

**PERFLUORINATED COMPOUNDS IN LANDFILL LEACHATE FROM
DISCARDED CARPETS**

by

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B.Sc., Sharif University of Technology, 2010

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)

June 2012

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Abstract

Perfluorinated compounds (PFCs) are a class of anthropogenic chemicals incorporated over six decades into a wide range of industrial and consumer-use products including surface treatments for carpets and textiles, paper and packaging, non-stick cookware, firefighting foams and insecticides. The extremely strong carbon-fluorine bond, "the strongest in organic chemistry", makes them thermally and chemically stable, and resistant to degradation. Several studies on toxicology of PFCs demonstrate negative health effects of these compounds. Some PFCs were added to the Stockholm convention on Persistent Organic Pollutants (POPs) in 2009, due to their persistence, toxicity, and widespread occurrence in the environment. Stain-resistant carpets comprise a major part of global historical PFC production and use. Landfills are a major source of PFC emissions to the environment as final destinations for discarded consumer articles, including carpets. This thesis explores how various PFCs leach from carpets to landfill leachate, and how factors like temperature, pH and contacting efficiency affect the transfer of PFCs into aqueous media.

Experiments were conducted in which a number of carpets manufactured in ~2000 to 2005 were contacted with landfill leachate and distilled water. Transfer of different PFCs into the aqueous phase increased with contacting time, with differences between 1 and 24 h much greater than between 24 and 168 h. A temperature increase from 5 to 35°C resulted in a significant increase in PFC leaching. Increasing the pH from 5 to 8 resulted in an increase followed by a decrease in leaching of most PFCs. The overall leaching rates of PFCAs into distilled water were somewhat greater than into landfill leachate. The majority of PFC exchange between carpets and leachate was more dependent on some factor (e.g. adsorption or desorption) rather than external mass transfer.

Preface

For all carpet and leachate samples in this study, sample extraction, clean-up and PFC analyses using LC/MS/MS were carried out at the Fisheries and Oceans Canada Institute of Ocean Sciences in Sidney, British Columbia by Dr. Jonathan Benskin, under the guidance of Dr. Michael Ikonomou.

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List of Abbreviations

AFFF	aqueous fire fighting foam
BC	British Columbia
CEPA	Canadian Environmental Protection Agency
DFO-IOS	Fisheries and Oceans Canada Institute of Ocean Sciences
ECF	electrochemical fluorination
EPA	United States Environmental Protection Agency
FTCA	fluorotelomer carboxylic acid
FTUA	fluorotelomer unsaturated acid HDPE
HDPE	high density polyethylene
HPLC	high pressure liquid chromatography
IDL	instrument detection limit
LC/MS/MS	liquid chromatography-tandem mass spectrometry
MDL	method detection limit
MSW	municipal solid waste
PFC	perfluorinated compound
PFCA	perfluorocarboxylic acid
PFSA	perfluorosulfonate
POP	persistent organic pollutant
R ²	Pearson's correlation coefficient
rpm	revolutions per minute
TCLP	toxicity characteristic leaching procedure
TDS	total dissolved solids
TOC	total organic carbon

UBC	University of British Columbia
WTP	water treatment plant
WWTP	wastewater treatment plant

List of Chemicals

6:2 FTOH	6:2 fluorotelomer alcohol
8:2 FTOH	8:2 fluorotelomer alcohol
10:2 FTOH	10:2 fluorotelomer alcohol
N-EtFOSE	n-Methyl perfluorooctane sulfonamido ethanol
N-MeFOSE	n-Ethyl perfluorooctane sulfonamido ethanol
PFBA	perfluorobutanoic acid
PFBS	perfluorobutane sulfonate
PFDA	perfluorodecanoic acid
PFDoA	perfluoroundecanoic acid
PFDS	perfluorodecane sulfonate
PFHpA	perfluoroheptanoic acid
PFHxA	perfluorohexanoic acid
PFHxS	perfluorohexane sulfonate
PFNA	perfluorononanoic acid
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonate
PFOSA	perfluorooctane sulfonamide
PFPA	perfluoropentanoic acid
PFTA	perfluorotetradecanoic acid
PFUnA	perfluoroundecanoic acid
POSF	perfluorooctanesulfonyl fluoride

Acknowledgements

Dr. Loretta Li and Dr. John Grace, my knowledgeable research supervisors: I express my sincere gratitude and appreciation for your guidance, support, and encouragement throughout my entire Master's journey. This dissertation would not have been possible without all your eternal patience, brilliant judgement and valuable advice, which inspired and motivated me from the very early stages of this research.

Dr. Michael Ikonomou, Dr. Jonathan Benskin, and the staff of the Fisheries and Oceans Institute of Ocean Sciences (DFO-IO): I owe my deepest gratitude to you for your knowledgeable advice, providing laboratory assistance, and all your support for my research chemical analyses. This thesis would have remained a dream had it not been for your patience in answering my many questions over emails about PFCs and analytical chemistry in my entire Master's program.

Dr. Gilles Hebrard: It gives me immense pleasure to acknowledge you for being there whenever I needed you. From carpet preparation and leachate collection for my experiments to providing advice for writing heat transfer and mass balance equations for my thesis, you were always helping me with a cheerful attitude. Honestly, this research would not have become reality if it were not for your invaluable advice, exceptional suggestions, encouragement and patience.

Mark Rigolo, Paula Parkinson, Timothy Ma, Bill Leung, Harald Schrempp and the staff of the UBC Civil Environmental Engineering Lab and Workshop: I consider it an honor to work with you. Thank you for your time and effort for not only providing the necessary equipment for this research, but also making the Environmental Laboratory a convivial place to work.

Without your constructive comments, laboratory assistance, and practical knowledge, I could not have done any part of this ambitious research.

The landfill operator: I extend my sincere appreciation to you, although I could not mention your name. Thank you for your assistance collecting huge amounts of leachate from your landfill.

All my wonderful friends and colleagues: A very special and heartfelt thanks to all my friends whose unconditional friendship and faith gave me such a pleasant time while working at UBC.

My parents: Your unconditional and unwavering support, endless love and dedication from across the miles inspired and motivated me in my darkest hours of this research. Thank you for your support and believing in me for my whole life.

I also would like to show my deepest gratitude to NSERC (Natural Sciences and Engineering Research Council of Canada) and to the Fisheries and Oceans Institute of Ocean Sciences (DFO-IO) for providing financial support for this research.

Chapter 1: Introduction

1.1 Problem statement

Perfluorinated compounds (PFCs) are a class of anthropogenic chemicals consisting of a fluorinated alkyl chain (4-14 carbons), with various functional groups attached (Corsini et al. 2012). Although PFCs include thousands of chemicals (Lindstrom et al. 2011), they are best known for two classes of substances, perfluorosulfonates (PFSA) and perfluorocarboxylic acids (PFCAs). These are degradation products or manufacturing residuals of fluorinated polymers and PFC precursors integrated into many consumer products (Giesy and Kannan 2002).

Several unique physical and chemical properties such as water and stain repellency, thermal stability, and surfactant properties are imparted by the strong fluorine-carbon bond in these compounds (Kissa 2001). PFCs have been incorporated into a wide range of industrial and consumer-use products including paper and packaging, non-stick cookware, surface treatments for carpets and textiles, firefighting foams, floor polishes, and insecticides for the past six decades (Prevedouros et al. 2006; 3M Company 1999a; Paul et al. 2009). The same properties that make the PFCs industrially beneficial also tend to make them accumulative and persistent environmental contaminants (Stock et al. 2004).

In recent years, detection of individual PFCs of very low concentrations (i.e. in range of ppb) has become possible through significant advances in analytical chemistry and application of high-performance liquid chromatography tandem mass spectrometry (Hansen et al. 2001; Sottani et al. 2002). This improvement has made it possible to detect even trace levels of PFCs, which are ubiquitous in environmental matrices including surface water, groundwater,

indoor and outdoor air, soil, sediment, wildlife, and human blood sera, even in remote locations (Ahrens et al. 2011; Paul et al. 2009; Olsen et al. 2005; Giesy and Kannan 2001). Several studies on toxicology and health effects of PFCs demonstrate negative health effects such as weight loss, increased liver weight, decreased thyroid hormone levels, and altered sex hormones in laboratory species and humans (Kennedy et al. 2004; Seacat et al. 2003).

Due to their persistence, toxicity, and widespread occurrence in the environment, PFOS, its salts, and perfluorooctane sulfonyl fluoride (PFOSF) were added to Annex B of the Stockholm convention on Persistent Organic Pollutants (POPs) in May 2009, resulting in global restrictions on the application and production of these compounds (Stockholm Convention 2009; Karrman et al. 2006; Lindstrom et al. 2011). In Canada, the manufacture and exportation of PFOS-related compounds (except for limited applications) has been discontinued since 2002 (Canada Gazette part I 2006).

Emissions of PFCs to the environment occur through direct and indirect means. Direct PFC releases (e.g. from PFC manufacturing facilities) comprise the majority of emissions (~95-99% of total emissions), while indirect sources (e.g. from PFC residuals or degradation of precursors in consumer products) comprise small contributions (Russell et al. 2008; Prevedouros et al. 2006).

Landfills are one of the point sources of PFC emissions to the environment as they are the final destination for many fluorochemicals widely incorporated in consumer articles. These PFCs might remain in the landfills for decades or more. Most current landfills are equipped with leachate collection systems. Leachate is then treated on-site or directed to a wastewater treatment plant (WWTP). Conventional treatment processes in a WWTP do not appear to influence the concentrations of PFCs contained in landfill leachate (Huset et al. 2008).

In a case study by Schultz et al. (2006) on 10 WWTPs, even higher concentrations of a few PFCs were observed in the effluent due to possible biodegradation of precursors. In addition, PFCs might be sorbed to bio-solids and sewage sludge in the WWTPs (Higgins et al. 2005) and return to landfills for disposal.

Between 1970 and 2002, stain-resistant carpets comprised approximately 50% of global historical PFC production and use (Paul et al. 2009). In Canada, 57.8% of total PFCs were applied to fabric and carpets between 1997 and 2000 (Footitt et al. 2004).

Carpet treatments may be applied by fiber manufacturers and carpet mills, or by customers after purchasing carpets. It has been estimated that nearly 53% of the PFCs applied as carpet treatments remain at the disposal time on average (3M Company 1999a). The most common disposal method for carpets at the end of their useful lives in many countries is landfilling. In Canada, more than 90% of discarded commercial and residential carpets were landfilled in 2010 (Canadian Carpet Recovery Effort 2010). After being landfilled, the PFCs in carpets may leach into the landfill leachate.

Considerable research has been carried out to determine the PFC concentrations in biota and environmental matrices, and to assess the associated health risks. In recent years, a few studies have aimed to document the concentrations of PFCs in different landfill sites in Canada (Li et al., 2012), the United States (Huset et al. 2011), Germany (Busch et al. 2010), and Denmark (Kallenborn et al. 2004). In addition, concentrations of PFCs in different consumer products have been reported in several articles (Begley et al. 2005; Sinclair et al. 2007; Fiedler et al. 2010; Guo et al. 2009; Washburn et al. 2005). However, no studies have been published about how PFCs leach from consumer products to landfill leachates and enter the environment. Residential and commercial carpets are disposed in landfills, and PFCs,

even those no longer being manufactured, will continuously enter the environment in future years, making it crucial to understand how the PFCs in carpets leach into landfill leachate.

1.2 Objectives

The overall objective of this thesis is to comprehensively study the leaching of different poly- and per-fluorinated compounds from discarded carpets into landfill leachate and to shed light on how these materials behave in landfills. Specific objectives of this study were:

- To determine the levels and types of PFCs and their precursors in old and new carpets;
- To characterize and measure PFC concentrations of leachate from a landfill in western Canada;
- To determine the leaching extent and leaching rate of different PFCs from used and unused carpets to landfill leachate;
- To study the effect of changes in contact time, contacting efficiency, temperature and pH on leaching rates of different PFCs to landfill leachate and/or distilled water; and
- To investigate if the rate of leaching of PFCs from carpets to landfill leachate is externally mass-transfer controlled.

1.3 Plan of this thesis

Chapter 2 provides a review of the chemical and physical properties of the compounds of interest, their manufacture, applications and environmental factors, and specifies their incorporation in, and leaching from, carpets.

In order to achieve the objectives listed in the previous section, a number of leaching experiments were conducted, in which used and unused carpets were contacted with landfill leachate. To determine the leaching extent and leaching rate of different PFCs, carpet samples

were contacted with leachate for specific time periods under controlled pH and temperature conditions. In order to investigate the effect of different factors on PFC leaching rates, experiments were carried out at pH between 5 and 8, temperature between 5 and 35°C and varying contacting conditions. In addition to contacting carpet samples with leachate, a number of experiments were designed to contact carpets with distilled water, allowing PFC leaching rates to be determined in the absence of other agents, e.g. organic and inorganic matter, which may contribute to leaching.

The experiments were conducted in two levels of preliminary tests and final tests. Since no previous data about leaching rates of PFCs were available in the literature, preliminary tests were included to provide an overview of the PFC leaching rates and of PFC expected levels in the aqueous media after contact with PFC-containing compounds. For more details about the leaching test procedures, see Chapter 3. The experimental results are presented in Chapter 4, and conclusions and recommendations in Chapter 5.

Straight-chain perfluoroalkyl carboxylic acids (PFCAs) of 4 to 12 and 14 carbon atoms and straight-chain perfluoroalkyl sulfonates of 4, 6, 8, and 10 carbons were studied in this thesis. In addition to these PFCs, perfluorooctane sulfonamide (FOSA), an 8-carbon-length fluorinated sulfonamide was analysed.

Figure 1.1 presents a flowchart of the research plan, including the tasks designed to realize the objectives of this study. The various steps in the tests are described in detail in Chapter 3, with results then appearing in Chapter 4.

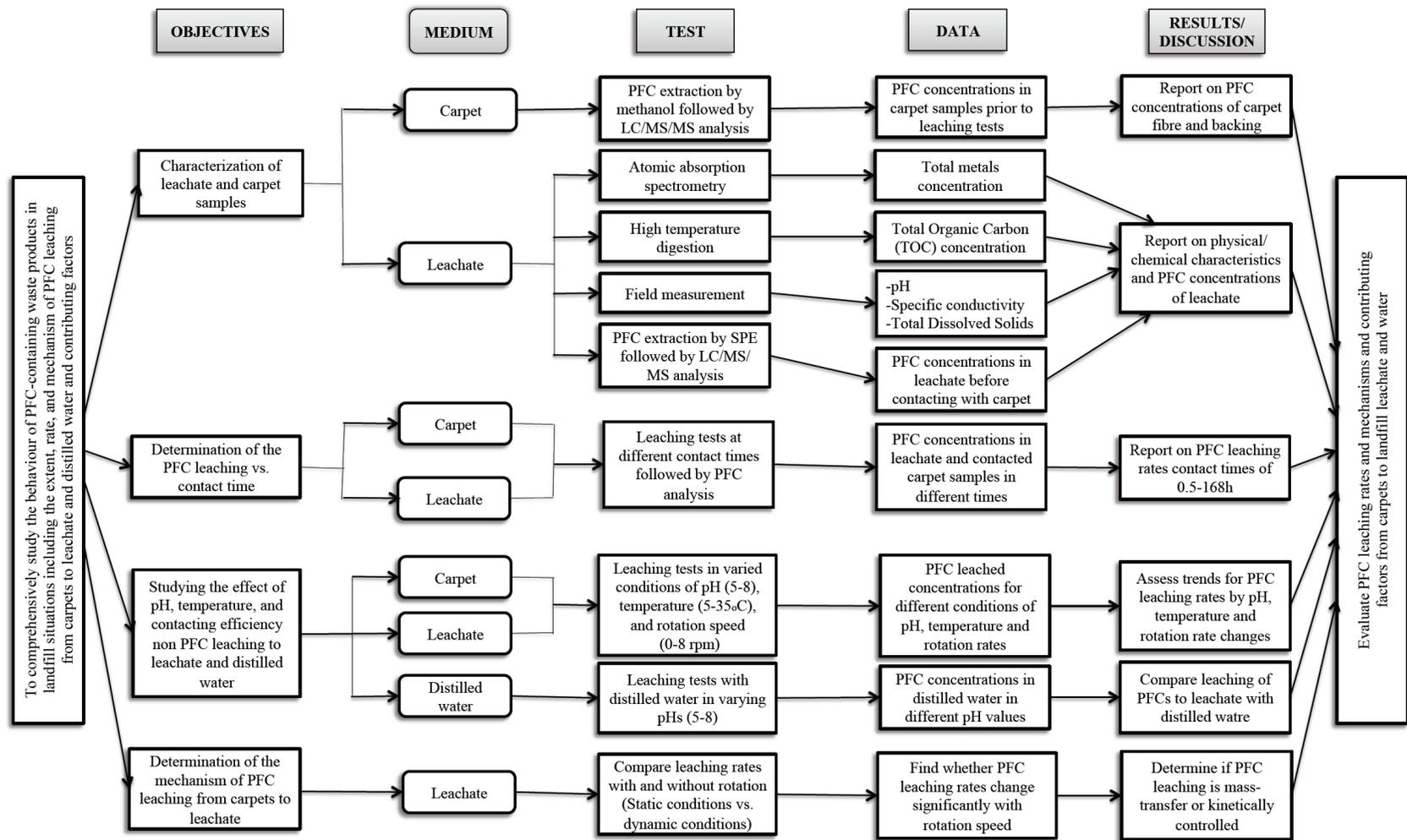


Figure 1.1: Research plan

1.4 Research contributions

This study is intended to clarify the leaching extents and rates of different perfluorinated compounds and their precursors from waste materials to landfill leachate. The results are intended to contribute to a comprehensive understanding of whether or not PFC-containing waste could have a significant effect on leachate quality. In addition, the study sheds light on the parameters (e.g. pH and temperature) influencing the leaching of PFCs from waste, and ultimately to groundwater. These results would provide further information for regulators helpful in developing best management practices. This could aid in making decisions about more appropriate ways for disposal of PFC-containing waste and regulation of PFCs in consumer products to benefit both the environment and public health.

