0.34	0.24	0.33	0.44	1.00	0.12	0.20	0.29	0.10	0.33	0.61	0.42	0.39	0.36	0.17	0.00	0.04	0.05	0.24	0.12	0.02		
PFBS	0.07	0.40	0.06	0.01	0.10	0.07	0.15	0.07	0.25	0.12	1.00	0.34	0.09	0.00	0.12	0.16	0.21	0.15	0.18	0.01	0.00	0.74	0.08	0.04	0.76	0.01		
PFHxS	0.70	0.08	0.61	0.43	0.75	0.22	0.19	0.07	0.36	0.20	0.34	1.00	0.33	0.20	0.31	0.36	0.23	0.14	0.71	0.12	0.27	0.16	0.03	0.00	0.51	0.00		
PFOS	0.02	0.00	0.01	0.00	0.62	0.92	0.90	0.67	0.89	0.29	0.09	0.33	1.00	0.26	0.99	0.68	0.81	0.72	0.80	0.07	0.06	0.12	0.09	0.08	0.00	0.13		
PFDS	0.20	0.18	0.03	0.02	0.24	0.30	0.20	0.18	0.25	0.10	0.00	0.20	0.26	1.00	0.27	0.22	0.19	0.29	0.26	0.07	0.06	0.07	0.01	0.05	0.19	0.07		
PFOSA	0.01	0.01	0.00	0.00	0.56	0.95	0.94	0.74	0.94	0.33	0.12	0.31	0.99	0.27	1.00	0.71	0.86	0.80	0.77	0.11	0.07	0.14	0.11	0.11	0.00	0.07		
6:2FTUA	0.07	0.15	0.03	0.01	0.57	0.66	0.70	0.42	0.81	0.61	0.16	0.36	0.68	0.22	0.71	1.00	0.80	0.73	0.74	0.16	0.02	0.07	0.09	0.12	0.02	0.00		
8:2FTUA	0.00	0.11	0.01	0.03	0.38	0.80	0.89	0.64	0.91	0.42	0.21	0.23	0.81	0.19	0.86	0.80	1.00	0.94	0.63	0.27	0.13	0.17	0.30	0.18	0.00	0.01		
10:2FTU	0.00	0.04	0.03	0.06	0.28	0.80	0.86	0.68	0.87	0.39	0.15	0.14	0.72	0.29	0.80	0.73	0.94	1.00	0.50	0.35	0.15	0.12	0.30	0.17	0.00	0.06		
A	0.30	0.05	0.23	0.17	0.91	0.65	0.63	0.35	0.75	0.36	0.18	0.71	0.80	0.26	0.77	0.74	0.63	0.50	1.00	0.00	0.02	0.14	0.01	0.01	0.09	0.02		
TotPFC	0.31	0.00	0.56	0.49	0.04	0.16	0.17	0.28	0.14	0.17	0.01	0.12	0.07	0.07	0.11	0.16	0.27	0.35	0.00	1.00	0.38	0.05	0.26	0.50	0.43			
pH	0.71	0.03	0.65	0.76	0.09	0.07	0.16	0.10	0.05	0.00	0.00	0.27	0.06	0.06	0.07	0.02	0.13	0.15	0.02	0.38	1.00	0.01	0.60	0.24	0.90			
EC	0.00	0.30	0.02	0.00	0.07	0.09	0.17	0.10	0.21	0.04	0.74	0.16	0.12	0.07	0.14	0.07	0.17	0.12	0.14	0.05	0.01	1.00	0.15	0.00	0.55			
TSS	0.24	0.27	0.34	0.38	0.02	0.07	0.18	0.06	0.12	0.05	0.08	0.03	0.09	0.01	0.11	0.09	0.30	0.30	0.01	0.26	0.60	0.15	1.00	0.21	0.20			
Temp	0.10	0.04	0.22	0.26	0.01	0.10	0.11	0.16	0.12	0.24	0.04	0.00	0.08	0.05	0.11	0.12	0.18	0.17	0.01	0.50	0.24	0.00	0.21	1.00	0.00			
Rain-2wk	0.78	0.09	0.70	0.64	0.09	0.02	0.04	0.05	0.01	0.12	0.76	0.51	0.00	0.19	0.00	0.02	0.00	0.00	0.09	0.43	0.90	0.55	0.20	0.00	1.00			
TOC	0.04	0.01	0.07	0.25	0.01	0.14	0.17	0.01	0.04	0.02	0.01	0.00	0.13	0.07	0.07	0.00	0.01	0.06	0.02									
Rain-24h	Log-log R ² for all but Rain-24h																											

Appendix C: Raw data tables for samples processed by liquid-liquid extraction at DFO-IOS

Table C.1: PFCs in landfill A samples

Sample ID	Concentration (ppb)																	
	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTA	PFBS	PFHxS	PFOS	PFDS	PFOSA	6:2 FTUA	8:2 FTUA	10:2 FTUA
LH9	<MDL	0.113	0.166	0.0994	0.281	<MDL	N/A	<MDL	N/A	0.0624	0.0652	0.348	0.0628	<MDL	N/A	N/A	N/A	<MDL
LH11	0.189	0.092	0.1058	0.082	0.3	N/A	N/A	<MDL	0.027	0.0636	0.0612	0.374	0.0416	<MDL	N/A	N/A	N/A	N/A
LH13	<MDL	0.1158	0.1468	0.0958	0.32	<MDL	N/A	N/A	0.0262	N/A	0.0638	0.332	0.0484	<MDL	N/A	N/A	N/A	<MDL
LH16	<MDL	0.1322	0.158	0.1144	0.332	N/A	N/A	<MDL	N/A	0.0662	0.0626	0.4	0.0338	<MDL	N/A	N/A	N/A	<MDL
LH22	<MDL	0.0752	0.1308	0.1102	0.322	N/A	N/A	<MDL	0.0272	0.0632	0.0588	0.37	0.0492	<MDL	N/A	N/A	N/A	N/A
LH2	<MDL	<MDL	0.092	0.0612	0.212	N/A	N/A	<MDL	0.0284	N/A	0.0484	0.218	0.0342	<MDL	N/A	N/A	N/A	<MDL
LH4	N/A	0.272	0.222	0.1044	0.346	<MDL	N/A	<MDL	0.0318	N/A	0.0774	0.466	0.0638	0.0298	N/A	N/A	N/A	<MDL
Avg	0.189	0.133	0.146	0.095	0.302	-	-	-	0.028	0.064	0.062	0.358	0.048	0.030	-	-	-	-
RSD (%)	-	53.061	29.456	19.275	14.880	-	-	-	7.833	2.575	13.785	21.073	25.721	-	-	-	-	-
MDL (ppb)	0.28	0.14	0.06	0.06	0.28	0.14	0.06	0.06	0.04	0.06	0.02	0.02	0.04	0.04	0.04	0.04	0.04	0.04
<MDL: Less than method detection limit; N/A: Not analyzed																		

Table C.2: PFCs in landfill B samples

Sample	Concentration (ppb)																	
	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTA	PFBS	PFHxS	PFOS	PFDS	PFOSA	6:2 FTUA	8:2 FTUA	10:2 FTUA
Dec2-1a-ss1	0.200	0.438	0.330	0.152	0.254	< 0	< 0	< 0	<MDL	<MDL	0.145	0.400	0.200	< 0	0.234	No Peak	< 0	<MDL
Dec2-1a-ss2	0.192	0.422	0.338	0.143	<MDL	< 0	< 0	< 0	No Peak	<MDL	0.140	0.386	0.166	< 0	0.234	<MDL	< 0	<MDL
Dec2-1b-ss1	0.206	0.438	0.362	0.178	<MDL	< 0	< 0	< 0	<MDL	<MDL	0.144	0.376	0.151	< 0	0.234	<MDL	< 0	<MDL
Dec2-1b-ss2	0.206	0.442	0.364	0.155	<MDL	< 0	< 0	< 0	<MDL	<MDL	0.151	0.416	0.166	< 0	0.236	<MDL	< 0	<MDL
Dec2-2a-ss1	0.216	0.416	0.354	0.152	<MDL	< 0	< 0	<MDL	<MDL	<MDL	0.165	0.408	0.114	< 0	0.236	No Peak	< 0	<MDL
Dec2-2a-ss2	0.212	0.402	0.422	0.169	0.230	< 0	< 0	< 0	<MDL	<MDL	0.151	0.444	0.128	< 0	0.236	<MDL	< 0	<MDL
Dec2-2b-ss1	0.210	0.436	0.418	0.157	<MDL	< 0	< 0	<MDL	<MDL	<MDL	0.148	0.364	0.125	< 0	0.236	<MDL	< 0	0.009
Dec2-2b-ss2	0.242	0.430	0.368	0.156	<MDL	< 0	< 0	< 0	<MDL	<MDL	0.139	0.396	0.158	< 0	0.236	<MDL	< 0	0.014
Feb2-1	0.176	0.422	0.370	0.159	<MDL	< 0	< 0	<MDL	<MDL	<MDL	0.134	0.398	0.132	< 0	0.240	<MDL	0.022	<MDL
Feb2-2	0.202	0.384	0.356	0.155	<MDL	< 0	< 0	< 0	<MDL	<MDL	0.144	0.390	0.141	< 0	0.236	<MDL	0.039	0.009
Feb16-1	0.145	0.320	0.210	0.085	<MDL	< 0	<MDL	< 0	<MDL	<MDL	<MDL	0.202	0.216	< 0	0.240	<MDL	0.022	0.010
Feb16-2	<MDL	0.356	0.208	0.089	<MDL	< 0	0.020	<MDL	<MDL	<MDL	<MDL	0.176	0.232	< 0	0.244	<MDL	0.008	0.010
Mar2B-1	0.224	0.496	0.422	0.150	0.282	< 0	<MDL	< 0	<MDL	<MDL	0.157	0.486	0.362	< 0	0.240	<MDL	< 0	<MDL
Mar2B-2	0.230	0.450	0.408	0.183	0.298	< 0	<MDL	< 0	<MDL	<MDL	0.144	0.498	0.326	< 0	0.238	<MDL	< 0	<MDL
Mar2P-1	0.264	0.558	0.460	0.176	0.296	< 0	< 0	<MDL	<MDL	<MDL	0.194	0.620	0.153	< 0	0.238	<MDL	0.075	0.023
Mar2P-2	0.266	0.668	0.456	0.158	0.266	< 0	< 0	<MDL	<MDL	<MDL	0.175	0.578	0.150	< 0	0.238	No Peak	0.072	0.020
Mar16-1	0.222	0.502	0.440	0.164	0.310	< 0	0.087	<MDL	<MDL	<MDL	0.164	0.456	0.782	< 0	0.270	<MDL	0.298	0.038
Mar16-2	0.234	0.454	0.388	0.158	0.300	< 0	0.091	<MDL	<MDL	<MDL	0.163	0.478	0.756	< 0	0.266	<MDL	0.224	0.030
Mar30-1	0.187	0.416	0.302	0.117	0.580	< 0	0.310	<MDL	<MDL	<MDL	<MDL	0.432	2.080	< 0	0.282	<MDL	0.620	0.041
Mar30-2	0.165	0.376	0.292	0.114	0.504	< 0	0.260	<MDL	<MDL	<MDL	<MDL	0.438	1.792	< 0	0.274	<MDL	0.636	0.038
Apr13-1	0.276	0.570	0.422	0.194	0.680	<MDL	0.368	<MDL	<MDL	<MDL	0.190	0.634	2.720	< 0	0.350	No Peak	< 0	<MDL
Apr13-2	0.238	0.498	0.428	0.144	0.670	<MDL	0.354	<MDL	<MDL	<MDL	0.172	0.592	2.520	< 0	0.340	<MDL	< 0	<MDL
Apr27-1	0.316	0.768	0.720	0.280	0.400	< 0	0.051	< 0	<MDL	<MDL	0.602	0.896	0.340	< 0	0.240	<MDL	<MDL	<MDL
Apr27-2	0.376	0.824	0.754	0.392	0.440	< 0	0.039	<MDL	<MDL	<MDL	0.706	0.994	0.282	< 0	0.240	0.096	0.014	0.017
MDL (ppb)	0.28	0.14	0.06	0.06	0.28	0.14	0.06	0.06	0.04	0.06	0.02	0.02	0.04	0.04	0.04	0.04	0.04	0.04
<MDL: Less than method detection limit; No peak or < 0: No quantifiable peak * Samples from May-June 2010 were not analyzed																		