Chapter 2: Background and Literature Review

2.1 Introduction and physical/chemical properties

Poly- and per-fluorinated compounds involve a heterogeneous class of chemicals consisting of a fluorinated alkyl chain (4–14 carbons), with various functional groups attached (Corsini et al. 2012). In poly-fluorinated hydrocarbons, hydrogen atoms are replaced by fluorine atoms in multiple sites (e.g., telomer alcohols); while in perfluorinated species all of the hydrogen atoms are replaced by fluorine atoms (e.g., PFOS and PFOA) (Lindstrom et al. 2011). Figure 2.1 shows the chemical structures of two classes of PFCs and their precursors. Note that the perfluorinated carboxylic acids are expected to dissociate in the environment almost entirely to their anionic forms.

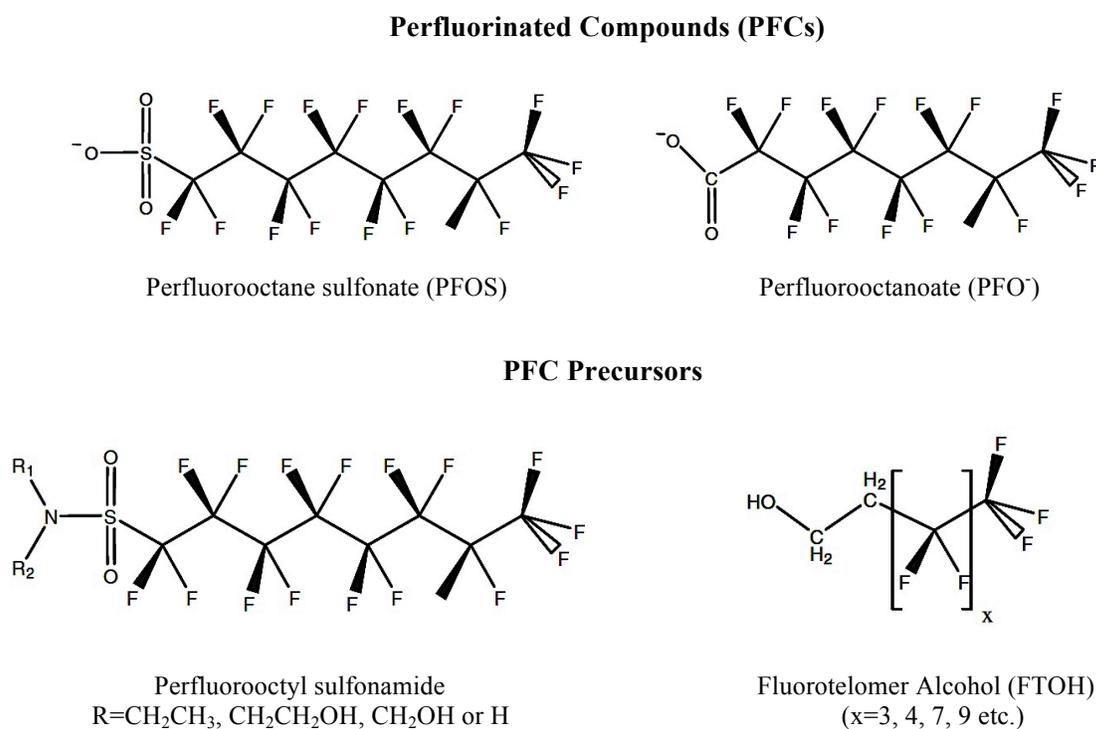


Figure 2.1: Structure of PFCs and some of their precursors (adapted from Giesy et al. 2006)

PFCs are mostly comprised of a hydrophilic head of sulfonates or carboxylates and a hydrophobic tail of fluorinated carbon chain (Bhatarai and Gramatica, 2011). Polyfluorinated sulfonamidoethanols (FOSEs) and telomer alcohols (FTOHs) are broadly used to incorporate perfluorinated alkyl groups into various polymeric materials. (N-MeFOSE) and (N-EtFOSE) are two major sulfonamides incorporated into numerous fluoropolymers. The FTOHs are usually referred to as X:Y FTOH, with X showing the perfluorinated carbon atoms and Y representing non-substituted methylene groups. These compounds have elicited considerable attention recently since they are suspected to be precursors of (PFOS) and longer-chain PFCAs (Lei et al. 2004). Table 2.1 represents names, acronyms, Chemical Abstracts Services (CAS) numbers, chemical structures and molecular weights of different classes of PFCs of direct interest in this study.

Most of the unique physical and chemical properties of PFCs are due to the extremely strong Carbon-Fluorine bond, labelled as "the strongest in organic chemistry" (O'Hagan 2008), with a Bond Dissociation Energy (BDE) of up to 544 kJ/mol (Lemal 2004). This strong bond is resistant to heat, strong acids and bases, oxidizing and reducing agents, photolysis, microbes, and metabolic processes (Schultz et al. 2003; Kissa 2001). Unfortunately, there is currently little information on the chemical-physical properties of most PFCs since their properties change with varying physical and chemical conditions. Experimental studies on physical/chemical properties of poly- and per- fluorinated compounds mainly focus on PFC precursors rather than PFSA and PFCAs. Table 2.2 shows empirical results for vapor pressure and solubility of various PFC precursors from different studies. Differences between similar values are mostly due to different analytical methods and test conditions.

Table 2.1: PFCs analysed in this study (Giesy et al. 2010; OECD 2007)

Group	Compound name	Acronym	CAS No.	Molecular structure	Molecular wt. (g/mol)
Perfluoroalkyl Sulfonate	Perfluorobutane sulfonate	PFBS	375-73-5	C ₄ F ₉ SO ₃ H	300
	Perfluorohexane sulfonate	PFHxS	355-46-4	C ₆ F ₁₃ SO ₃ H	400
	Perfluorooctane sulfonate	PFOS	1763-23-1	C ₈ F ₁₇ SO ₃ H	500
	Perfluorodecane sulfonate	PFDS	335-77-3	C ₁₀ F ₂₁ SO ₃ H	600
Perfluoroalkyl Carboxylic Acid	Perfluorobutanoic acid	PFBA	375-22-4	C ₃ F ₇ COOH	214
	Perfluoropentanoic acid	PFPA	2706-90-3	C ₄ F ₉ COOH	264
	Perfluorohexanoic acid	PFHxA	307-24-4	C ₅ F ₁₁ COOH	314
	Perfluoroheptanoic acid	PFHpA	6130-43-4	C ₆ F ₁₃ COOH	364
	Perfluorooctanoic acid	PFOA	335-67-1	C ₇ F ₁₅ COOH	414
	Perfluorononanoic acid	PFNA	375-95-1	C ₈ F ₁₇ COOH	464
	Perfluorodecanoic acid	PFDA	335-76-2	C ₉ F ₁₉ COOH	514
	Perfluoroundecanoic acid	PFUnA	2058-94-8	C ₁₀ F ₂₁ COOH	564
	Perfluorododecanoic acid	PFDoA	307-55-1	C ₁₁ F ₂₃ COOH	614
Perfluorotetradecanoic acid	PFTA	376-06-7	C ₁₃ F ₂₇ COOH	714	
Fluoroalkyl Sulfonamide	Perfluorooctane sulfonamide	FOSA	754-91-6	C ₈ F ₁₇ SO ₂ NH ₂	499

Table 2.2: Properties of PFCs and their precursors.

Acronym	Compound Name	Molecular Structure CAS No.	Vapor Pressure (Pa)	Solubility (mg/L)
PFOA	Perfluorooctanoic acid	C ₇ F ₁₅ COOH 335-67-1	4.2 (25°C) (Prevedouros et al. 2006) 7.0 (25°C) (Hekster et al. 2002)	9.5 (25°C) (Hekster et al. 2002)
PFOS, K ⁺	Potassium perfluorooctane sulfonate	C ₈ F ₁₇ SO ₃ K 68391-09-3	0.0003 (20°C) (3M Company 2000a)	680 (25°C) (Ellefson 2001) 570 (25°C) (3M Company 2000a)
4:2 FTOH	4:2 Fluorotelomer alcohol	CF ₃ (CF ₂) ₃ C ₂ H ₄ OH 2043-47-2	990 (25°C) (Dinglasan et al. 2004) 992 (25°C) (Stock et al. 2004) 1670 (25°C) (Lei et al. 2004)	974 (22°C) (Liu and Lee 2007)
6:2 FTOH	6:2 Fluorotelomer alcohol	CF ₃ (CF ₂) ₅ C ₂ H ₄ OH 647-42-7	713 (25°C) (Stock et al. 2004) 876 (25°C) (Lei et al. 2004)	18.8 (22°C) (Liu and Lee 2007) 12-17 (25°C) (Hekster et al. 2002)
8:2 FTOH	8:2 Fluorotelomer alcohol	CF ₃ (CF ₂) ₇ C ₂ H ₄ OH 678-39-7	2.93 (25°C) (Hekster et al. 2002) 3 (21°C) (Kaiser et al. 2004) 227 (25°C) (Lei et al. 2004) 254 (25°C) (Stock et al. 2004) 270 (25°C) (Dinglasan et al. 2004)	0.137 (21°C) (Kaiser et al. 2004) 0.14 (25°C) (Hekster et al. 2002)
10:2 FTOH	10:2 Fluorotelomer alcohol	CF ₃ (CF ₂) ₉ C ₂ H ₄ OH 865-86-1	53 (25°C) (Lei et al. 2004) 140 (25°C) (Dinglasan et al. 2004) 144 (25°C) (Stock et al. 2004)	0.006-0.885 (22°C) (Liu and Lee 2007)
n-MeFOSE	n-Methyl perfluorooctane sulfonamido ethanol	C ₈ F ₁₇ SO ₂ N(CH ₃)C ₂ H ₄ O H 24448-09-7	0.002 (23°C) (Shoeib et al. 2004) 0.7 (25°C) (Lei et al. 2004)	N/A
n-EtFOSE	n-Ethyl perfluorooctane sulfonamido ethanol	C ₈ F ₁₇ SO ₂ N(C ₂ H ₅)C ₂ H ₄ OH 1691-99-2	0.009 (23°C) (Shoeib et al. 2004) 0.35 (25°C) (Lei et al. 2004)	0.151 (25°C) (Hekster et al. 2002)

From Table 2.2, it appears that the water solubilities of fluorotelomer alcohols are relatively low. Typically, the major structural feature influencing water solubility of fluorotelomer alcohols is the fluorocarbon chain length; higher chain length fluorotelomer alcohols have lower solubility (Liu and Lee 2007).

The vapor pressures of fluorotelomer alcohols are usually higher than those of their parent alcohols; for example, 10:2 FTOH is 1000 times more volatile than dodecanol (Stock et al. 2004).

Properties of most sulfonates and carboxylic acids are not yet available, even though knowledge of the physical and chemical properties of PFCs is crucial to study their environmental fate and transport, in particular their leachability in landfills. In order to fill this gap for PFC properties, software packages are utilized to estimate these properties and to give insight into understand the relative behavior of these compounds. Table 2.3 shows the solubility and vapor pressure of various carboxylic acids predicted by models based on theoretical molecular descriptors (Bhatarai and Gramatica 2011).

Table 2.3: Solubility and vapor pressure of perfluorinated carboxylic acids (adapted from Bhatarai and Gramatica 2011).

Name	Solubility (mg/L)	Vapor Pressure (Pa)
PFBA	446.7	131.8
PFPA	120.2	338.8
PFH _x A	29.5	120.2
PFHpA	6.6	39.0
PFOA	1.7	12.0
PFNA	0.2	3.5
PFDA	0.0	1.0
PFUnA	0.0	0.3
PFDoA	7.6x10 ⁻⁵	0.1

The vapor pressure of perfluorinated carboxylic acids decreases with increasing fluorocarbon chain length (Kaiser et al. 2005). The acids and their free salts are reasonably soluble in water and insoluble in lipids. Increasing the chain length decreases the aqueous solubility of these acids (Kaiser et al. 2006).

2.2 Synthesis

Two major manufacturing processes are adopted to produce fluorinated compounds: electrochemical fluorination (ECF) and telomerization (Kissa 2001). The former was established by Simons in 1944. 3M Company, the major manufacturer of POSF-based chemicals up to 2002, used this route after 1956 (3M Company 1950). In the ECF process, all hydrogen atoms of a straight chain hydrocarbon are substituted with fluorine atoms as a result of electricity-promoted reaction with hydrogen fluoride (Kissa 2001). The major target compound in this process is perfluorooctane sulfonyl fluoride (POSF). The ECF is a relatively impure process, leading to approximately 35-40% straight chain POSF, with the remainder being a mixture of branched and cyclic isomers, primarily from 4 to 9 carbons, as byproducts. The POSF product is used in a series of reactions to produce N-methyl and N-ethyl perfluorooctane sulfonamidoethanol (N-MeFOSE and N-EtFOSE), with historical applications in producing surface coatings for textiles and paper products (Paul et al. 2009; Olsen et al. 2005). An example of the ECF process is illustrated in Figure 2.2. Note that all compounds produced from POSF have the potential to degrade or transform to PFOS ultimately; therefore these materials may be considered to be “PFOS equivalents” (Lindstrom et al. 2011). From 1947 through 2002, most (80-90% in 2000) ammonium perfluorooctanoate (APFO) worldwide was manufactured through the ECF process (Prevedouros et al. 2006).

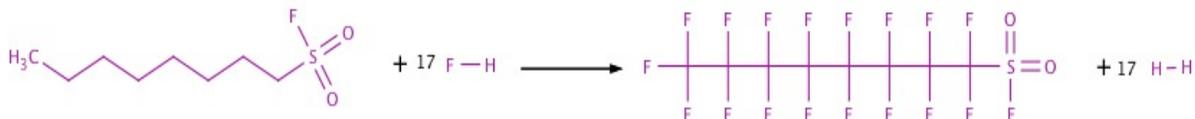


Figure 2.2: An example of an electrochemical fluorination process (adapted from Hekster et al. 2003).

Haszeldine developed another method for producing perfluorinated compounds in 1964 (DuPont Company 1964; Rao and Baker 1994). This method, called Telomerization, was adopted first by the DuPont Company in the 1969s, and it has been used by AsahiGlass, AtoFina, Clariant, Daikin, and DuPont Companies since then (Hekster et al. 2003). In this process, fluorinated chemicals are produced by iterative reaction of perfluoroethyl iodide (telogen) with perfluoroethylene (taxogen), yielding perfluoroalkyl chains, which differ in length by CF_2 CF_2 (D'eon and Mabury 2011). The transfer of iodine produces a mixture of linear perfluorinated iodides (Paul et al. 2009). Reaction with ethylene yields fluorotelomer iodides (x:2 FTI), which can produce fluorotelomer alcohols (X:Y FTOH) after being hydrolyzed (D'eon and Mabury 2011). Unlike the ECF process, telomerization products are linear process compounds, containing a small percentage of branched products (Kissa 2001). Note that the final fluorinated polymers produced through both ECF and telomerization usually contain unreacted or partially reacted starting materials or intermediates, which end up in the final products (Olsen et al. 2005). Figure 2.3 presents the major characteristics of the ECF and telomerization processes for manufacturing perfluorinated compounds.

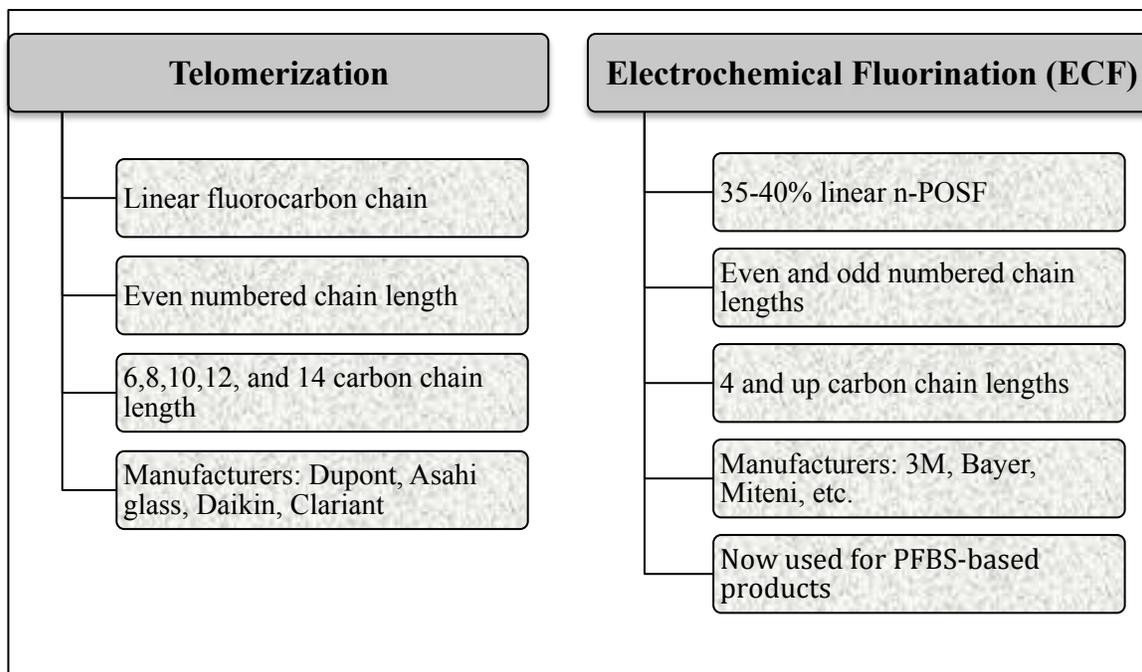


Figure 2.3: Key aspects of the electrochemical fluorination (*right*) and telomerization (*left*) processes.