Appendix D: Raw data tables for batch adsorption tests

Table D.1: Mixed PFCs

Sample	Concentration (ppb)																	
	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTA	PFBS	PFHxS	PFOS	PFDS	PFOSA	6:2 FTUA	8:2 FTUA	10:2 FTUA
R 1:100-1	0.075	0.424	0.311	0.153	0.362	0.35	0.705	0.777	0.857	0.382	0.152	0.259	0.502	0.238	0.422	0.0467	0.138	0.218
1:100-1 Rinse	0.0145	0.0859	0.0197	0.0194	< 0	0.0132	0.0275	0.0269	0.0377	0.0304	< 0	0.0102	0.0171	0.0148	0.027	0.013	0.0089 8	0.013
1:100-1	1.24	7.09	5.21	3.27	5	3.94	4.2	2.32	0.874	0.0416	5.67	3.81	3.23	0.359	1.95	0.954	1.32	0.581
1:100-1 duplicate	1.26	6.95	5.33	3.73	4.9	3.58	4.18	2.36	1.02	0.0324	5.43	3.72	3.18	0.377	1.94	1.01	1.35	0.59
1:100-2	1.36	6.81	5.43	3.61	4.88	4.03	4.47	2.42	0.924	0.0321	5.69	3.97	3.29	0.362	3.72	0.938	1.39	0.625
1:100-3	1.31	5.57	5.24	3.38	4.88	3.88	4.31	2.22	0.86	0.0363	5.02	3.51	3.09	0.359	3.15	0.89	1.3	0.637
1:100-4	1.25	5.29	5.23	3.37	4.63	4.01	4.17	2.19	0.875	0.0316	5.75	3.85	3.13	0.307	1.79	1.03	1.38	0.592
1:200-1	1.24	5.53	5.2	3.25	4.62	3.99	4.25	2.17	0.977	0.0381	5.45	3.71	3.06	0.341	2.34	0.874	1.31	0.624
R 1:200-1	0.0627	0.233	0.254	0.148	0.396	0.484	0.765	0.707	0.884	0.628	0.129	0.25	0.542	0.254	0.63	0.038	0.18	0.197
1:200-1 Rinse	0.0765	0.23	0.343	0.169	0.471	0.532	0.896	0.927	1.35	1.26	0.166	0.315	0.658	0.304	0.368	0.0479	0.201	0.208
1:200-1 duplicate	1.39	5.79	5.63	3.69	5.13	3.68	4.66	2.53	1.1	0.0388	5.6	3.92	3.44	0.388	2.73	0.897	1.44	0.696
1:200-2	1.29	5.74	5.41	3.55	4.87	4.03	4.35	2.07	0.815	0.0421	5.94	3.97	3.23	0.317	2.29	1.1	1.59	0.617
1:200-3	1.32	5.43	5.45	3.43	4.98	4.09	4.38	2.17	1	0.0967	6.08	4.06	3.28	0.323	2.58	0.967	1.52	0.653
1:200-4	1.41	6.21	5.57	3.66	5.16	4.38	4.27	2.03	0.617	0.0284	5.77	4.02	3.3	0.322	2.74	1.01	1.48	0.543
R 1:400-1	0.0718	0.287	0.331	0.226	0.425	0.471	0.728	0.826	1.19	1.15	0.147	0.289	0.568	0.327	0.568	0.0414	0.145	0.19
1:400-1 Rinse	0.769	0.384	0.339	0.401	0.859	0.574	0.793	2.07	4.8	10.1	0.0429	0.125	0.564	1.16	0.268	0.0184	0.0387	0.202
1:400-1	1.41	7.4	5.59	3.82	5.21	4.33	4.61	2.6	1.27	0.109	5.87	4.1	3.44	0.342	1.83	1.2	1.24	0.588
1:400-2	1.22	6.97	4.97	3.15	4.58	4	3.94	2.08	0.952	0.0641	5.42	3.59	2.96	0.34	3.04	0.941	1.12	0.518
1:400-3	1.34	7.42	5.57	4.18	4.9	4.06	4.32	2.42	1.09	0.0448	5.58	3.8	3.28	0.394	2.72	1.18	1.21	0.559
1:400-4	1.3	6.72	5.48	4.72	5.21	4.35	4.45	2.42	1.21	0.0766	5.33	3.92	3.28	0.402	3.43	1.26	1.24	0.581
RH2O-1:200-1	0.0304	0.0737	0.019	0.02	0.0124	0.0273	0.0282	0.038	0.0434	0.0358	< 0	0.0105	0.0224	0.0154	0.0281	0.0112	0.0088 4	0.014
H2O-1:200-1 rinse	0.0214	No Peak	0.0186	0.023	0.0062 1	0.0111	0.025	0.0303	0.0422	0.0344	< 0	0.0114	0.0231	0.0161	0.0259	0.0177	0.0237	0.0383
H2O-1:200-1 duplicate	0.0103	0.0772	0.025	0.024	0.0050 3	0.0080 2	0.035	0.0281	0.0378	0.0307	< 0	0.0121	0.0232	0.0141	0.0282	0.0114	0.0083 7	0.0119
H2O-1:200-2	< 0	0.102	0.018	0.0207	0.0021 7	0.0114	0.0363	0.032	0.0516	0.0359	< 0	0.0105	0.0247	0.0139	0.0283	0.0121	0.0096 6	0.0208

Table D.1 continued

Sample	Concentration (ppb)																	
	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTA	PFBS	PFHxS	PFOS	PFDS	PFOSA	6:2 FTUA	8:2 FTUA	10:2 FTUA
H2O-1:200-3	0.0022 8	0.084	0.0243	0.0221	0.0070 7	0.0096 4	0.0384	0.0344	0.0439	0.0309	< 0	0.0115	0.0226	0.0143	0.03	0.0143	0.0161	0.0206
RH2O-1	0.0214	0.0782	0.0188	0.0279	0.0203	0.0245	0.0423	0.0419	0.0545	0.0366	< 0	0.012	0.0255	0.0161	0.0199	0.0153	0.0135	0.0207
H2O-1	0.038	0.0826	0.02	0.0235	0.0275	0.0301	0.0563	0.0541	0.0668	0.0315	< 0	No Peak	0.0314	0.0195	0.0258	0.0212	0.0305	0.0215
H2O-2	0.0138	0.106	0.0312	0.027	0.0265	0.0313	0.06	0.0635	0.0632	0.0401	< 0	0.0103	0.0273	0.015	0.0304	0.0236	0.025	0.0457
H2O-3	0.0299	0.0877	0.0174	0.0181	0.0013 2	0.0133	0.0376	0.0327	0.0284	0.0348	< 0	0.0096 9	0.0234	0.0156	0.0254	0.0183	0.0081	0.0283
RH2O-S-1:200-1	< 0	0.106	0.0673	0.0684	0.0737	0.146	0.321	0.466	0.763	0.622	0.0274	0.0503	0.167	0.012	0.0915	0.0126	0.0102	0.0153
H2O-S-1:200-1 rinse	No Peak	0.15	0.0653	0.0694	0.0927	0.146	0.292	0.463	0.812	0.801	0.0593	0.0761	0.17	0.0181	0.0286	0.0327	0.0258	0.0468
H2O-S-1:200-1	0.0565	7.88	5.55	5.34	4.99	4.36	4.78	4.72	3.03	0.0704	3.82	3.41	3.41	0.0171	1.3	0.018	0.014	0.0284
H2O-S-1:200-2	0.0122	6.28	5.01	5.01	4.56	4.06	4.74	6.61	5.48	0.0478	3.13	3.06	3.27	0.0249	0.659	0.0238	0.0069 8	0.0191
H2O-S-1:200-3	0.036	6.09	4.91	4.72	4.51	4.38	4.67	2.65	1.18	0.0297	3.59	3.32	3.14	0.0153	2.13	0.0129	0.0069 4	0.016
RH2O-S-1	0.0247	0.0918	0.0478	0.0462	0.0545	0.113	0.253	0.512	0.73	0.294	0.0104	0.0343	0.135	0.0183	0.055	0.0168	0.0113	0.0326
H2O-S-1 rinse	< 0	0.0863	0.0341	0.0452	0.0276	0.0845	0.253	0.468	0.616	0.158	0.0128	0.0309	0.133	0.0129	0.182	0.0132	0.0069 7	0.0179
H2O-S-1	< 0	5.41	5.14	5.23	4.8	4.63	4.86	2.91	2.53	0.242	4.98	4.65	3.36	0.0198	0.523	0.0145	0.0124	0.0165
H2O-S-2	0.0014 2	5.67	5.2	4.77	4.61	4.46	4.88	2.63	1.76	0.0556	4.93	4.27	3.18	0.0203	0.314	0.019	0.0211	0.0442
H2O-S-3	0.0053 2	5.32	5.01	5.03	4.79	4.72	4.96	3.28	2.64	0.307	3.61	3.36	3.21	0.0198	0.157	0.0342	0.0337	0.0807
RLEA-N-1	0.0443	0.143	0.175	0.0454	0.133	0.0093 7	0.0128	< 0	0.0116	0.0284	0.038	0.0971	0.0772	0.0118	0.0266	0.0153	0.017	0.0122
LEA-N-1 rinse	0.0653	0.149	0.191	0.0753	0.126	0.0031 3	0.0079 8	< 0	0.0085 8	0.0286	0.0388	0.0995	0.0761	0.0118	0.022	0.0133	0.01	0.0117
LEA-N-1	0.0313	0.231	0.312	0.0801	0.271	0.0658	0.0071 4	0.0063 3	0.0124	0.0345	0.0127	0.0334	0.0634	0.0124	0.0161	0.0119	0.0085 7	0.0088 5
LEA-N-1 triplicate	0.0523	0.199	0.172	0.0533	0.149	0.0029 6	0.0105	< 0	0.0066 5	0.0286	0.0407	0.108	0.0719	0.0118	0.0263	0.0132	0.0093	0.0105
LEA-N-2	0.0337	0.149	0.173	0.0492	0.123	0.0022 9	0.0084 6	< 0	0.0071 9	0.0285	0.0407	0.107	0.0622	No Peak	0.0229	0.0115	0.0083 7	0.0095 3
LEA-N-2a	0.0372	0.144	0.161	0.0454	0.125	0.0043 2	0.0158	0.0118	0.0215	0.0283	0.0382	0.102	0.0674	0.0131	0.0304	0.0117	0.0093 4	0.0122
LEA-N-2b	0.041	0.134	0.161	0.0477	0.119	0.0031 2	0.0059 7	< 0	0.0149	0.0291	0.0231	0.0905	0.0631	0.0114	0.0481	0.0141	0.0078 2	0.0096 3

Table D.1 continued

Sample	Concentration (ppb)																	
	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTA	PFBS	PFHxS	PFOS	PFDS	PFOSA	6:2 FTUA	8:2 FTUA	10:2 FTUA
LEA-N-3	0.0403	0.169	0.188	0.0644	0.142	0.0063 7	0.0095 4	< 0	0.0082 9	0.0284	0.0451	0.105	0.0726	0.0131	0.0163	0.0127	0.0082 5	No Peak
LEA-N-4	0.067	0.166	0.177	0.0571	0.122	0.0011 7	0.0064 3	< 0	0.0086 2	0.0285	0.0332	0.0927	0.0653	0.0118	0.0176	0.0116	0.0064 9	0.0083 5
RLEA-S-1	0.0933	0.325	0.365	0.17	0.403	0.362	0.66	0.966	1.27	0.837	0.204	0.28	0.458	0.385	0.546	0.0407	0.145	0.264
LEA-S-1 rinse	0.0978	0.3	0.289	0.205	0.417	0.33	0.666	1.43	2.41	3.09	0.143	0.23	0.453	0.621	0.211	0.0244	0.075	0.246
LEA-S-1	1.37	5.74	5.85	3.75	5.29	3.94	5.05	2.47	1.17	0.0559	6.44	4.4	3.53	0.385	2.13	1.12	1.83	0.746
LEA-S-1 duplicate	1.34	5.68	5.57	3.53	5.17	4.31	4.78	2.45	1.19	0.0342	5.91	4.05	3.4	0.418	3.21	0.873	1.43	0.696
LEA-S-2	1.37	5.41	5.39	3.32	4.89	3.93	4.53	2.23	0.882	0.043	5.87	3.93	3.26	0.304	1.91	1.04	1.66	0.695
LEA-S-3	1.23	4.97	4.97	3.18	4.63	3.79	4.41	2.25	0.981	0.0758	5.47	3.77	3.08	0.32	1.51	0.915	1.51	0.617
LEA-S-4	1.29	5.34	5.17	3.33	4.63	4.09	4.38	2.29	0.961	No Peak	5.48	3.73	3.09	0.35	2.15	0.866	1.38	0.596
No Peak or < 0: Peak was not quantifiable																		