2.3 Applications

Poly- and perfluorinated compounds have been incorporated into a wide range of industrial and consumer products for the past six decades due to their unique physical and chemical properties. The major commercial applications of PFCs fall into these groups (3M Company 1999a; Prevedouros et al. 2006; Washburn et al. 2005):

- Surface treatments,
- Paper and packaging protectors, and
- Performance chemicals.

Surface treatments provide soil, water, and stain resistance to residential and commercial furnishings and apparel, lowering the surface energy of the material to which they are applied and significantly increasing the useful lifetime and sustaining the appearance of carpets,

fabric, leather and upholstery. The PFCs in surface treatment chemicals are primarily manufactured as high-molecular-weight polymers (mostly with a perfluorinated chain length of 8 carbons) and could be either N-MeFOSE or fluorotelomer based (D'eon and Mabury 2011). In 2004, Dupont (2004) announced that the major portion of its fluorotelomer-based commercial products (~80%) were fluorinated polymers applied as surface treatments, while only 20% were used as fluorosurfactants.

Paper and packaging protectors are applied by paper mills and packaging manufacturers to food packaging and papers to improve their moisture and oil barrier properties. The phosphate esters of N-EtFOSE alcohol, acrylate copolymers of N-MeFOSE (3M Company 1999a), or low molecular weight mixtures of C₆, C₈, C₁₀, and C₁₂ fluotelomers are commonly used in the production of these chemicals (Begley et al. 2005).

Performance chemicals are typically low-molecular-weight surface-active monomers (3M Company 1999a), preferentially with a perfluorinated chain length of six carbons (D'eon and Mabury 2011). These compounds could be used either directly in consumer products or as intermediates in manufacturing finished products. Fluorochemical surfactants normally result in surface tensions as low as 15-16 dynes/cm at concentrations of 100 ppm or less, making them suitable for applications in the mining and oil industries, carpet spot cleaners, insecticide raw materials, metal plating, and household additives (e.g. floor polishes). Besides surface tension reduction, some POSF-based performance chemicals have the ability to form tough and resilient foams, useful for production of Aqueous Fire Fighting Foams (AFFFs) to resist the action of high temperature or aggressive chemicals and vapors (3M Company 1999a,b).

In addition to various fluorinated polymers, PFCs have direct commercial applications. PFOS can be incorporated in AFFFs, hydraulic fluids, and photolithography (OECD 2002; Paul et

al. 2009). No direct application of PFOA in commercial products has been reported; however the ammonium salts of PFOA are an essential processing aid in manufacturing of PTFE, the functional component of non-stick pans (D'eon and Mabury 2011; Prevedouros et al. 2006) and to a lesser extent in industrial applications in the electronic industry and as an anti-static additives (OECD 2002). Note that since PFOA degrades at the high temperatures applied in cookware manufacturing, non-stick pans do not contain any detectable PFOA (Washburn et al. 2005).

2.4 Toxicology and health effects

Several research studies have been conducted recently on the toxicological effects of PFCs and their concentrations in humans and wildlife. It is well known that both PFOA and PFOS can be easily absorbed orally; however it takes a long time for them to be eliminated or degraded in the human body, as well as in wildlife (Johnson et al. 1984; Kemper and Nabb 2005). Although the elimination rates of PFCs vary significantly among species (Olsen et al. 2005) and even between genders of a specific species (Kemper and Jepson 2003), the elimination potential decreases with increasing fluorinated carbon chain length (Lau et al. 2007).

PFCs are highly bio-accumulative in humans and wildlife. Approaches for studying PFC bioaccumulation differ totally from those used to study other fat-soluble persistent organic pollutants; because PFCs have a high tendency to bind to protein albumin (Rayne et al. 2009; Kelly et al. 2009). This is why greater concentrations of PFCs have been observed in protein-rich tissues, specifically liver, kidney and blood serum (to a lesser extent) in both monitoring and laboratory studies (Quinete et al. 2009; Hundley et al. 2006; Seacat et al. 2002,2003). The bioaccumulation potential of PFCs depends greatly on the carbon chain length, as well as on

the attached functional group. Long-chain PFCAs and PFSAAs have the highest bioaccumulation potential, with perfluorinated sulfonates more likely to accumulate than perfluorinated carboxylates of the same length (Martin et al. 2003). For example, the bioaccumulation rate of PFOA has been observed to be 20 times lower than for PFOS (Liu et al. 2011).

Greater concentrations of PFCs in animals high in a food chain (i.e. top predators) compared with those in their diets provide strong evidence for bioaccumulation and biomagnification of PFCs (Giesy and Kannan 2001; Houde et al. 2006; Tomy et al. 2004). The trends for biomagnification potential in PFCs are similar to those for bioaccumulation; the highest biomagnifications have been observed for PFNA to PFUnA, as well as PFOS (Kelly et al. 2007; Houde et al. 2006).

The potential toxicities of PFOS and PFOA in monkeys (Seacat et al. 2002), rats (Austin et al. 2003; Seacat et al. 2003), fish (Hoff et al. 2005; Martin et al. 2003), and humans (Olsen et al. 1999, 2003) have been widely characterized in recent years; however, less is known about the toxicology of PFCs of carbon chain lengths other than C-8 perfluorochemicals, (Lau et al. 2007). Early responses to exposure to PFOA and PFOS are reported to include reduced body weight, increased liver weight, and serum cholesterol and thyroid hormones reduction in experimental animals (Kennedy et al. 2004; Seacat et al. 2003). Studies examining hormone levels in workers reported an increase in serum estradiol levels among individuals with the highest PFOA serum levels (Olsen et al. 1998). A significant inverse association of serum PFOA concentrations with birth weight and birth length has been reported in Denmark (Fei et al. 2008). Notably increased diabetes mortality in occupationally exposed groups compared with non-exposed workers has also been observed (Lundin et al. 2009). Melzer et al. (2010)

reported a statistical increase in Odds Ratio (OR) of having thyroid disease in women with elevated blood PFOA concentrations. In addition, PFOA and PFOS are known to affect the immune system (White et al. 2011).

In general, the toxicity behavior of PFCs follows similar trends as bioaccumulation; PFOS and its derivatives are more toxic than PFOA, and toxicity of PFCs increases with chain length (Jensen et al. 2008). Furthermore, linear PFCs show higher toxicities than their branched analogues (Kawashima et al. 1995).

Studying the PFC levels in human blood sera has revealed some findings about general PFC exposure. A strong correlation between blood concentrations of PFOA and PFOS implies that similarities exist between human exposure pathways to these compounds (Apelberg et al. 2007). In addition, after 3M's phase-out of the production of POSF-based compounds, a 60% decrease in PFOS concentrations and a 25% drop in PFOA concentrations were observed in blood samples collected in the United States over the 2000-2006 period (Olsen et al. 2008).

2.5 PFCs in Canada

Prior to 2002, most PFOS-based compounds in Canada were imported as raw chemicals and as components in products, formulations and manufactured items. The manufacture and exportation of these compounds was discontinued in 2002 (Canada Gazette part I 2006). The total amount of PFCs imported into Canada from 1997 to 2000 was estimated to be 600 tonnes, with PFOS-based substances comprising 43% of imported PFC compounds. As in many other countries, the main applications of these substances were as surface treatments, providing water, oil, soil and grease repellency for fabric, leather, paper and packaging, carpets and rugs, as well as AFFFs, and paint and coatings additives. Footitt et al. (2004) estimated the percentage of total fluorochemicals tonnages used for different applications in

Canada between 1997 and 2000. Based on their study, 57.8% of total PFCs were used in fabric and carpets, 28.9% in paper and packaging products, 6% in AFFF products, and the remainder in other areas (e.g. processing aids, leather protection and polymer additives).

The use of PFOS-based compounds in Canada dropped sharply after 2000, when the major global manufacturer of perfluorinated sulfonamides voluntarily phased-out of the manufacture of PFOS-based compounds. The only permitted applications of PFCs in Canada now are in metal plating, photography and photolithography, semiconductor industries, hydraulic fluids, papers and printing plates and, while current stocks last, PFOS-based AFFFs (Canada Gazette part II 2008). Although PFOS-based substances have not been manufactured in Canada since 2002 and importing them is limited to specific applications, there is a growing concern associated with increasing imports from Asia, especially in apparel products, since these may be a potential source of PFCs.

Canada was the first government to ban three fluoropolymer stain repellents containing telomer alcohols in December 2004 (Renner et al. 2005). In addition, in July 2006, the ministers of the Environment and Health proposed to add PFOS and its salts to the List of Toxic Substances in Schedule 1 of the Canadian Environmental Protection Agency (CEPA) 1999 Act. Their final decision was published on the screening assessment of PFOS in the Canada Gazette, Part I, and (Canada Gazette part II 2008). On April 17th, 2008, the PFOS Virtual Elimination Act received Royal Assent and became law. The objective was to demonstrate the Government's continuing commitment to virtually eliminate PFOS and to meet the requirements of the CEPA 1999 Act (Government of Canada 2009).

2.6 Sources and human exposure

PFC emission sources can be classified as direct and indirect sources. Direct sources include all environmental emissions resulting from PFC and polymer manufacturing, AFFF products, and consumer products in which the perfluorinated compounds and their derivatives are used. Indirect emissions might result from release of the PFCs in consumer products as unwanted manufacturing residuals, or degradation of POSF-based and fluorotelomer-based products, as well as fluorinated polymers (Prevedouros et al. 2006). The concentration of the fluorochemical residuals in commercial products is typically less than 1% (Olsen et al. 2005) and might include PFHxS, PFOSA, N-MePFOSE, and N-EtPFOSE in sulfonamide-based products, and PFOA and other perfluorinated carboxylic acids in telomere-based products (Parsons et al. 2008). Direct PFC releases comprise the majority of emissions, while indirect sources contribute little (Russell et al. 2008). The total emissions of PFCAs from 1951 to 2004 have been estimated to be between 3200 and 7300 tonnes, with indirect sources accounting for ~1-5% of the total (Prevedouros et al. 2006). Uncertainty exists in the assessment of indirect sources due to the complexity of the degradation mechanism for fluorinated polymers incorporated into commercial products and for fluorotelomer alcohols and perfluorinated sulfonamides contained as residuals in these substances (Myers et al. 2010). Degradation mechanisms of these compounds are considered in the next section.

Human exposure might occur through the following mechanisms (Shoeib et al. 2011), which are similar to environmental emissions.

- Directly from manufacturing and use of PFOA and PFOS in commercial products;
- Atmospheric oxidation and breakdown of precursors that degrade to PFOS and PFOA;
- Absorption of the precursors into the body and their metabolic transformation.

The main pathways of human exposure to PFOS, PFOA and their precursors include diet and drinking water (Vestegren and Cousins 2009), air inhalation, dust ingestion (Shoeib et al. 2011) and absorption from dermal contact (Fasano et al. 2006).

2.7 Environmental fate and transport

The strength of the carbon-fluorine bond is the key contributor to the unique physical and chemical properties of PFCs; however, it appears to be the major factor in restraining the biodegradability of PFCs. In general, perfluorinated compounds are more resistant to biodegradation than poly-fluorinated compounds. While neither PFOS nor PFOA show any aerobic biodegradation (Parsons et al. 2008), several recent investigations for determination of the environmental fate of FTOHs and perfluorinated sulfonamides have shown potential degradation pathways by which these compounds end up as PFCAs and PFSA in the environment. Atmospheric oxidation (Ellis et al. 2004) and aerobic biodegradation, e.g. detected in microbial cultures (Dinglasan et al. 2004; Wang et al. 2005), liver tissues (Martin et al. 2005; Nabb et al. 2007) and rat models (Fasano et al. 2006) are considered the key PFC degradation pathways. The most important final product of FTOH transformation is a PFCA shorter by two carbon units than the parent FTOH (Dinglasan et al. 2004); low conversions (1-10%) are observed in activated sludge, mixed bacterial cultures, and mammalian metabolism, while higher conversions (up to 40%) could be obtained in aerobic soil samples (Wang et al. 2009). In addition to PFOA, the FTCAs and FTUCAs are two known intermediates in biodegradation of FTOH to PFCAs in all studies. Due to the somewhat shorter lifetimes of FTCAs in the environment, the FTUCAs are normally expected to be observed in environmental samples (Myers et al. 2010). Rapid biodegradation of 6:2 FTOH, the second dominant FTOH in fluorinated polymer products, occurs in both aerobic soils and

mixed bacterial culture with a degradation half-life of less than 2 days (Liu et al. 2010). Note that both even and odd chain length PFCAs are produced in biodegradation of FTOHs to PFCAs, although PFCAs resulting from the telomerization process comprise only even chain length PFCs (Liu et al. 2010). In the case of POSF-based precursors, N-EtFOSA, FOSA and FOSAA were formed in the first day as biodegradation products of N-EtFOSE in activated sludge, while PFOS appeared as the final degradation compound after 3 days (Rhoads et al. 2008).

Unlike fluorotelomers and POSF-based precursors, few studies have been carried out to investigate the biodegradation of fluorinated polymers, the main active ingredients in manufacturing of commercialized products. In the environment, these polymers undergo sequential transformation to their poly-fluorinated components, and ultimately to PFCAs. However, a recent study by Van Zelm et al. (2008) has been reported that the emissions from fluoroacrylate polymers, one of the most important classes of PFCs in surface treatment products (3M Company 1999a; Rao et al. 1994), currently comprise a minor fraction of total PFOA emissions. Thus, degradation of the residuals in the polymeric products is the chief contributor to PFOA generated from fluorotelomer acrylate production and use. Note that the residual amounts of 8:2 FTOH and PFOA in the fluorotelomer acrylate polymers are typically 0.5 and 0.013% by weight respectively (Russell et al. 2008). Furthermore, hydrolysis of Fluoroacrylate polymer does not break down the ester linkage at pH of 4, 7 or 9 at 50°C (Dupont Company 2004).

In urban areas, the presence of PFCs in food (Begley et al. 2005; Young et al. 2012; Fromme et al. 2009; Domingo 2012), air (Shoeib et al. 2004; Fraser et al. 2012; Shoeib et al. 2011), house dust (Liu et al. 2011; Shoeib et al. 2005), and drinking water (Skutlarek et al. 2006;

Lange et al. 2007) has been widely reported in the literature. In addition, PFCs have been studied in rivers, lakes and oceans worldwide have been studied. Typically high PFC concentrations are observed in regions with direct industrial emissions, since they have an impact on fresh water lakes and rivers, with concentrations ranging from 1-1000s ng/L (Saito et al. 2004; Skutlarek et al. 2006; Nakayama et al. 2010). In oceans, the concentrations of perfluorinated acids are approximately three orders of magnitude lower than in lakes and rivers (Yamashita et al. 2005). Trace levels of PFOA (N.D.-11.3 µg/L) and (0.3-7.5 µg/kg) have been detected in Canadian fresh water and fresh water sediments respectively (Environment Canada 2010). These findings are in agreement with negligible concentrations of PFOA and PFOS (i.e. 0.2 ng/L and N.D., respectively) detected in Vancouver and Calgary (Fuji et al. 2007).

PFCs are ubiquitous in humans (Kannan et al. 2004), with much higher concentrations in occupationally exposed workers (Ehresman et al. 2007). In addition, PFCs occur widely in biota, especially in fish (Bossi et al. 2005), aquatic invertebrates (Kannan et al. 2001), fish-eating birds (Kannan et al. 2001) and marine mammals (Houde et al. 2006; Butt et al. 2007). Moreover, fluorochemicals are detected widely in mammals, birds, and several other species, found only in remote regions (Paul et al. 2009; Olsen et al. 2005).

Wastewater treatment plants (WWTPs) are a major point source for PFCs to the environment. Conventional WWTPs are not effective for removing PFCs; hence similar or even higher PFC concentrations have been reported in the effluent of WWTP in comparison to the influent (Huset et al. 2008; Schultz et al. 2006). The biotransformation of precursor compounds within the WWTP might be the chief contributor to increase concentrations of PFCAs and PFSAs in the influent. In the effluent from Canadian WWTP facilities, the concentration of PFOA

ranges from 0.007 to 0.055 µg/L (Environment Canada 2010).

Landfills also play a critical role in the release of PFCs to soil, air, surface water and groundwater, as they are the final destination for many fluorochemicals used in consumer articles. Release of PFCs to the environment depends highly on the concentration of remaining PFCs at disposal time, landfilling practices and leachate collection systems. Leachates containing PFOS and PFOA are normally sent to municipal treatment facilities after collection; however, since these compounds are not removed from the influent of these facilities, they either pass directly into the downstream aquatic environment, or are contained in bio-solids, which are whether applied directly onto land or returned to the originating landfills (Environment Canada 2006). In a study on leachate samples from seven municipal landfills in the United States (Huset et al. 2011), PFCAs were the dominant compounds (~67%) in leachate, followed by PFSAAs (~22%), perfluoroalkyl sulfonamides (~8%), and fluorotelomer sulfonates (~2.4%). Emissions to air also occur in municipal landfills due to volatilization of precursors contained in disposed compounds, or water-air transfer of water-soluble PFCs that have readily transferred to landfill leachate. In a recent study by Ahrens et al. (2011), FTOHs have been reported to be the major class (~93-98% of the Σ PFCs), with dominance of the even chain-length PFCAs in air for two solid waste landfill sites in Ontario. However, in the same study, PFOS contributed ~2% of the total emissions, possibly due to partitioning to landfill leachate, or strong sorption to landfill solids.