Table D.2: Single PFCs

Sample	Conc (ng/L)	Mean (ng/L)	St Dev (ng/L)	95% CI (ng/L)	RSD
SLE-PFBA-1	2.8				
SLE-PFBA-2	2.92				
SLE-PFBA-3	3	2.91	0.10	0.11	3%
PFBA-100-1	2.82				
PFBA-100-2	3.04				
PFBA-100-3	3.06	2.97	0.13	0.15	4%
PFBA-200-1	2.96				
PFBA-200-2	2.72				
PFBA-200-3	3.12	2.93	0.20	0.23	7%
PFBA-400-1	2.68				
PFBA-400-2	3.04				
PFBA-400-3	2.74	2.82	0.19	0.22	7%
SLE-PFBS-1	19.58				
SLE-PFBS-2	22.6				
SLE-PFBS-3	22.4	21.53	1.69	1.91	8%
PFBS-100-1	21				
PFBS-100-2	20.2				
PFBS-100-3	19.96	20.39	0.54	0.62	3%
PFBS-200-1	20.6				
PFBS-200-2	21.8				
PFBS-200-3	20.4	20.93	0.76	0.86	4%
PFBS-400-1	21.8				
PFBS-400-2	25.6				
PFBS-400-3	20.4	22.60	2.69	3.04	12%
SLE-PFHxA-1	10.44				
SLE-PFHxA-2	10.46				
SLE-PFHxA-3	10.96	10.62	0.29	0.33	3%
PFHxA-100-1	11.18				
PFHxA-100-2	11.1				

Table D.2 continued

Sample	Conc (ng/L)	Mean (ng/L)	St Dev (ng/L)	95% CI (ng/L)	RSD
PFHxA-100-3	10.9	11.06	0.14	0.16	1%
PFHxA-200-1	11.48				
PFHxA-200-2	11.24				
PFHxA-200-3	10.94	11.22	0.27	0.31	2%
PFHxA-400-1	10.8				
PFHxA-400-2	10.96				
PFHxA-400-3	11.44	11.07	0.33	0.38	3%
SLE-PFOA-1	13.18				
SLE-PFOA-2	Not analyzed				
SLE-PFOA-3	Not analyzed	13.18			
PFOA-100-1	15.74				
PFOA-100-2	17.28				
PFOA-100-3	15.88	16.30	0.85	0.96	5%
PFOA-200-1	17.48				
PFOA-200-2	18.16				
PFOA-200-3	15.72	17.12	1.26	1.42	7%
PFOA-400-1	16.84				
PFOA-400-2	16.5				
PFOA-400-3	14.08	15.81	1.50	1.70	10%
SLE-PFOS-1	11.7				
SLE-PFOS-2	12.12				
SLE-PFOS-3	12.38	12.07	0.34	0.39	3%
PFOS-100-1	12.72				
PFOS-100-2	11.12				
PFOS-100-3	12.46	12.10	0.86	0.97	7%
PFOS-200-1	12.62				
PFOS-200-2	12.82				
PFOS-200-3	12.72	12.72	0.10	0.11	1%
PFOS-400-1	12.84				
PFOS-400-2	12.26				

Table D.2 continued

Sample	Conc (ng/L)	Mean (ng/L)	St Dev (ng/L)	95% CI (ng/L)	RSD
PFOS-400-3	11.96	12.35	0.45	0.51	4%
SH2O-PFBA-1	2.64				
SH2O-PFBA-2	2.82				
SH2O-PFBA-3	2.6	2.69	0.12	0.13	4%
SH2O-PFBA-200-1	2.54				
SH2O-PFBA-200-2	2.7				
SH2O-PFBA-200-3	2.82	2.69	0.14	0.16	5%
SH2O-PFBS-1	13.66				
SH2O-PFBS-2	14.52				
SH2O-PFBS-3	13.26	13.81	0.64	0.73	5%
SH2O-PFBS-200-1	14.32				
SH2O-PFBS-200-2	13.8				
SH2O-PFBS-200-3	13.92	14.01	0.27	0.31	2%
SH2O-PFHxA-1	12.48				
SH2O-PFHxA-2	11.02				
SH2O-PFHxA-3	11.56	11.69	0.74	0.84	6%
SH2O-PFHxA-200-1	11.82				
SH2O-PFHxA-200-2	11.7				
SH2O-PFHxA-200-3	11.9	11.81	0.10	0.11	1%
SH2O-PFOA-1	11.62				
SH2O-PFOA-2	11.24				
SH2O-PFOA-3	13.52	12.13	1.22	1.38	10%
SH2O-PFOA-200-1	11				
SH2O-PFOA-200-2	13.76				
SH2O-PFOA-200-3	10.68	11.81	1.69	1.92	14%
SH2O-PFOS-1	11.7				
SH2O-PFOS-2	12.18				
SH2O-PFOS-3	11.8	11.89	0.25	0.29	2%
SH2O-PFOS-200-1	13.48				
SH2O-PFOS-200-2	11.84				
SH2O-PFOS-200-3	13.1	12.81	0.86	0.97	7%

Appendix E: Optimum dry density of sand-bentonite admix

The optimum dry density of the sand-bentonite admix was determined by following the Laboratory Compaction Characteristics of Soil Using Standard Effort (ASTM D698-07) method (ASTM International, n.d.a), as mentioned in section 3.6.2. The optimum dry density of the sand-bentonite admix was determined based on a quadratic curve fitted to six points ranging in water content from 8 to 18% (Figure E.1). The optimum dry density was 1.8 g/cm^3 at a water content of 13%. Table F.1 summarizes the data for the optimum dry density determination.

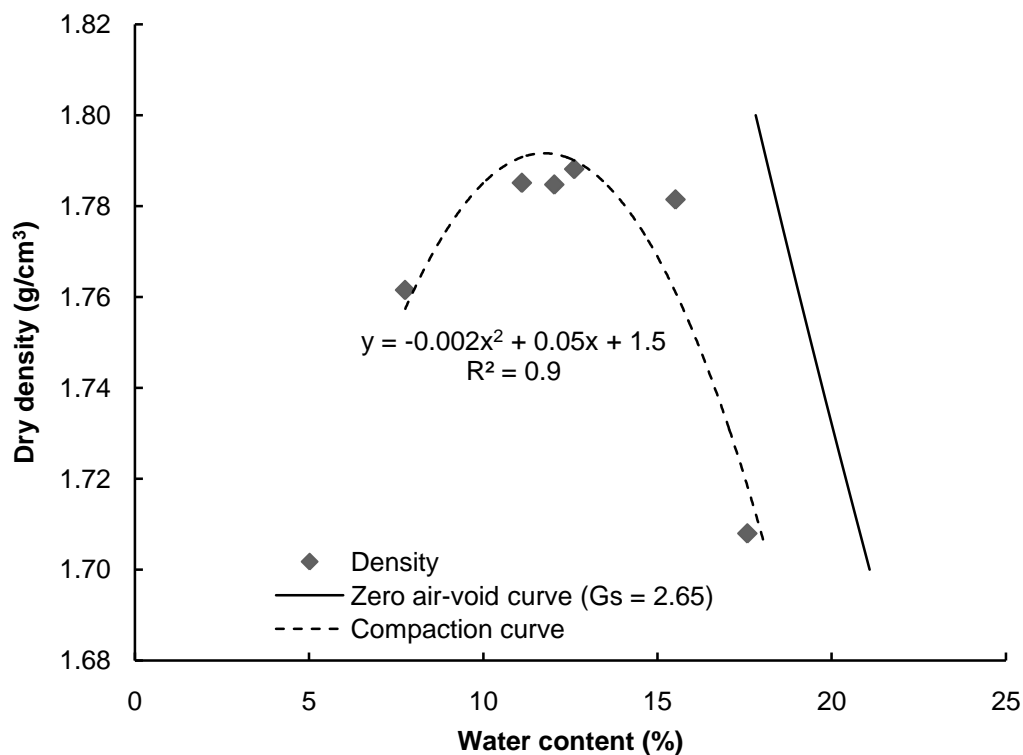


Figure E.1: Compaction curve for sand-bentonite admix

Appendix F: Raw data tables for leaching cell tests

Table F.1: Compaction test data for optimum dry density and leaching cell tests

	Optimum Dry Density Determination						Leaching Cell Tests				
	1	2	3	4	6	7	Water	Leachate 1	Leachate 2	Spiked Leachate 1	Spiked Leachate 2
Empty cell (g)	4165	4166	4166	4166	4165	4165	4566	4561	4554	4561	4560
Cell with soil (g)	5924	6004	6019	6032	6072	6026	5433	5425	5413	5425	5426
Soil (g)	1759	1838	1853	1866	1907	1861	867	864	859	864	866
Volume of cell (cm ³)	926.67	926.67	926.67	926.67	926.67	926.67	411.85	411.85	411.85	411.85	411.85
Wet density (g/cm ³)	1.90	1.98	2.00	2.01	2.06	2.01	2.11	2.10	2.09	2.08	2.10
Dry density (g/cm ³)	1.76	1.79	1.78	1.79	1.78	1.71	1.82	1.80	1.79	1.80	1.81
Dry weight (g)								743.18	736.63	745.44	746.59
Empty container (g)	40	32	27	28	32	32	32	28.64	27.27	32.09	31.95
Container with soil (g)	140	134	134	128	131	137	133	124.54	125.76	136.08	136.96
Container with dry soil (g)	132.8	123.8	122.5	116.8	117.7	121.3	119.3	111.13	111.73	121.81	122.48
Wet soil (g)	100	102	107	100	99	105	101	95.9	98.49	103.99	105.01
Dry soil (g)	92.8	91.8	95.5	88.8	85.7	89.3	87.3	82.49	84.46	89.72	90.53
Water in soil (g)	7.2	10.2	11.5	11.2	13.3	15.7	13.7	13.41	14.03	14.27	14.48
Water content (%)	7.76	11.11	12.04	12.61	15.52	17.58	15.69	16.26	16.61	15.91	15.99

Table F.2: Flow volumes and hydraulic conductivities for water permeating through sand-bentonite admix