2.8 Perfluorinated compounds in carpets: from manufacturing to disposal

For over half a century, fluorinated compounds have been incorporated into carpet finishing treatments to provide stain resistance (Kissa 2001). The carpet treatments are applied by fiber manufacturers, carpet mills, and customers as post-application treatments under trade names

like Scotchgard® (from the 3M company), Teflon® Advance, Zonyl®, and Stainmaster® (from Dupont company), which are readily available at hardware and carpet retail stores. The primary “active ingredients” in carpet and textile treatments (e.g. ScotchGard and Stainmaster) are fluorinated polymers. Dupont’s carpet protector is typically a mixture containing both urethane and acrylic FTOH based copolymers (Dupont Company 2001). Scotchgard carpet protector contains a mixture of fluoroalkyl copolymers as well as other acrylic based polymers (3M Company 2003). The 3M carpet protection products contain approximately 15% fluoroalkyl polymers (Hekster et al. 2002). Upon application, these compounds are adsorbed or chemically bound to the treated textile.

Figure 2.4 presents an overview of the significant points of contact where PFCs are used in carpets. Note that the flowchart describes the typical carpet product line, and not every product necessarily goes through all steps.

The total environmental releases through the life cycle of a stain resistant carpet can be studied in three stages:

- Carpet treatment,
 - Carpet mills and fiber manufacturers
 - Application of spray cans
- Customer usage, and
- Disposal.

Carpet mills and fiber manufacturers: Typically 0.05-0.5% by weight of fluorochemical is added to carpets to provide long-lasting repellency (Rao et al. 1994). Initial application of surface treatment products to uncut carpet or fiber through several methods including spray, foam, pad, or co-application might end up as PFC losses to air and wastewater. Furthermore,

throughout shearing, cutting and other packaging operations, solid wastes are generated, which finally end up in landfills. In addition to carpet and fiber manufacturers, PFC treatments might be applied by professional carpet steam cleaners, showing similar wear patterns to mill-applied treatments (3M Company 1999a).

Application of spray can products: Environmental releases during the application of these products depend on the size and shape of the carpet and accuracy of the applicator. The 3M Company estimated that the transfer efficiency across all sizes and shapes was ~66%; therefore 34% of the PFCs are initially released to air, with a potential for deposition (3M Company 2000b). In addition to losses during application, approximately 12.5% of the original spray contents remain in the can at the time of disposal; since a small percentage of these cans are recycled or incinerated, spray products represent a significant potential source of PFC release to landfills.

Customer usage: Substantial release (up to 50%) of the fluorochemical treatment is expected during the estimated nine-year average life of a carpet due to traffic and vacuuming (3M Company 2000b), with the release ending up in air and landfills. In a recent Japanese study (Liu et al. 2011), PFCAs were widely detected in vacuum cleaner dust samples, with the odd-numbered long-chain PFCAs (e.g. PFNA, PFUnDA, and PFTrDA) as the major components. PFC losses to wastewater treatment plants and possibly landfills (i.e. as biosolids) are also expected from steam cleaning. Table 2.4 presents PFC exposure routes during usage of both mill-treated and spray-treated carpets. Tittlemier et al. (2007) identified treated carpeting as the second major contributor to daily intake of PFCAs and PFOS after ingestion of food in a typical Canadian house.

Disposal: On average, more than half (53%) of PFCs initially applied as carpet treatments

remain at the disposal time (3M 2000b). At this stage, used carpets are either incinerated or sent to landfills. During incineration, both acrylate polymer and other PFC residuals are completely destroyed (Yamada et al. 2005); however, in Canada, municipal incineration of solid waste represents approximately 5% of total solid waste disposal (Environment Canada 2006) and accounts for less than 10% of residential and commercial carpet removal in 2010 (Canadian Carpet Disposal Fact Sheet 2010).

Degradation conditions in landfills extensively vary in temperature, as well as in available oxygen and moisture levels (Russell et al. 2008). Fluoropolymers have a negligible chance of degradation in the short term, since the biodegradation half-life of Fluoroacrylate polymer in aerobic soils has been estimated to be 1200-1700 years (Russell et al. 2008). Note that although the perfluoroacrylate polymers are not a significant source of emissions, they remain in landfill soils for long periods and possibly become the major emission source of PFCs after the phase-out of global PFC production (Van Zelm et al. 2008).

The main releases from landfilled carpets to the environment are through residual PFCAs, PFSAs, or FTOH-based and sulfonamide-based precursors brought about by incomplete synthesis or lack of purification prior to marketing (Dinglasan et al. 2006). In a study by Dinglasan et al. (2006), free NMeFOSE was observed in a Scotchgard® carpet and rug protector manufactured pre-2002, while unbound telomer alcohols with chain lengths from 8 to 14 carbons (6:2 up to 12:2 FTOHs) were detected in a Teflon® Advance product. The extent of unbound residual PFOS, n-methyl and n-ethyl FOSA and N-MeFOSE and N-Et FOSE alcohols in 3M products is up to 1-2% (3M 1999a). For fluorotelomer acrylate, 0.5% by weight of 8:2 FTOH and 0.013% by weight of PFOA are normal in consumer products (Russell et al. 2008).

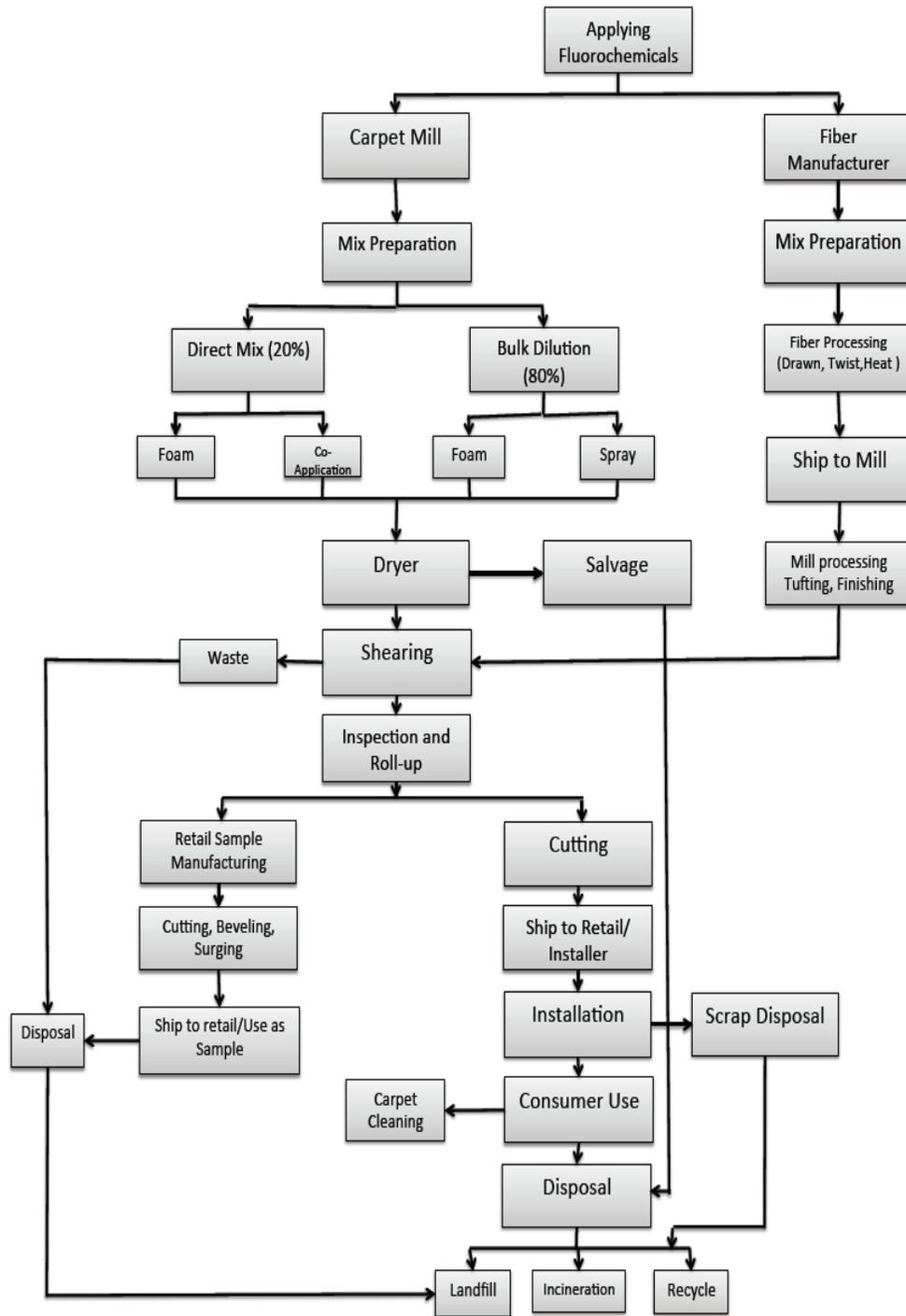


Figure 2.4: Overview of significant points of PFC emissions from carpet manufacturing to end-of-life.

Table 2.4: PFC exposure routes during usage of both mill-treated and spray-treated carpets (Source: Washburn et al. 2005)

Article Group	Dermal contact	Ingestion via hand-mouth contact	Incidental ingestion of dust	Inhalation of particulates	Inhalation of vapor	Ingestion of contacted food	Inhalation of droplets
Mill treated carpet	Yes	Yes	Yes	Yes	Yes	Yes	No
Solution treated carpet	Yes	Yes	Yes	Yes	Yes	Yes	Yes

Due to high vapor pressure and low water solubility of the PFC precursors, the residual telomer or sulfonamide alcohols in carpets preferentially partition into air during the carpet life (Lei et al. 2004). Sulfonamide alcohols have a higher chance of remaining in the carpet surface in old carpets, since their vapor pressures are approximately 3 orders of magnitude lower than for FTOHs. The vapor pressures of precursor residuals are so high that most of them volatilize during the drying process in carpet mills (Buck et al. 2005). Therefore, the only compounds expected to mostly end up in the landfills from old carpets are residual PFCAs and PFSAs, which have low vapor pressures. Since these compounds are quite water soluble, transfer from old carpets to landfill leachate is very likely.

The total annual amounts of PFC emissions to landfill leachates can be calculated by multiplying the average concentration of PFCs in leachate samples, which might have seasonal variations (Li et al. 2012), by the annual leachate flow. Table 2.5 shows the annual leachate flows, served populations, and total waste quantities from three different landfills in Canada.

Table 2.5: Landfill specifications of different landfill sites in Canada

Landfill name and location	Leachate flow (m ³ /year)	Year	Population served	Total landfilled waste (tonnes)
Hope landfill, BC ¹	107,000	2009	7,840	6,746
Vancouver landfill, BC ²	2,080,000	2011	1,060,000	1,299,279
Eastview landfill, ON (closed in 2003) ³	120,000	2010	Not available	No waste

¹ From Hope Landfill 2009 Annual Report (2011)

² From Vancouver Landfill 2010 Annual Report (2011)

³ From Eastview Road Landfill Site 2010 Annual Report (2011)

2.9 Leaching test procedures and factors affecting leaching rates

Although no studies have been published about leaching of PFCs from carpets into landfill leachate at this point, several experiments have been carried out on mechanisms of leaching of other compounds, most of which following directly the procedures of Toxicity Characteristic Leaching Procedure (TCLP) under the EPA SW846 Method 1311 (1992) (US EPA 2009). The TCLP method simulates contaminant leaching in MSW landfills, using a solution of acetic acid as an extraction fluid. Acetic acid is produced in landfills during anaerobic decomposition of waste. In addition to TCLP, other standards e.g. Synthetic Precipitation Leaching Procedure (SPLP) EPA Method 1312 (1994) and California's Waste Extraction Test (WET) (1985) (US EPA 2009) are widely used in leaching studies (Townsend et al. 2004; Lincoln et al. 2007). Care must be taken while using different standard procedures since the composition of extraction fluids in different test methods might not always represent what is encountered in actual landfill conditions. For example, Jang and Townsend (2003) reported a dramatic difference between concentrations of leached lead using the TCLP

method and those measured using real landfill leachate. Real landfill leachate is preferred to simulated extraction fluids in batch leaching tests to provide more realistic landfill conditions. Many different factors such as waste type, analyte concentration in waste, solution pH and ionic strength, leaching test solid wt./liquid wt. ratio, samples size and contact time might have an impact on leaching amounts and rates (Townsend et al. 2004). For instance, noticeable increases in leachability of lead were reported at both low and high pH values, while minimum leachability was witnessed at neutral pH (Townsend et al. 2004). In addition to these factors, temperature is expected to alter the leaching rates of PFCs, whether by affecting the solubility of different PFCs (Bhatarai and Gramatica 2011) or influencing the bacterial activity (Wang et al. 2008).

Chapter 3: Materials and Methods

3.1 Introduction

This chapter describes the experimental equipment, procedures, and analysis used to study the transfer of PFCs from carpets to aqueous media. All leaching experiments were conducted in bench- and pilot-scale “end-over-end” contactors. Figure 3.1 provides an overall flowchart of these experiments.

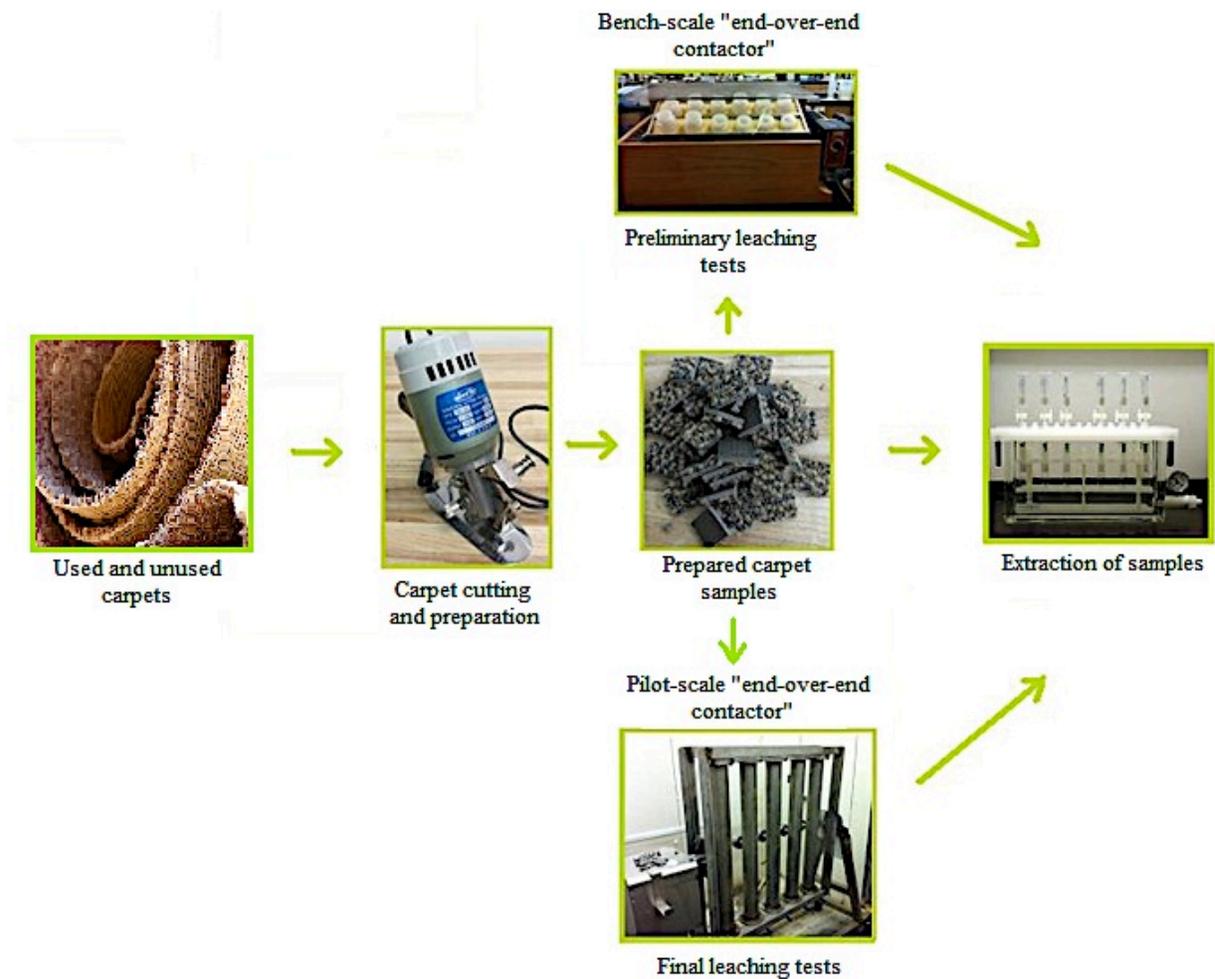


Figure 3.1: Overall work flow of the leaching experiments

3.2 Utilized materials

3.2.1 Carpets

Carpet samples were the main constituent in all leaching experiments. A number of used and new carpets were collected from suppliers in Vancouver, thrift stores, and departments of UBC. Table 3.1 summarizes the approximate date of manufacture, appearance, fibre thickness, location of usage, and possible previous treatment types for each of the collected carpets. Carpets N₁, N₂, and N₃ were not selected for this study due to their negligible concentrations of PFCs. Details of the PFC concentrations in each carpet sample are described in Section 4. The extraction and analysis methods for different PFCs are described in Sections 3.6 and 3.7 below.

3.2.2 High-pressure liquid chromatography (HPLC) grade water

HPLC grade water was used in the experiments to minimize the level of contamination. The suspended solids of tap water were first removed by pre-filtration. A Barnstead Thermolyne (Model A1013-B) water still was then used to evaporate and condensate the pre-filtered water. The distilled water was then collected in two 45 L high density polyethylene (HDPE) bottles and fed to a Synergy UV Millipore system. Finally, ultrapure HPLC grade water with resistance of 18.2 MΩ.cm at 25°C and pH of 7.65 was obtained from the UBC Department of Civil Engineering.

Table 3.1: Details of collected carpets

No.	Source	Approximate Date of Manufacture	Physical conditions	Fibre thickness (mm)	Previous treatments
N ₁	Carpet retailer	2011	Brand new, unused	20	Treatment by Scotchgard at carpet mill
N ₂	Carpet retailer	2011	Brand new, unused	10	Treatment of fibre by Dupont products (Stainmaster)
N ₃	Carpet retailer	2011	Brand new, unused	10	Treatment of fibre by Dupont products (Stainmaster) “Highly stain resistant” on the label, one of the very recent products
N ₄	Commercial carpet used in UBC CHBE building when it was opened.	2005	Maintained in boxes in the warehouse- unused	10	Treatment of carpet through a heat-and-force actuated cohesion process – Contains high MW polymers – no further info provided
N ₅	Used in UBC Pulp and Paper Centre when some offices were upgraded.	~2000	Maintained in boxes in the warehouse- unused and clean	10	Treatment of carpet through a heat-and-force actuated cohesion process – Contains high MW polymers – no further info provided
N ₆	Thrift store	N/A, ~2000	Contains heavy dust- used conditions	15	Unknown, possible treatment by mills, steam cleaners, or aerosol sprays
N ₇	Thrift store	N/A, ~2000	Contains heavy dust- used conditions	15	Unknown, possible treatment by mills, steam cleaners, or aerosol sprays
N ₈	Commercial collected by UBC APSC	N/A	Unused and clean	10	Unknown, possible treatment by carpet mill or fibre manufacturer

3.3 Experimental set-up

3.3.1 Bench-scale “end-over-end contactor”

Preliminary tests were carried out in the initial experiments in a small Dayton bench-scale “end-over-end contactor” model 5X412. This contacting apparatus, shown in Figure 3.2, holds 12 x 500 mL HDPE bottles and rotates at rotation rates from 0 to 25 revolution(s) per minute. The rotation speed was set to 8 rpm during the preliminary tests. The HDPE bottles

were rinsed with methanol and air-dried prior to the experiments to remove possible PFC contamination.



Figure 3.2: Bench-scale “end-over-end contactor”

3.3.2 Pilot-scale “end-over-end contactor”

The results from preliminary leaching tests allowed the conditions for the final tests to be chosen in a more effective way. Details of the analysis are provided in Section 3.7. All final experiments were conducted in the custom-built “pilot-scale end-over-end contactor”, shown in Figure 3.3. Details of the design and operation of this facility are given by Danon-Schaffer (2010).

This contacting device included 5 parallel cylindrical vessels, each simultaneously contacting carpets with leachate, in most cases, at a rotational speed of 8 revolutions per minute (rpm).

Rotation promoted contact between carpet and leachate by creating turbulence and forcing liquid to flow through the pieces of carpet. The rotation speed was changed by a transformer changing the input voltage to the electric motor as required. The contactor was built and assembled by the UBC Department of Chemical and Biological Engineering workshop in 2005. Each vessel has an inner diameter of 82 mm and an inside length of 900 mm, providing a capacity of ~ 5 L for each vessel. More details about the rotator are provided in Figure 3.4.



Figure 3.3: Pilot-scale “end-over-end contactor”

A 1-inch (25 mm) ball valve is located at the bottom of each vessel for sub-sampling. All components of the apparatus were fabricated from food-grade stainless steel to minimize adsorption of PFCs onto the vessel walls.

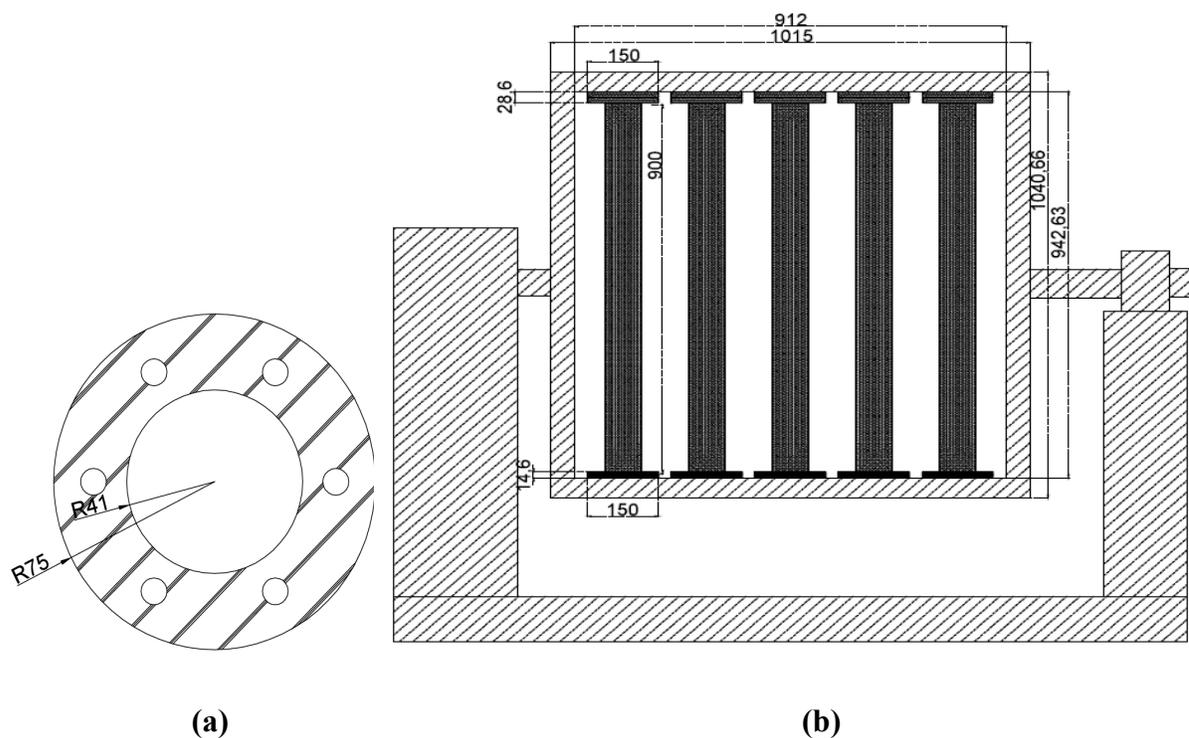


Figure 3.4: (a) Plan-view of a single vessel and (b) side-view of pilot-scale end-over-end contactor (all dimensions are in mm).

Unlike the preliminary tests, whole pieces of carpet (i.e. fibres attached to their backings) were utilized for the final tests, better representing what is encountered in real landfill situations. Figure 3.5 provides a flow chart of the final leaching experiments. Altogether this included 30 contacting tests carried out in duplicate.

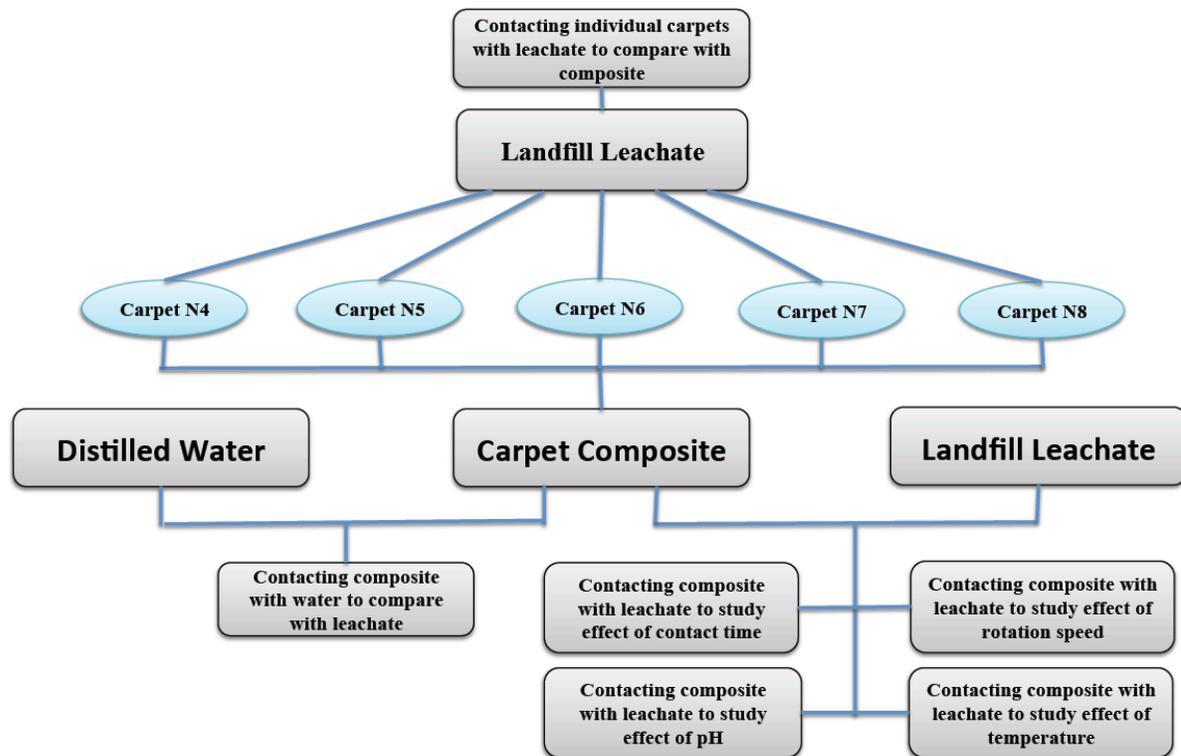


Figure 3.5: Flowchart of final experiments

3.4 Experimental methodology

3.4.1 Carpet preparation

Particle size is one of the most important factors affecting leaching rates (Townsend et al. 2004). In preliminary tests, where only carpet fibres were utilized, carpet fibres was simply separated from the attached backings. The separated carpet fibres were then mixed thoroughly by hand to improve the homogeneity of the matrix. In the final tests, where carpet fibres were not separated from backings, carpet samples were cut with a Microtop industrial cutting machine into 20 x 20 mm squares in order to maintain the consistency in all experiments. In order to examine more realistic conditions where several carpets might enter the landfill at the same time, composite carpet samples were tested in some contacting experiments. Nitrile gloves were employed to handle carpet samples. To ensure homogeneity of the carpet

samples, a method similar to quartering (split sampling) was used to thoroughly mix the carpet pieces, with this method applied separately for each carpet type (i.e. N₄, N₅, N₆, N₇, and N₈). The steps to mix and prepare carpet samples were as follows:

- a. On a clean surface, all carpet pieces were divided into quarters and the contents of each quarter were mixed thoroughly. Care was taken to ensure that the surface was not contaminated with PFCs.
- b. Two quarters were then mixed together to form halves.
- c. The two halves were then combined and blended to form a more homogeneous matrix.

This procedure was repeated 10 times for each type of carpet. Figure 3.6 shows a schematic of the quartering method.

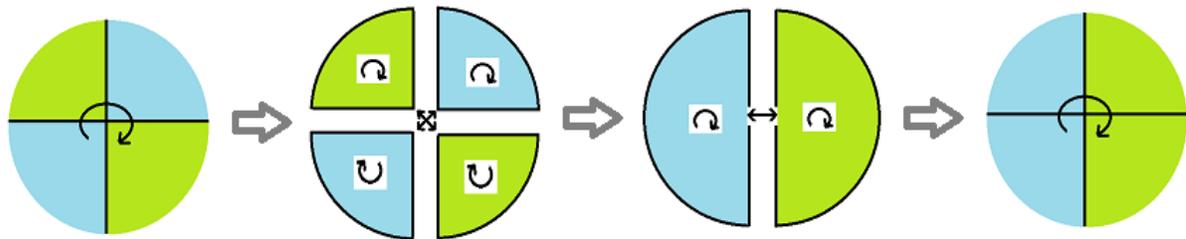


Figure 3.6: Schematic of carpet mixing method (i.e. quartering).

Thereafter, 100 g composites of N₄, N₅, N₆, N₇ (22.5 wt. % each), and N₈ (10 wt. %) were weighed, mixed, and stored in clean plastic bags, which did not contain any PFCs. The proportions were chosen based on the availability of each carpet. In addition to composites, 2 x 100 g of each individual carpet were also stored in plastic bags. Figure 3.7 shows a photo of a composite carpet sample.



Figure 3.7: 100 g of composite carpet sample after preparation.

3.4.2 Leachate collection

The leachate was collected by the author on Jan 30th, 2012 from an urban landfill in Canada¹, which accepted municipal waste as well as residuals and sludge from WWTPs and Water Treatment Plants (WTPs). The landfill was equipped with a double ditch leachate collection system, where the inner ditch collected the leachate and the outer one water. The leachate was pumped to a WWTP for treatment.

Prior to sampling, 20 L HDPE carboys were rinsed first with HPLC grade water followed by methanol and air-dried afterwards. Nitrile gloves were used for sample handling.

Approximately 270 L of leachate was collected from the landfill's leachate well using a bailer and transferred to the carboys. In order to minimize any changes in leachate quality as a result of biological activity or evaporation of volatile precursors, samples were shipped to the UBC

¹ The identity of the landfill cannot be disclosed because of a confidentiality agreement with the landfill operator.

Department of Civil Engineering immediately after collection and stored in a 4 - 6°C walk-in fridge.

The leachate was characterized for pH, conductivity and Total Dissolved Solids (TDS) by the author before being stored in the fridge. A ϕ 44 Beckman pH meter (Model PHI 44) was used for the pH measurements. Prior to each use, the instrument was calibrated using buffer solutions with pH of 4, 7 and 10. For conductivity and TDS measurement, a Pionner 30 portable conductivity meter was used, which was calibrated with a KCl standard with a known electric conductivity prior to each use. The fresh leachate was also preserved and characterized for Total Organic Carbon (TOC) and total metals including Al, As, Be, Ca, Fe, Mg and Zn. by the UBC Environmental Engineering Laboratory. The EPA Standard Methods 5310B (2000) and 3120 (1999) were followed to characterize the TOC and total metals of the leachate respectively (US EPA 2009).

3.4.3 Preliminary leaching experiments in the bench-scale “end-over-end contactor”

The main objective of the preliminary tests was to determine the leaching of PFCs from carpet to leachate and distilled water at different contact times. Carpet N₅, an unused carpet with an approximate manufacture date of 2000, was used for the preliminary tests. Analysis of a sample of this carpet prior to the leaching experiments demonstrated high concentrations of PFCs (~543 ng of Σ PFCAs per g of carpet) in this carpet. Detailed information on the analysis methods is provided in Section 3.7. In the preliminary tests, the carpet backings were separated from the fibres, and only the fibres were utilized. The leachate was collected by Li (2011) from a landfill² serving a large urban area. This leachate had been stored in a 15 L

² The identity of the landfill cannot be disclosed because of a confidentiality agreement with the landfill operator.

HDPE carboy since being collected in August 2010 at -20°C to prevent changes in the PFC concentrations. Storing at this temperature is one the most appropriate ways of PFC sample preservation (Leeuwen et al. 2007), stopping bacterial activity causing biodegradation and preventing losses from evaporation of volatile PFCs, e.g. sulfonamides.

Two days prior to starting, the frozen leachate was removed from the fridge to thaw at room temperature (21°C). During the preliminary experiments, the carboy was stored in a $4 - 6^{\circ}\text{C}$ walk-in fridge. 400 mL aliquots of leachate were collected in 500mL HDPE bottles after shaking the carboys thoroughly by hand for 30 s. Before introducing carpet samples to the leachate, the bottles were left in the room for 2 h in order to reach room temperature. Otherwise, the creation of a temperature profile might impact the results. Carpet samples were next added to the bottles with a solid/liquid (w/w) ratio of 1:20 and placed in the contactor, rotating at a speed of 8 rpm. The carpet-leachate contact times ranged from 0.5 h to 3 days. Since the leaching rates were expected to decrease as time passed (because of a decrease in concentration gradient), shorter sampling time intervals were chosen at the beginning of experiments than the end. Due to the high cost of analysis, only 2 experiments were carried out in triplicate. All preliminary tests were conducted at $21 \pm 2^{\circ}\text{C}$. In addition to leaching of PFCs from carpets to the leachate, the biodegradation of precursors of the leachate was a possible contributor to the increase in PFC concentration in the leachate. Therefore, 10 experiments were conducted to monitor possible changes of PFC concentrations in landfill leachate at various time intervals from 0.5 h to 3 days.

At the end of each run, a 45 mL aliquot of each sample was passed through a $200\ \mu\text{m}$ stainless steel mesh and collected in a 50 mL polypropylene centrifuge tube. The mesh had been washed with methanol and air-dried prior to each test to prevent from contamination. It

successfully separated the floating carpet fibres from the liquid. The pH, electrical conductivity and total dissolved solids of the leachate were then measured and recorded. The tubes were filled up to 90% of their total volume, leaving a 5 mL headspace to prevent cracking the tubes due to expansion of their contents while stored in fridge at -20°C. The samples were shipped to the Department of Fisheries and Oceans Canada Institute of Ocean Sciences (DFO-IOS) in Sidney, BC in coolers packed with ice for extraction and analysis.

3.4.4 Final leaching experiments in the pilot-scale “end-over-end contactor”

The leaching tests conducted in the pilot-scale “end-over-end contactor” followed a method similar to the EPA Toxicity Characteristic Leaching Procedure (TCLP), described in Section 2.9. Table 3.2 summarizes the leaching experiments carried out in the pilot-scale end-over-end rotating apparatus.

In each experiment, 100 g of composite or individual carpet was cut, mixed (as explained in section 3.4.1) and added to each vessel, together with 4 L of leachate or distilled water. A headspace of ~20% of the total vessel volume (i.e. ~1 L) was provided in each test. The solid/liquid ratio (wt./wt.) was 1:40 in all tests. The results from the preliminary tests implied that higher solid/liquid ratios might need dilution for the analysis, while lower values might have led to concentrations below the limit for detection of some PFCs.