Time	Time (days)	Pressure (kPa)	Volume (mL)	Total discharge volume	Flow rate, Q (mL/d)	Hydraulic conductivity, k (cm/s)
5/18/10 10:45	0	5	0	0		
5/18/10 12:45	0	15	0	0	0.000	0.00E+00
5/19/10 10:45	1	25	0	0	0.000	0.00E+00
5/19/10 11:45	1	35	0	0	0.000	0.00E+00
5/19/10 12:45	1	45	0	0	0.000	0.00E+00
5/20/10 11:00	2	45	0	0	0.000	0.00E+00
5/25/10 11:30	7	45	0	0	0.000	0.00E+00
5/26/10 16:00	8	45	1	1	0.842	1.31E-09
5/28/10 10:15	10	45	2.5	3	0.852	1.32E-09
5/31/10 13:00	13	45	5	5	0.803	1.25E-09
6/2/10 13:00	15	45	7.5	8	1.250	1.94E-09
6/3/10 13:45	16	45	8	8	0.485	7.52E-10
6/7/10 10:25	20	45	12	12	1.036	1.61E-09
6/9/10 13:40	22	47	14	14	0.937	1.41E-09
6/11/10 10:30	24	45	15.5	16	0.803	1.25E-09
6/21/10 13:40	34	45	24	24	0.839	1.30E-09
6/23/10 13:35	36	45	27	27	1.503	2.33E-09
6/25/10 12:25	38	45	28	28	0.512	7.95E-10
6/28/10 9:45	41	45	31	31	1.038	1.61E-09
6/30/10 14:15	43	45	32.5	33	0.686	1.06E-09
7/5/10 13:15	48	45	37.5	38	1.008	1.56E-09
7/8/10 15:50	51	45	2.5	40	0.804	1.25E-09
7/12/10 11:45	55	45	7	45	1.175	1.82E-09
7/21/10 9:50	64	44	15	53	0.897	1.42E-09
7/26/10 10:00	69	44	19	57	0.799	1.27E-09
7/29/10 15:45	72	45	23	61	1.235	1.92E-09

Table F.3: Flow volumes and hydraulic conductivities for landfill leachate permeating through sand-bentonite admix

Time	Time (days)	Pressure (kPa)	Volume 1 (mL)	Volume 2 (mL)	Total discharge volume 1 (mL)	Total discharge volume 2 (mL)	Flow rate, Q 1 (mL/d)	Flow rate, Q 2 (mL/d)	Hydraulic conductivity, k (cm/s)	Hydraulic conductivity, k (cm/s)
8/27/10 9:30	0	5	0	0	0	0				
8/27/10 11:30	0	15	0	0	0	0	0.000	0.000	0.0E+00	0.0E+00
8/27/10 12:30	0	25	0	0	0	0	0.000	0.000	0.0E+00	0.0E+00
8/27/10 13:30	0	35	0	0	0	0	0.000	0.000	0.0E+00	0.0E+00
9/7/10 11:00	11	35	2	2	2	2	0.184	0.184	3.7E-10	3.7E-10
9/10/10 13:45	14	35	4	4	4	4	0.642	0.642	1.3E-09	1.3E-09
9/14/10 13:45	18	35	8	8	8	8	0.875	0.875	1.7E-09	1.7E-09
9/20/10 15:55	24	35	12	13	12	13	0.739	0.821	1.5E-09	1.6E-09
9/23/10 16:55	27	35	14	15	14	15	0.658	0.822	1.3E-09	1.6E-09
9/30/10 16:50	34	35	19	22	19	22	0.715	1.000	1.4E-09	2.0E-09
10/6/10 15:32	40	35	5	5	24	27	0.757	0.841	1.5E-09	1.7E-09
10/14/10 8:31	48	35	11	12	30	34	0.843	0.908	1.7E-09	1.8E-09
10/20/10 15:55	54	35	16	18	35	40	0.793	0.872	1.6E-09	1.7E-09
10/27/10 15:55	61	35	25	23	44	45	1.214	0.714	2.4E-09	1.4E-09
11/3/10 15:56	68	35	32	31	51	53	1.071	1.143	2.1E-09	2.3E-09
11/12/10 10:35	77	35	43	50	62	72	1.196	2.222	2.4E-09	4.4E-09
11/17/10 12:30	82	35	25	48	87	120	4.921	9.449	9.8E-09	1.9E-08
11/18/10 16:08	83	35	16	8	103	128	13.896	6.514	2.8E-08	1.3E-08
11/19/10 12:45	84	35	20	10	107	130	4.656	2.910	9.3E-09	5.8E-09

Table F.4: Flow volumes and hydraulic conductivities for PFC-spiked landfill leachate permeating through sand-bentonite admix

Time	Time (days)	Pressure (kPa)	Total discharge volume 1 (mL)	Total discharge volume 2 (mL)	Flow rate, Q 1 (mL/d)	Flow rate, Q 2 (mL/d)	Hydraulic conductivity, k (cm/s)	Hydraulic conductivity, k (cm/s)
11/24/10 2:15 PM	0	5						
11/24/10 4:30 PM	0	15			0.000	0.000	0.0E+00	0.0E+00
11/25/10 2:15 PM	1	25			0.000	0.000	0.0E+00	0.0E+00
11/25/10 4:45 PM	1	35			0.000	0.000	0.0E+00	0.0E+00
11/26/10 10:25 AM	2	35			0.000	0.000	0.0E+00	0.0E+00
11/26/10 5:00 PM	2	35			0.000	0.000	0.0E+00	0.0E+00
12/7/10 1:10 PM	13	35		1	0.000	0.092	0.0E+00	1.8E-10
12/9/10 4:00 PM	15	35	2	2	0.944	0.472	1.9E-09	9.4E-10
12/10/10 1:25 PM	16	35	Compressor broke					
12/14/10 9:30 AM	20	25	5	5	0.634	0.634	1.8E-09	1.8E-09
12/14/10 11:00 AM	20	15	Compressor broke					
12/14/10 11:20 AM	20	20						
12/14/10 12:20 PM	20	35						
12/16/10 10:00 AM	22	25						
12/16/10 11:30 AM	22	20						
12/16/10 1:25 PM	22	35						
12/17/10 10:00 AM	23	0						
12/17/10 10:15 AM	23	15						
12/17/10 11:00 AM	23	35	7	7	0.653	0.653	1.3E-09	1.3E-09
12/21/10 12:50 PM	27	35	9	9	0.491	0.491	9.8E-10	9.8E-10
12/27/10 12:20 PM	33	35	14	13	0.836	0.669	1.7E-09	1.3E-09
12/30/10 2:10 PM	36	35	16	15	0.650	0.650	1.3E-09	1.3E-09
1/3/11 11:30 AM	40	35	18	18	0.514	0.771	1.0E-09	1.5E-09
1/10/11 9:00 AM	47	35	23	23	0.725	0.653	1.4E-09	1.3E-09
1/17/11 10:30 AM	54	35	28	28	0.708	0.708	1.4E-09	1.4E-09
1/24/11 1:15 PM	61	35	33	32	0.633	0.633	1.3E-09	1.3E-09
1/31/11 8:30 AM	68	35	37	35	0.662	0.441	1.3E-09	8.8E-10
2/4/11 1:05 PM	72	35	38	36	0.239	0.239	4.7E-10	4.7E-10
2/8/11 9:30 AM	76	35	40	38	0.390	0.519	7.7E-10	1.0E-09