Table 3.2: Summary of leaching experiments conducted in pilot-scale end-over-end contactor.

Type of Experiment	Contact time (h)	pH	Wt. liq./ wt. carpet	Carpet	Liquid	Rotation speed (rpm)	Average temperature (°C)
Effect of contact time	1	6	40	¹ Composite	Leachate	8	15
	2	6	40	¹ Composite	Leachate	8	15
	6	6	40	¹ Composite	Leachate	8	15
	24	6	40	¹ Composite	Leachate	8	15
	168	6	40	¹ Composite	Leachate	8	15
	6	6	40	¹ Composite	Leachate	0	15
Effect of rotation speed	6	6	40	¹ Composite	Leachate	4	15
	6	6	40	¹ Composite	Leachate	8	15
	6	5	40	¹ Composite	Leachate	8	15
Effect of pH	6	7	40	¹ Composite	Leachate	8	15
	6	8	40	¹ Composite	Leachate	8	15
	6	6	40	¹ Composite	Leachate	8	15
	6	5	40	¹ Composite	Water	8	15
Contact with distilled water	6	6	40	¹ Composite	Water	8	15
	6	7	40	¹ Composite	Water	8	15
	6	8	40	¹ Composite	Water	8	15
	6	6	40	N ₄	Leachate	8	15
Individual carpets vs. composite	6	6	40	N ₅	Leachate	8	15
	6	6	40	N ₆	Leachate	8	15
	6	6	40	N ₇	Leachate	8	15
	6	6	40	N ₈	Leachate	8	15
	6	6	40	¹ Composite	Leachate	8	15
	6	6	40	¹ Composite	Leachate	8	5
Effect of temperature	2	6	40	¹ Composite	Leachate	8	5
	24	6	40	¹ Composite	Leachate	8	5
	6	6	40	¹ Composite	Leachate	8	35
	2	6	40	¹ Composite	Leachate	8	35
	24	6	40	¹ Composite	Leachate	8	35

¹ Mixture of carpet samples, including 22.5 (wt. %) each of N₄, N₅, N₆, N₇, and 10 (wt.%) of N₈.

In order to explore the effect of pH, temperature and rotation speed on PFC leaching rates, a base condition was set for the experiments, and all conditions were varied around the corresponding specific value. The base condition included:

- Contact time: 6 h,
- pH: 6, one of the most common pH values for landfill leachates,
- Temperature: room temperature ($\sim 15 \pm 3^\circ\text{C}$),

- Rotation speed: 8 revolutions per minute,
- Solid/liquid mass ratio: 1:40,
- Carpet type: Composite.

Prior to starting each test, a leachate carboy was taken out of the fridge and shaken thoroughly by hand for 30 s to obtain a homogeneous matrix. Precisely 4 L of leachate was then transferred to a 5L HDPE container, which had previously been rinsed in order by hot water and soap, HPLC water, and methanol, then air-dried. The initial pH of the collected leachate was ~7. Glacial acetic acid, an organic acid formed during the anaerobic decomposition of organic compounds in landfills, was applied to the leachate to reduce the pH to 6 ± 0.05 . Pure glacial acetic acid (99.7%) from Fisher Scientific was first diluted with HPLC grade water to obtain a diluted solution of 10% acetic acid. This diluted solution was then used to reduce the pH of 1L leachate sample by trial and error through a method similar to titration.

Approximately 3.5 mL of diluted acetic acid were required to reduce the leachate pH from 7 to 6, so that ~15 mL of diluted acetic acid was added to 4L of leachate. The pH was measured and recorded next to ensure a pH of 6 ± 0.05 . The electrical conductivity and TDS were also recorded. The container was then left for 2 hours to reach room temperature before transferring the leachate to the “end-over-end contactor” vessels through a HDPE funnel, which had previously been rinsed with methanol and then air-dried. The temperature of the room in which the experiments were conducted was subject to fluctuations throughout the tests. When the doors were opened in winter, sudden temperature drops (down to $\sim 8^{\circ}\text{C}$) were witnessed. Despite the extent of these changes, the leaching rates were not affected significantly as long as these changes did not have a noticeable intermediate-term effect on the mean temperature of room, which was $15 \pm 3^{\circ}\text{C}$ for the majority of tests. This is because of

a time lag between changes in temperature of the ambient air and the temperature of the aqueous media due to the heat transfer resistance and thermal inertia, mainly from the steel walls of the vessels. See Appendix A an analysis of the time lag and energy balance equations for this system.

The experiments summarized in Table 3.2 are discussed below. Note that at the end of all leaching tests, 45 mL aliquots of corresponding samples were collected and stored following the same procedure as discussed in Section 3.3.1.

3.4.4.1 Effect of contact time

Composite carpets were contacted with leachate samples separately for 0.5, 1, 2, 6, 24, and 168 h, each in duplicate. This range of contact times was chosen based on the preliminary test results in which the concentrations of most PFCs appeared to approach their asymptotic values after 3 days of contact. As discussed previously, the time intervals between sampling at the beginning of the tests were shorter than towards the end. These experiments were carried out at room temperature with a rotation speed of 8 rpm.

3.4.4.2 Effect of rotation speed

It is assumed that the rotation provides enhanced contact between the carpet particles and aqueous media; this assumption was verified by conducting tests with three different rotation speeds: 0 (static), 4, and 8 rpm. These tests were carried out at the base case conditions, except that the rotation speed was varied.

3.4.4.3 Effect of temperature

To explore the effect of temperature on leaching rates of various PFCs and their precursors, 100 g of composite carpet sample was contacted with 4L landfill leachate over a temperature

range of 5-35°C, covering the temperature range of most municipal solid waste (MSW) landfills. The upper limit indicates the generation of heat as a result of waste oxidation. Due to the high cost of analysis, the leaching experiments were conducted at two temperatures: 5±1, and 35±1°C. The temperature was maintained during the period of experiments by placing the contactor at a walk-in temperature chamber at the UBC Environmental Engineering Laboratory. The contactor was placed in the chamber 14-15 h prior to each test so that all vessels reached the desired temperature.

3.4.4.4 Effect of pH

The pH of the leachate used in the experiments was ~7. To study the effect of pH on leaching rates, the pH was changed over the range of 5 to 8, which covers the pH for most MSW landfills. Typically, the leachate of younger landfills have lower pH and, with time, increases in pH tend to occur for landfill leachates (Slomczynska and Slomczynski 2004). Reagent grade glacial acetic acid was used to reduce the leachate pH to 5±0.05 and 6±0.05, whereas reagent grade sodium hydroxide was applied to increase the leachate pH to 8±0.05. To obtain a pH of 7±0.05, the leachate was used, with no acid or base added.

Although no data were available about leaching rates of PFCs and the affecting factors, the effect of pH on other compounds e.g. metals were explored previously. In a study by Warner and Solomon (1990), the leaching rates of arsenic, chromium and copper were increased up to certain point by increasing pH, but decreased by further increasing the pH.

3.4.4.5 Individual carpets vs. composite

Some experimental runs were designed to compare the leaching of PFCs from individual carpets with leaching from composite carpets. 100 g of each carpet sample (N₄, N₅, N₆, N₇, and N₈) were contacted with 4 L of leachate in duplicate. These tests were carried out at room

temperature with a rotational speed of 8 rpm.

3.4.4.6 Contacting with distilled water

PFC leaching rates were explored in the absence of other agents e.g. organic and inorganic matter, metals, etc. This set of experiments was also intended to shed light on how the PFCs enter the aqueous media. HPLC grade water was used in these experiments to minimize cross-contamination. Similar to the experiments in section 3.4.3.4, the pH of distilled water was adjusted to 5 ± 0.05 , 6 ± 0.05 , 7 ± 0.05 , and 8 ± 0.05 using glacial acetic acid or sodium hydroxide.

3.5 Quality Assurance/Quality Control (QA/QC) procedures

3.5.1 Leachate blank tests

Leachate blank tests were conducted using 4 L of leachate with no pieces of carpet added. These tests were carried out to rule out possible changes in PFC concentration in leachate as a result of degradation of precursors during experiments and storage. A single leachate blank was associated with each set of experiments (except for the tests conducted with distilled water and for exploring the effect of pH). Table 3.3 represents the conditions of the leachate blank tests.

3.5.2 Operational blank test

A single blank test was conducted with HPLC grade water. The objective was to determine the degree of probable cross-contamination from use of the sampling containers or tubes, sample handling, storage, and transportation. The blank test was carried out in the contacting device for 6 hours at 8 rpm and at room temperature. The pH, conductivity, and total dissolved solids were measured and recorded before and after each test.

Table 3.3: Leachate blank test conditions.

Blank sample No.	Experiment type	Duration (h)	pH	Rotation speed (rpm)	Temperature (°C)
B.1	Effect of contact time	168	6	8	15 ± 3
B.2	Effect of rotation rate	6	6	8	15 ± 3
B.3	Effect of temperature	6	6	8	35 ± 1
B.4	Individual carpets vs. mixture	6	6	8	15 ± 3
B.5	Additional leachate blank test	6	6	8	20 ± 1

3.5.3 Base case experiments

A single base case experiment was carried out for each set of tests (except for one conducted with distilled water). Since the operational conditions in all of the base case experiments were similar, the results of these five tests provide an indication of the precision of the entire test series. QA/QC procedures for extraction and analysis are described in Sections 3.6 and 3.7.

3.6 Carpet and leachate sample extraction (DFO-IOS)

Extraction and clean-up of the samples are essential elements in concentrating and purifying the extract prior to analysis. The extraction and analysis of the samples in this study were performed at the Fisheries and Oceans Canada Institute of Ocean Sciences in Sidney, BC, by Dr. Jonathan Benskin under the guidance of Dr. Michael Ikonou. Two different methods were used for extraction and analysis of carpet and leachate samples. This section describes each extraction method.

3.6.1 Extraction of carpet samples

PFCs from carpet samples were extracted by the method described by L'Empereur et al.

(2008), with all carpet samples extracted in triplicate. Two, 2x2 cm carpet pieces were used for each extraction (approximately 5 g). Carpets were weighed and placed into a 50 ml polypropylene tube, then spiked with 22.5 ng of mass-labelled internal standards ($^{13}\text{C}_4$ 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). Internal standards were applied to correct for the loss of analyte during sample preparation or sample inlet once required. The spiked carpets were allowed to sit for a few minutes until the solvent dried. Next, the extraction was carried out by adding 15 mL of methanol to the carpets for five times. After each stage of extraction with methanol, the centrifuge tubes were shaken in a vortex shaker for ~15 minutes. The extracts were reduced under nitrogen to a final volume of 45 mL and then spiked with 22.5 ng recovery standard (500 μg of a 500 ppb standard). The solution was then vortex-mixed and a portion of the extract was transferred to a 300 μL PP microvial for analysis by HPLC-MS/MS.

In order to assess % recoveries, a spike-recovery experiment was performed in triplicate by spiking native PFC and precursor standards onto a blank carpet (containing no PFC), allowing it to dry, and then extracting with the above method. In addition, untreated carpet samples were extracted with the same method to determine any major problem with recovery of the analytes of interest.

Extraction efficiency experiments were carried out for all carpet samples by performing a sixth methanol extraction, and analysing it separately. These experiments were conducted to confirm that all PFCs were extracted in the first five methanol extractions. Extraction efficiencies for each carpet were calculated through the following equation:

$$\text{Extraction Efficiency (\%)} = \left[\frac{\text{Analyte concentration obtained from the first five extractions}}{\text{Analyte concentration detected in the 6}^{\text{th}} \text{ methanol extract}} \right] \times 100$$

3.6.2 Extraction of leachate samples

The leachate extraction procedure was adopted from a previously developed USEPA method (US EPA 2011) for 45 mL leachate samples. Prior to extraction, the pH of samples was checked. Since all samples displayed a pH of 6 to 7, no pH adjustment was made. All samples and blanks were spiked with 2 ng of isotopically-labelled internal standards ($^{13}\text{C}_4$ 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). SPE cartridges (Oasis® WAX 6cc, 500mg 30 μm) were conditioned with 5 mL of 0.3% NH_4OH in methanol, 5 mL of 0.1M formic acid, and 5 mL of reagent HPLC-grade water prior to loading. Samples were vortex-mixed, then loaded drop-wise (5 mL/min) under vacuum. After loading, the cartridges were washed with 5 mL of 20% methanol and 80% of 0.1 M formic acid in reagent water. The cartridges were dried under vacuum and eluted with 4 mL of 0.3% NH_4OH in methanol afterwards. The extracted solution was spiked with recovery standard (2 ng $^{13}\text{C}_2\text{FDUEA}$) and a portion was transferred into a conical vial for analysis by HPLC-MS/MS.

3.7 Instrumental analysis (DFO-IOS)

The PFCs were analysed by liquid chromatography tandem mass spectrometry (LC/MS/MS) at the Fisheries and Oceans Canada Institute of Ocean Sciences (DFO-IOS) in Sidney, BC. 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 was utilized to separate the target analytes. In addition, the PFCs in the pump were separated from PFCs in

the samples by two Waters Xterra C18 (5 μm , 4.6 mm x 30 mm) columns, linked in series and placed upstream of the injector. In the initial conditions, the mobile phase consisted of 10% solvent A (100% MeOH) and 90% solvent B (0.1% ammonium hydroxide/ 0.1% ammonium acetate). The gradient elution program was: 0-1 min, 90% B, increase to 0% B by 8 min, maintain at 0% B until 12 min, return to starting conditions by 12.1 min, equilibrate for 4 min. Throughout the injection, the flow rate was held constant at 250 $\mu\text{L}/\text{min}$. Analysis of the samples was performed by an API 5000Q triple-quadrupole mass spectrometer (AB Sciex, Concord, ON, Canada) operating in negative ion Multiple Reaction Monitoring (MRM) mode. For each analyte, one or two precursor-product transitions were monitored. For the first 4.0 min of each run, the flow was diverted from the mass spectrometer by a Vici Valco diverter valve. The source temperature was 400°C. In order to target and quantify the analytes, Analyst v. 1.5.1 software was used.

Weighted (1/x) linear regression calibrations were used to determine the concentration ranges. Analyte concentrations were then determined with respect to the mass-labelled internal standards, shown in Table 3.5. Each batch consisted of 12 samples. Four blanks (methanol) and one calibration standard (1 ppb) were processed between each batch. Method detection limits (MDLs) were assigned as 3 standard deviations above the mean blank levels. In cases when the blanks displayed non-detectable analyte concentration levels, the MDL was set equal to the instrument detection limit (IDL). The IDL was determined from the analyte peak response with a signal-to-noise ratio of 3:1. The MDL values in the analysis of leachate samples are summarized in Table 3.4. For purpose of statistical analysis, values of 0.5 MDL were assigned for the analytes for which the concentrations were below MDL.

Since the extracted carpet weights were not equal for all samples, the measured MDL values

for carpet samples were sample-specific, i.e. each individual sample had a unique MDL. Thus the MDLs are not summarized in this section and were directly applied to the data reported in Section 4.1 where required.

Table 3.4: Method Detection Limits (MDLs) for different PFCs in leachate sample analysis.

PFC	MDL (ng/mL)	PFC (continued)	MDL (ng/mL)
PFBA	0.019	PFDoA	0.009
PFPA	0.077	PFTA	0.009
PFHxA	0.125	PFBS	0.003
PFHpA	0.080	PFHxS	0.008
PFOA	0.887	PFOS	0.008
PFNA	0.381	PFDS	0.003
PFDA	0.013	FOSA	0.001
PFUnA	0.009	---	---

Adopting internal standards in the analysis is essential to obtain data of as high a quality as possible in ultra-trace analysis. Under ideal conditions, each analyte should have an individual mass-labelled internal standard for maximum quantification accuracy. In this study, mass-labelled internal standards were available for 7 of the 18 PFCs of interest. Analytes with corresponding mass-labelled standards are highlighted by a (*) sign in Table 3.5. These analytes are expected to have the highest precision and accuracy in analyses. The mass-labelled internal standards could also be used for quantification of the remaining 11 analytes, for which the mass-labelled standards are lacking (e.g. $^{13}\text{C}_2$ -PFHxA for quantification of PFHpA). The mass-labelled internal standards are assigned to these analytes based on similarities in physical and chemical properties of the compounds, such as chemical structure and functional groups.

Table 3.5: Mass-labelled internal standards used in DFO-IOS lab.

PFC	Mass-labelled internal standard
* PFBA	$^{13}\text{C}_4$ -PFBA
PFPeA	$^{13}\text{C}_4$ -PFBA
* PFHxA	$^{13}\text{C}_2$ -PFHxA
PFHpA	$^{13}\text{C}_2$ -PFHxA
* PFOA	$^{13}\text{C}_2$ -PFOA
* PFNA	$^{13}\text{C}_5$ -PFNA
* PFDA	$^{13}\text{C}_2$ -PFDA
PFUnA	$^{13}\text{C}_2$ -PFDA
PFDoA	$^{13}\text{C}_2$ -PFDA
PFTA	$^{13}\text{C}_2$ -PFDA
PFBS	$^{13}\text{C}_4$ -PFOS
PFHxS	$^{13}\text{C}_4$ -PFOS
* PFOS	$^{13}\text{C}_4$ -PFOS
PFDS	$^{13}\text{C}_2$ -PFOA
FOSA	$^{13}\text{C}_4$ -PFOS

* Analytes for which mass-labelled internal standards are available in this study.

Chapter 4: Results and Discussion

4.1 Quality Assurance/Quality Control (QA/QC)

4.1.1 Leachate blank tests

Concentrations of PFCs undergo changes over time due to biodegradation of precursors in raw leachate (See Section 3.5.1). Measured PFC levels in blank leachate samples (i.e. leachate samples having no contact with carpet) for different test conditions are summarized in Table 4.1. Samples are tagged with the same labels as in Table 3.3. Note that since a set of duplicate samples was available for blank leachate at a pH of 6, temperature of 15°C and contact time of 6 h, both mean and standard deviation values are provided. Figure 4.1 compares concentrations of PFCs of interest in blank leachate after 6 and 168 h at a pH of 6 and a temperature of 15°C. Except for PFBA, detected levels of PFCs were higher after 168 h than after 6 h, suggesting that biodegradation of precursors in blank leachate samples resulted in more PFC generation as time passed.

Table 4.1: Concentrations of different PFCs in leachate blank samples for various test conditions and pH of 6 in all cases. Underlined numbers show that corresponding PFC concentration was below MDL, and a value of 0.5 MDL was assigned.

Test Type	Sample No.	PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTA	PFBS	PFHxS	PFOS	PFDS	FOSA
<ul style="list-style-type: none"> • 6 h • 8 rpm • 15°C 	B.2 (ng/mL)	0.054	0.329	0.201	0.097	<u>0.044</u>	<u>0.191</u>	0.019	<u>0.004</u>	0.007	0.010	<u>0.001</u>	0.046	0.053	<u>0.002</u>	<u>0.000</u>
	B.4 (ng/mL)	0.120	0.538	0.345	0.114	<u>0.044</u>	<u>0.191</u>	0.010	<u>0.004</u>	<u>0.005</u>	0.012	<u>0.001</u>	0.063	0.073	<u>0.002</u>	<u>0.000</u>
	Mean (ng/mL)	0.087	0.434	0.273	0.106	<u>0.044</u>	<u>0.191</u>	0.015	<u>0.004</u>	0.006	0.011	<u>0.001</u>	0.055	0.063	<u>0.002</u>	<u>0.000</u>
	¹ S.Dev (ng/mL)	0.047	0.148	0.102	0.012	0.000	0.000	0.006	0.000	0.001	0.002	<u>0.000</u>	0.012	0.014	0.000	<u>0.000</u>
<ul style="list-style-type: none"> • 168 h • 8 rpm • 15°C 	B.1 (ng/mL)	0.065	0.605	0.357	0.134	<u>0.044</u>	<u>0.191</u>	0.026	0.011	0.019	0.021	0.011	0.064	0.068	<u>0.002</u>	<u>0.003</u>
<ul style="list-style-type: none"> • 6 h • 8 rpm • 35°C 	B.3 (ng/mL)	0.124	0.115	0.159	0.117	<u>0.044</u>	<u>0.191</u>	0.033	0.019	0.016	0.018	<u>0.001</u>	0.052	0.059	<u>0.002</u>	<u>0.000</u>
<ul style="list-style-type: none"> • 6 h • 8 rpm • 20°C 	B.5 (ng/mL)	0.071	0.338	0.373	0.093	<u>0.044</u>	<u>0.191</u>	0.011	0.003	0.007	0.014	0.006	0.060	0.062	<u>0.002</u>	<u>0.000</u>
<ul style="list-style-type: none"> • 0 h 	Mean (ng/mL)	<u>0.009</u>	<u>0.038</u>	0.324	<u>0.079</u>	<u>0.044</u>	<u>0.191</u>	0.013	<u>0.004</u>	<u>0.005</u>	<u>0.004</u>	<u>0.001</u>	0.057	0.081	<u>0.002</u>	<u>0.000</u>

¹ Standard deviation, in ng/mL.

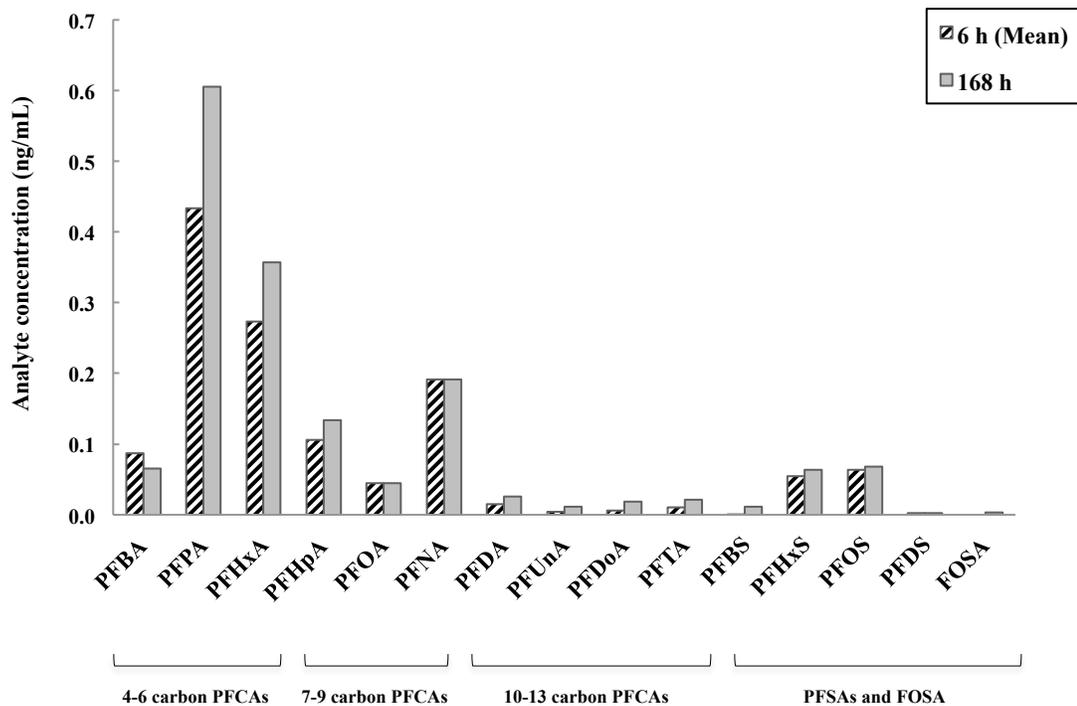


Figure 4.1: Concentrations of different PFCs in blank leachate after 6 and 168 h at pH of 6, temperature of 15°C and rotation speed of 8 rpm.

4.1.2 Operational blank test

A single operational blank test with distilled water was conducted for 6 h at a pH of 6, temperature of 15°C and rotational speed of 8 rpm in order to ensure that no cross-contamination occurred. Concentrations of all analytes of interest in this sample were below the corresponding MDL, indicating that there was negligible cross-contamination during the experimental runs, sample handling, storage, extraction and analysis.

4.1.3 Base case experiments

Table 4.2 summarizes the PFC concentrations leached from composite carpets to landfill leachate at base case conditions of pH 6, temperature 15°C, and rotation speed 8 rpm carried out in the pilot-scale “end-over-end contactor”. Data obtained from 0.5 MDL are excluded. Altogether, there were 5 samples at the base case conditions, providing a much greater sample

Table 4.2: Different PFC concentrations obtained for tests conducted under base-case conditions (time=6 h, pH=6, temperature=15°C and rotation speed=8 rpm). Mean, standard deviation and standard error of mean are also included.

No.	PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTA	PFBS	PFHxS	PFOS	PFDS	FOSA
Base Case. 1 (ng/mL)	0.133	0.685	2.005	1.632	0.563	0.829	0.405	0.085	0.328	0.610	0.5MDL	0.062	0.104	0.5MDL	0.001
Base Case. 2 (ng/mL)	0.132	0.740	1.360	1.321	0.407	0.679	0.324	0.122	0.219	0.412	0.5MDL	0.049	0.060	0.5MDL	0.5MDL
Base Case. 3 (ng/mL)	0.145	0.666	1.510	1.549	0.434	0.774	0.362	0.099	0.242	0.607	0.5MDL	0.066	0.077	0.5MDL	0.001
Base Case. 4 (ng/mL)	0.126	0.714	1.557	1.672	0.506	0.921	0.560	0.154	0.394	0.807	0.5MDL	0.070	0.102	0.5MDL	0.003
Base Case. 5 (ng/mL)	0.145	0.656	1.034	1.303	0.426	0.726	0.372	0.108	0.295	0.564	0.013	0.052	0.077	0.5MDL	0.001
Mean (ng/mL)	0.136	0.692	1.493	1.495	0.467	0.786	0.405	0.114	0.296	0.600	0.003	0.060	0.084	0.5MDL	0.001
Standard deviation (ng/mL)	0.009	0.035	0.352	0.173	0.065	0.094	0.092	0.026	0.070	0.141	0.006	0.009	0.019	0.000	0.001
Standard error of mean (ng/mL)	0.004	0.016	0.157	0.078	0.029	0.042	0.041	0.012	0.031	0.063	0.002	0.004	0.008	0.000	0.000

size obtained over several weeks of experimentation, than for the other data. No systematic variation with time is apparent in the data.

The standard errors for PFC concentrations in Table 4.13 are small enough that the entire experimental series can be regarded as providing accurate and reproducible data.

4.2 PFC concentrations in carpet samples

The concentrations of PFCs of interest in five different used and unused carpets are shown in Table 4.3. Note that since each carpet sample was extracted and analysed in triplicate, the mean value, standard deviation and standard error are displayed for each sample. The raw data and extraction efficiencies provided by the DFO-IOS lab are presented in Appendix C. Based on the data in Table 4.3, possible treatments for each carpet are proposed below:

N_4 : Very high concentrations of perfluorinated carboxylic acids (over 1000 ng/g of Σ PFCAs), which are residuals or degradation products of fluorotelomer alcohols (D'eon and Mabury 2011), indicate probable application of a Dupont Stainmaster product on this mill-treated carpet, which is primarily a mixture of both urethane and acrylic FTOH-based copolymers (Dupont Company 2001). Very low (~2 ng/g) concentrations of perfluorinated sulfonates, which are not typically present in Dupont Stainmaster products (Dupont Company 2001), support this assessment. PFHpA is the major contributor to PFC in this carpet (28% of total), followed by PFNA, PFPA and PFHxA, with these PFCAs accounting for more than 75% of the total PFC content of this carpet.

Table 4.3: Mean, standard deviation and standard errors of PFC concentrations (all in ng/g) in carpet samples analysed in this stud Underlined numbers show that corresponding PFC concentrations were below MDL, and a value of 0.5 MDL was assigned.

No.	Conc.	PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTA	PFBS	PFHxS	PFOS	PFDS	FOSA
N4	Mean	9.0	171.8	160.6	302.0	57.9	185.7	91.8	22.5	30.2	21.80	<u>0.1</u>	<u>0.1</u>	2.0	<u>0.1</u>	<u>0.0</u>
	¹ S.Dev	2.9	1.8	6.0	20.7	1.9	3.2	1.8	1.2	0.5	1.5	0.0	0.0	0.4	0.0	0.0
	² S.E.M	1.7	1.0	3.5	12.0	1.1	1.8	1.1	0.7	0.3	0.9	0.0	0.0	0.2	0.0	0.0
N5	Mean	3.8	55.7	94.7	150.8	38.0	104.3	54.7	19.9	10.3	11.6	<u>0.1</u>	4.74	4.5	<u>0.1</u>	<u>0.1</u>
	S.Dev	1.5	2.7	5.3	8.3	2.2	4.6	3.8	1.5	0.5	2.0	0.0	0.83	0.8	0.0	0.0
	S.E.M	0.9	1.6	3.1	4.8	1.2	2.6	2.2	0.8	0.3	1.1	0.0	0.5	0.4	0.0	0.0
N6	Mean	8.5	102.3	170.6	122.7	103.5	125.9	273.6	81.4	180.4	291.6	3.0	0.4	76.6	1.0	13.8
	S.Dev	1.5	17.9	38.8	24.9	16.3	16.4	36.3	8.7	64.5	86.4	4.8	0.3	16.2	0.9	0.2
	S.E.M	0.9	10.3	22.4	14.4	9.4	9.5	21.0	5.0	37.2	49.9	2.8	0.2	9.4	0.5	0.1
N7	Mean	<u>2.4</u>	7.7	32.3	46.7	9.7	28.9	12.4	3.3	1.8	2.90	<u>0.2</u>	0.4	26.5	<u>0.2</u>	<u>0.1</u>
	S.Dev	0.0	8.5	3.4	39.1	2.9	5.2	2.8	1.4	0.7	0.4	0.0	0.2	3.7	0.0	0.00
	S.E.M	0.0	4.9	2.0	22.6	1.7	3.0	1.6	0.8	0.4	0.2	0.0	0.1	2.1	0.0	0.00
N8	Mean	<u>2.4</u>	<u>7.7</u>	<u>1.1</u>	<u>1.2</u>	<u>0.2</u>	<u>0.5</u>	<u>0.23</u>	<u>0.2</u>	<u>0.1</u>	<u>0.2</u>	<u>0.1</u>	<u>0.1</u>	2.1	<u>0.1</u>	<u>0.0</u>
	S.Dev	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.8	0.0	0.0
	S.E.M	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0	0.0
³ Composite (Mean)		5.6	76.7	103.2	140.1	47.1	100.1	97.3	28.6	50.1	73.8	0.8	1.3	24.9	0.3	3.2

¹ Standard Deviation

² Standard Error of Mean

³ PFC concentrations in composite carpet have been calculated based on the following formula (as discussed in Chapter 3):

$$\text{Mean Composite} = 0.225 \times (\text{Mean } N_4 + \text{Mean } N_5 + \text{Mean } N_6 + \text{Mean } N_7) + 0.1 \times \text{Mean } N_8$$

*N*₅: Perfluorinated carboxylic acids in this mill-treated carpet are similar to PFCAs in carpet *N*₄, but their concentrations are roughly half those in *N*₄. Like *N*₄, this carpet might have been treated with a Dupont Stainmaster product. PFHpA is the major component in this carpet (27% of total).

*N*₆ : This relatively old carpet contains significant amounts of both perfluorinated carboxylic acids and sulfonates. It has the highest PFC content among the carpets tested in this study: 44% more PFCs than *N*₄, 3 times more than *N*₅, 10 times more than *N*₇ and 38 times more than *N*₈. The presence of both PFCAs and PFSA and their high concentrations in this carpet suggest that it was treated several times with different products. Higher concentrations of PFCAs compared to PFSA and FOSA might be due to earlier treatments with Scotchgard, which contains NMeFOSE and perfluorosulfonate precursors (Dinglasan et al. 2006), followed by more recent treatments with Dupont Stainmaster products.

*N*₇ : This old and dusty carpet seems to have been treated several times with different products, but its low concentrations of PFCs suggest that several years have passed since the last treatment. PFHpA and PFHxA account for more than half of the PFC content of this carpet.

*N*₈ : Very low levels of PFCs (less than 20 ng/g of Σ PFCs) were detected in this carpet. Except for PFOS and PFPA, the PFC concentrations, displayed in Table 4.3, are simply the 0.5 Method Detection Limit (MDL) values of each of the corresponding analytes since no signal was detected when analysing the carpet samples for these PFCs.

Note that all extraction efficiencies of carpet samples in this study were more than 95%, suggesting that at least 95% of the PFCs were completely extracted from the carpet samples. For extraction efficiencies, see Table C.3 Appendix C.

4.3 Landfill leachate characterization

Table 4.4 summarizes characterization results for pH, electrical conductivity, total dissolved solids (TDS), metals and total organic carbon (TOC) of leachate samples immediately after collection from the landfill and after 50 days of storage at 4°C. The physical and chemical characteristics of the leachate samples do not appear to have changed notably during storage at this temperature. PFC concentrations in leachate are presented in Table 4.5. Except for PFHxA, the background concentrations of PFCs in the urban landfill leachate sample are very low, in some cases below the method detection limits (MDL), where a value of 0.5MDL was assigned to the corresponding PFC.

Figure 4.2 shows the percentage of each analyte in the leachate. Items along the x-axis are sorted in order of increasing number of carbon atoms in the PFCA and PFSA structure. Note that the major component of the leachate is PFHxA (38.0% of total PFCs), followed by PFNA (22.4%) and PFOS (9.5%). Among PFCAs present in the landfill leachates, perfluorinated carboxylic acids with 6 to 9 carbon atoms in their fluorinated chain are more dominant than PFCAs, with higher numbers of carbon atoms. This could be related to two factors: First, as discussed in Section 2.1, water solubilities of PFCAs decrease with increasing molecular weight, so that PFCAs with fewer carbon atoms have a higher tendency to solubilize in aqueous media. Second, perfluorinated compounds with 6 to 8 carbon atoms are preferred in manufacturing of polymeric materials and surfactants (D'eon and Mabury 2011), making their

corresponding PFCAs (as residuals in fluorinated polymers) dominant in commercial products and ultimately in landfill leachate.

Table 4.4: Blank-corrected physical properties and chemical concentrations analysed for leachate immediately after collection and after 50 days of storage at 4°C.

Test type	Analysed Parameters	Leachate after collection	Leachate after 50 days storage at 4°C
Physical tests	pH	7.03	7.05
	Conductivity (µs/cm)	1392	1402
	Total dissolved solids (TDS) (mg/L)	674	678
Metals (mg/L)	As	0.000	0.000
	Be	0.000	0.000
	Cd	0.011	0.005
	Ca	91.880	85.088
	Cr	0.007	0.001
	Co	0.006	0.004
	Cu	0.028	0.031
	Fe	9.673	9.096
	Pb	0.008	0.011
	Mg	21.740	22.100
	Mn	0.600	0.432
	Mo	0.011	0.009
	Ni	0.000	0.017
	Se	0.035	0.047
	Zn	0.039	0.075
	Sr	0.496	0.519
	Al	1.049	0.645
	Na	95.340	99.206
	K	18.200	36.647
	Ag	0.000	0.000
Ba	0.182	0.195	
Sb	0.025	0.036	
Sn	0.051	0.039	
Organics (mg/L)	Total organic carbon (TOC)	66.0	71.4

Table 4.5: PFC concentrations in leachate. Mean values and standard deviations are calculated for each PFC. The Underlined numbers show that the corresponding PFC concentrations were below MDL and values of 0.5 MDL were assigned.