Table F.5: PFC concentrations in influents and effluents

Sample	Concentration (ppb)																	
	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTA	PFBS	PFHxS	PFOS	PFDS	PFOSA	6:2 FTUA	8:2 FTUA	10:2 FTUA
Water Day 72	0.187	0.016	0.056	0.021	0.049	0.065	0.006	0.003	0.003	0.002	0.008	0.001	0.031	0.000	0.002	0.013	0.006	0.001
Leachate Reservoir	0.271	0.196	1.016	0.304	0.320	1.188	0.110	1.153	0.046	0.025	0.079	0.298	0.218	0.000	0.0029	0.0000	0.0027	0.0035
Leachate Day 34	0.147	0.114	0.040	0.017	0.027	0.014	0.005	0.006	0.003	0.002	0.007	0.004	0.074	0.000	0.0028	0.0030	0.0018	0.0007
Leachate Day 77	0.233	0.052	0.201	0.068	0.070	0.019	0.003	0.002	0.002	0.002	0.020	0.055	0.025	0.000	0.0029	0.0033	0.0025	0.0006
Leachate Day 82	0.349	0.130	0.711	0.170	0.177	0.031	0.005	0.012	0.001	0.001	0.055	0.175	0.036	0.000	0.0026	0.0024	0.0017	0.0004
Leachate Day 84	0.347	0.215	1.059	0.258	0.271	0.072	0.007	0.043	0.003	0.002	0.081	0.253	0.061	0.000	0.0019	0.0000	0.0013	0.0005
Spiked Leachate Day 76	0.215	0.658	2.400	1.487	0.519	0.124	0.004	0.002	0.001	0.001	1.182	0.862	0.013	0.000	0.006	0.003	0.002	0.001
Spiked Leachate Reservoir	0.031	30.486	18.845	20.483	4.618	20.066	9.270	9.073	6.876	7.735	4.899	6.137	6.733	0.022	5.919	0.016	0.028	0.042

Table F.6: PFC concentrations in sand-bentonite admix

Sample	Concentration (ng/g dry)																	
	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTA	PFBS	PFHxS	PFOS	PFDS	PFOSA	6:2 FTUA	8:2 FTUA	10:2 FTUA
Leachate a 1	0.019	0.533	0.078	0.063	0.059	0.040	0.017	0.001	0.001	0.009	0.001	0.001	0.143	0.000	0.041	0.038	0.006	0.005
Leachate b 1	0.019	0.997	0.113	0.079	0.082	0.035	0.043	0.001	0.001	0.019	0.001	0.001	0.848	0.000	0.056	0.039	0.010	0.005
Leachate c 1	0.019	0.478	0.067	0.057	0.058	0.027	0.018	0.001	0.001	0.009	0.001	0.001	0.056	0.000	0.039	0.038	0.008	0.002
Leachate d 1	0.191	0.477	0.082	0.058	0.057	0.027	0.016	0.001	0.001	0.009	0.001	0.001	0.032	0.000	0.047	0.037	0.006	0.005
Leachate a 2	0.191	0.467	0.065	0.069	0.059	0.027	0.013	0.001	0.001	0.009	0.001	0.001	0.040	0.000	0.036	0.038	0.010	0.005
Leachate b 2	0.019	0.459	0.101	0.074	0.066	0.027	0.016	0.001	0.001	0.009	0.001	0.001	0.028	0.000	0.035	0.040	0.008	0.005
Leachate c 2	0.019	0.664	0.151	0.075	0.070	0.030	0.022	0.001	0.001	0.009	0.001	0.001	0.208	0.000	0.044	0.042	0.019	0.005
Leachate d 2	0.019	0.615	0.156	0.078	0.072	0.027	0.021	0.001	0.001	0.019	0.001	0.001	0.119	0.000	0.038	0.039	0.006	0.002
Spiked Leachate a 1	0.191	1.093	0.951	0.613	0.267	0.343	0.043	0.001	0.001	0.009	0.378	0.236	0.512	0.000	0.054	0.040	0.014	0.005
Spiked Leachate b 1	0.019	1.334	1.057	0.685	0.300	0.555	0.352	0.001	0.001	0.019	0.443	0.298	1.230	0.000	0.116	0.038	0.006	0.002
Spiked Leachate c 1	0.019	0.763	0.892	0.659	0.230	0.379	0.580	0.130	0.001	0.009	0.465	0.242	0.292	0.000	0.232	0.036	0.006	0.002
Spiked Leachate d 1	0.019	0.710	0.961	0.619	0.197	0.196	0.250	0.352	0.275	0.065	0.483	0.214	0.139	0.000	0.156	0.040	0.006	0.002
Spiked Leachate a 2	0.019	0.726	0.758	0.571	0.264	0.295	0.014	0.001	0.001	0.009	0.347	0.248	0.083	0.000	0.053	0.040	0.006	0.005
Spiked Leachate b 2	0.019	0.708	0.788	0.602	0.339	0.612	0.130	0.001	0.001	0.009	0.382	0.326	0.248	0.000	0.109	0.045	0.016	0.007
Spiked Leachate c 2	0.019	0.752	0.945	0.743	0.609	0.791	0.712	0.045	0.019	0.038	0.428	0.353	0.508	0.000	0.245	0.040	0.015	0.008
Spiked Leachate d 2	0.019	0.831	1.022	0.766	0.539	0.583	0.703	0.694	0.325	0.086	0.445	0.356	0.367	0.000	0.313	0.040	0.009	0.005
Clean admix	0.019	0.019	0.040	0.052	0.049	0.188	0.018	0.001	0.001	0.009	0.001	0.001	0.024	0.000	0.042	0.038	0.008	0.002
MDL	0.191	0.194	0.040	0.024	0.013	0.027	0.007	0.005	0.011	0.019	0.013	0.009	0.003	0.002	0.005	0.011	0.006	0.005