Leachate Sample No.	Perfluorinated carboxylic acids (PFCAs) (ng/mL)										Perfluorinated sulfonates (PFASs) and sulfonamide (FOSA) (ng/mL)				
	PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTA	PFBS	PFHxS	PFOS	PFDS	FOSA
Leachate (1)	<u>0.009</u>	<u>0.038</u>	0.292	0.025	<u>0.044</u>	<u>0.191</u>	0.009	0.005	<u>0.005</u>	<u>0.004</u>	<u>0.001</u>	0.047	0.064	<u>0.002</u>	<u>0.000</u>
Leachate (2)	<u>0.009</u>	<u>0.038</u>	0.334	0.102	<u>0.044</u>	<u>0.191</u>	0.014	0.005	<u>0.005</u>	<u>0.004</u>	<u>0.001</u>	0.066	0.091	<u>0.002</u>	<u>0.000</u>
Leachate (3)	<u>0.009</u>	<u>0.038</u>	0.346	0.111	<u>0.044</u>	<u>0.191</u>	0.015	<u>0.004</u>	<u>0.005</u>	<u>0.004</u>	<u>0.001</u>	0.057	0.087	<u>0.002</u>	<u>0.000</u>
Mean (1,2,3)	<u>0.009</u>	<u>0.038</u>	0.324	0.079	<u>0.044</u>	<u>0.191</u>	0.013	<u>0.004</u>	<u>0.005</u>	<u>0.004</u>	<u>0.001</u>	0.057	0.081	<u>0.002</u>	<u>0.000</u>
Standard deviation	0.000	0.000	0.028	0.047	0.000	0.000	0.003	0.000	0.000	0.000	0.000	0.009	0.015	0.000	0.000

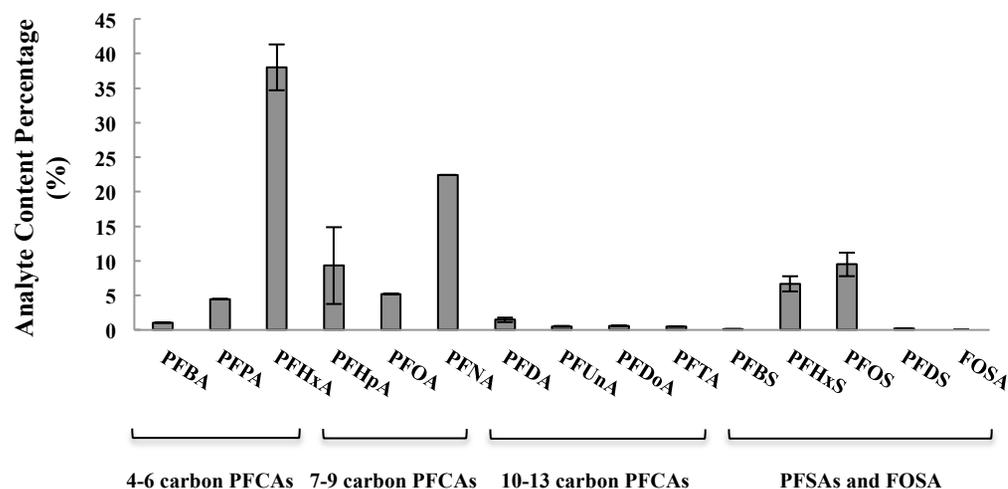


Figure 4.2: Percentages by mass of each PFC in total PFCs present in raw leachate. Compounds along the horizontal axis are in order of increasing number of carbon atoms for both PFCAs and PFASs.

4.4 Preliminary leaching experiments in bench-scale “end-over-end contactor”

As noted in Chapter 3, the leaching experiments were carried out in two phases: preliminary tests and final tests. Since a few tests were carried out in the first phase (i.e. preliminary tests) and the outcomes were similar to those of final leaching tests, the preliminary test results are not discussed here. Appendix B summarizes the preliminary test results.

4.5 Final leaching experiments in pilot-scale “end-over-end contactor”

The final leaching tests were intended to measure the leaching rates of different PFCs from carpet samples to real landfill leachate or distilled water for various contact times and operating conditions. Results are provided in this section.

4.5.1 Mass conservation equations in leaching experiments

In order to verify the mass conservation of different PFCs in leaching experiments, mass balance equations are applied to a few cases. Generally, for a certain species in a system, a mass balance can be written as:

$$\boxed{[\text{Net input to the system}] + [\text{Generation due to chemical reaction}] = [\text{Net output}] + [\text{Consumption due to chemical reaction}] + [\text{Accumulation rate}]}$$

To apply this approach to the leaching experiments, the following assumptions are made for the “system”, consisting of the carpet pieces and leachate in contact:

- $[\text{Net PFC input to the system}] = [\text{PFC input in carpet sample}] + [\text{PFC in leachate initially}]$
- $[\text{Net PFC output from the system}] = [\text{PFC remaining on the carpet after contact}] + [\text{PFC in the leachate after contact with carpet}]$

- Degradation and other reactions are ignored, given the limited duration of the experiments.
- It is assumed that no accumulation occurred in the system.

Six carpet samples were analysed after contact with leachate/distilled water, and mass balances were applied to them. Table 4.6 shows the net inputs and outputs of different perfluorinated compounds in these tests, as well as PFC inputs and outputs from carpet samples and leachate/distilled water separately. Plotting the net output PFC amounts against net input PFC amounts resulted in regression lines with slopes between 0.68 and 0.88, and correlation coefficient (R^2) values > 0.91 (indicating a good fit between the linear function and the experimental data), shown in Figure 4.3. Linear regression lines with slopes < 1 in these charts suggest that, except in a few cases, the total amounts of PFCs decreased during the leaching experiments. Degradation of PFC precursors increases total PFCA and PFSA concentrations and would not explain a reduction in total PFC amounts. In addition, PFCAs and PFSAs do not appear to undergo degradation at low temperatures (5 to 35°C). A possible reason for the observed decline in PFC amounts is transferring of dusts containing PFCs from carpet samples to aqueous media, which might have settled at the bottom of tubes or have separated by filtration prior to extraction and analysis. In addition, some PFCs from carpets might have been adsorbed onto fine particles in the leachate, which settled in the tubes or were separated by filtration.

A different trend was observed for PFBA net inputs and outputs. Unlike other PFCAs, in all mass balance equations in leachate samples (Mass balance No. 1, 2, 4, 5 and 6), the net output of PFBA was higher than the net input. Generation of PFBA as a result of biodegradation of PFC precursors, in particular 6:2 FTOH (Liu et al., 2010), during the experiments was

Table 4.6: Net inputs and outputs of different perfluorinated compounds from carpet and leachate samples in six leaching tests.

Test condition	Analysed parameters	PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTA	PFBS	PFHxS	PFOS	PFDS	FOSA
Mass Balance.1 -Liquid: leachate -Carpet: Composite -Time: 168 h -pH: 6 -Rotation: 8 rpm -Temp. : 15°C	Carpet input(ng)	464	7593	10309	14001	4705	10006	9731	2858	5010	7379	76	116	2281	20	310
	Leachate input (ng)	36	152	1295	316	177	764	50	17	20	16	4	226	323	8	1
	Carpet output (ng)	24	934	1122	2519	1081	2889	3398	920	1278	1865	76	291	1102	31	221
	Leachate output (ng)	608	3741	8492	9500	2608	3825	1841	836	1916	3960	4	216	176	8	9
	Net PFC input (ng)	500	7745	11604	14318	4882	10770	9781	2876	5030	7375	80	343	2605	28	311
	Net PFC output (ng)	632	4675	9614	12019	3689	6714	5239	1756	3194	5825	80	508	1279	39	230
Mass Balance.2 -Liquid: leachate -Carpet: Composite -Time: 6 h -pH: 6 -Rotation: 0 rpm -Temp. : 15°C	Carpet input(ng)	464	7593	10309	14001	4705	10006	9731	2858	5010	7379	76	116	2281	20	310
	Leachate input (ng)	36	152	1295	316	177	764	50	17	20	16	4	226	323	8	1
	Carpet output (ng)	124	1933	3566	5230	2042	3969	5234	1777	2691	3597	76	56	1239	21	322
	Leachate output (ng)	810	2311	4257	5456	1685	2693	2060	456	635	500	4	248	396	8	5
	Net PFC input (ng)	500	7745	11604	14318	4882	10770	9781	2876	5030	7395	80	343	2605	28	311
	Net PFC output (ng)	934	4244	7824	10687	3728	6662	7294	2234	3327	4097	80	304	1635	29	328
Mass Balance.3 -Liquid: water -Carpet: Composite -Time: 6 h -pH: 7 -Rotation: 8 rpm -Temp. : 15°C	Carpet input(ng)	464	7593	10309	14001	4705	10006	9731	2858	5010	7379	76	116	2281	20	310
	Leachate input (ng)	36	152	248	160	177	764	28.00	16	20	28	4	16	16	8	1
	Carpet output (ng)	62	1740	3148	4815	1656	3456	4417	1206	1969	2288	76	246	1055	20	275
	Leachate output (ng)	353	3483	4818	7175	1754	4103	2453	508	831	2199	4	56	276	8	6
	Net PFC input (ng)	500	7745	10557	14161	4882	10770	9759	2874	5030	7407	80	132	2297	28	311
	Net PFC output (ng)	416	5223	7967	11991	3410	7559	6870	1715	2800	4488	80	302	1332	28	282
Mass Balance.4 -Liquid: leachate -Carpet: Composite -Time: 6 h -pH: 6 -Rotation: 8 rpm -Temp. : 20°C	Carpet input(ng)	464	7593	10309	14001	4705	10006	9731	2858	5010	7379	76	116	2281	20	311
	Leachate input (ng)	36	152	1295	316	177	764	50	17	20	16	4	226	323	8	1
	Carpet output (ng)	163	2238	3972	5812	2308	5647	5599	1637	2959	4407	76	81	1313	19	295
	Leachate output (ng)	551	8930	6191	6191	1769	3180	1530	478	1377	3495	4	278	433	8	1
	Net PFC input (ng)	500	7745	11604	14318	4882	10770	9781	2876	5030	7395	80	343	2605	28	311
	Net PFC output (ng)	714	11168	10163	12003	4077	8827	7129	2115	4336	7902	80	359	1746	27	295

Table 4.6 (Continued): Net inputs and outputs of different perfluorinated compounds from carpet and leachate samples in six leaching tests.

Test condition	Analysed parameters	PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTA	PFBS	PFHxS	PFOS	PFDS	FOSA
Mass Balance.5 -Liquid: leachate -Carpet: Composite -Time: 6 h -pH: 6 -Rotation: 8 rpm -Temp. : 5°C	Carpet input(ng)	464	7593	10309	14001	4705	10006	9731	2858	5010	7379	76	116	2281	20	310
	Leachate input (ng)	36	152	1295	316	177	764	50	17	20	16	4	226	323	8	1
	Carpet output (ng)	141	2304	4843	7423	2547	5164	5454	1462	2339	3559	76	98	1326	20	263
	Leachate output (ng)	879	3669	5227	6319	1745	2604	1378	393	1494	3884	4	291	443	8	3
	Net PFC input (ng)	500	7745	11604	14318	4882	10770	9781	2876	5030	7395	80	343	2605	28	312
	Net PFC output (ng)	1020	5974	10071	13742	4292	7768	6832	1856	3834	7444	80	390	1769	28	266
Mass Balance.6 -Liquid: leachate -Carpet: Composite -Time: 24 h -pH: 6 -Rotation: 8 rpm -Temp. : 35°C	Carpet input (ng)	464	7593	10309	14001	4705	10006	9731	2858	5010	7379	76	116	2281	20	310
	Leachate input (ng)	36	152	1295	316	177	764	50	17	20	16	4	226	323	8	1
	Carpet output (ng)	9	444	923	1946	782	2511	3091	772	1490	2025	76	115	1034	19	170
	Leachate output (ng)	854	4200	9068	11464	3131	4910	2181	1009	1471	4123	4	182	187	8	12
	Net PFC input (ng)	500	7745	11604	14318	4882	10770	9781	2876	5030	7395	80	343	2605	28	312
	Net PFC output (ng)	863	4644	9992	13410	3914	7421	5272	1782	2962	6149	80	298	1221	27	183

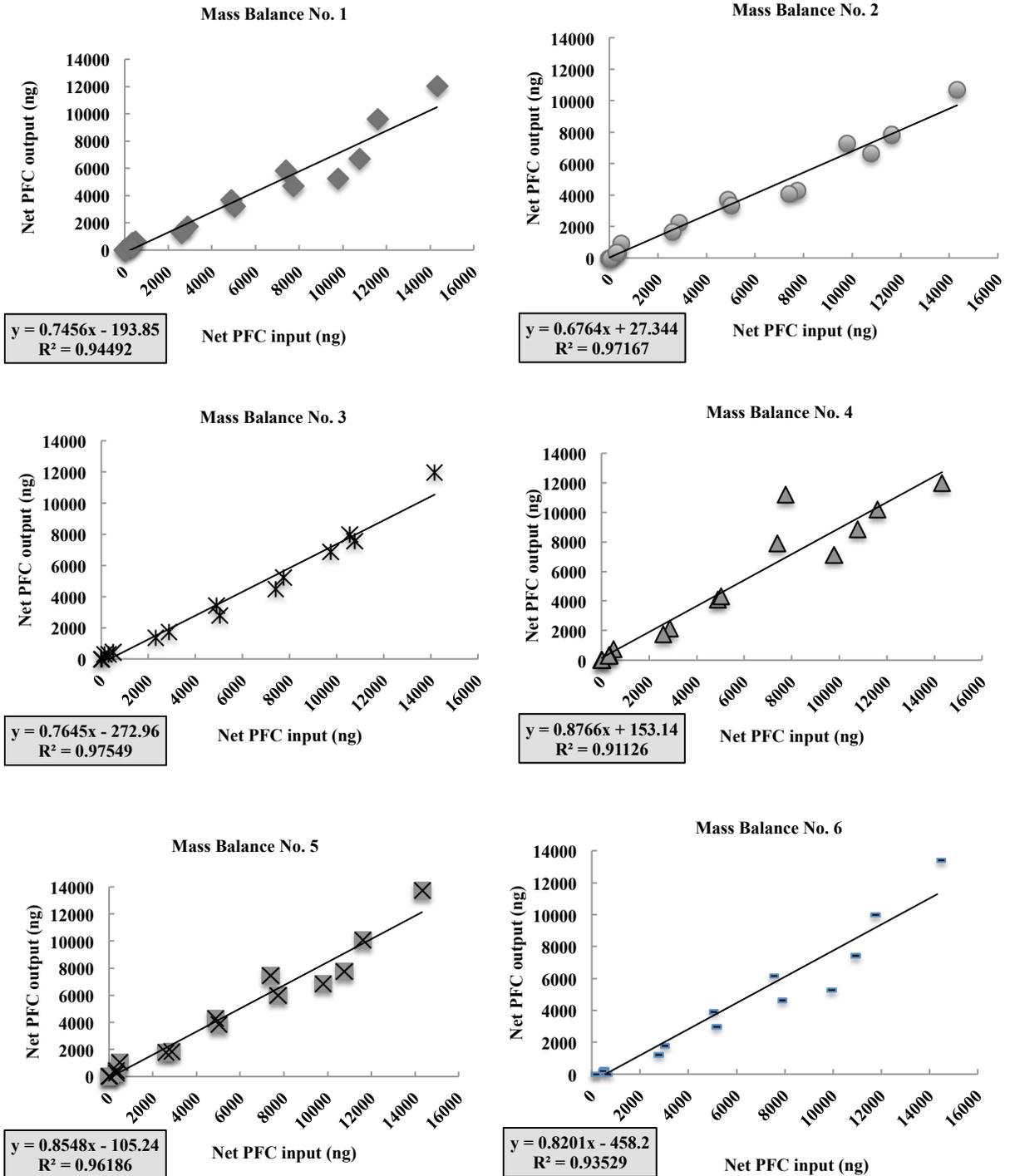


Figure 4.3: Net output PFC amounts vs. net input PFC amounts (presented in Table 4.6). The “Mass Balance No.” on top of each chart corresponds to the numbers in Table 4.6. Each point displays the amount of a specific PFC in both the input and output of the system.

probably the major contributor to the observed elevated PFBA outputs. Note that this trend only occurred in leachate media; in distilled water, the PFBA output was lower than the input, because unlike landfill leachate, distilled water contained no PFC precursors.

Generally, in all mass balances, the highest net PFC inputs and outputs were observed for PFHpA among the perfluorinated carboxylic acids (PFCAs), and for PFOS among the perfluorinated sulfonates (PFSAs).

4.5.2 Effect of contacting time on leaching rates

As discussed in Section 3.4.4, experiments were performed where composite carpet samples were contacted with landfill leachate for contacting time intervals of 1 to 168 h in the pilot-scale end-over-end contactor. Table 4.7 summarizes the results for leaching rates of different PFCs in five contacting time periods. Since all tests were in duplicate, the mean values and standard deviations are included in Table 4.7. Generally for PFCAs, a concentration increase was observed in leachate samples from 1 to 168 h, as shown in Figures 4.4(a) and 4.4(b).

From Figure 4.4, except for PFPA and PFTA, all PFCA concentrations underwent a rapid initial increase followed by a slower increase during the 168 h contacting, i.e. leaching rates were higher for the first few hours compared to the last hours. Some PFCAs appear to have approached an equilibrium concentration after seven days of contact, while for others, considerable changes were witnessed in the PFC concentration gains between 24 h and 168 h. PFHxA, PFHpA, PFOA, PFNA, PFDA, and PFUnA were subject to minor (10% or less) concentration increases between 1 and 7 days, and it appears that these compounds either reached equilibrium (PFNA and PFDA), or nearly reach equilibrium shortly (PFHxA, PFHpA, PFOA, and PFUnA). The concentration of PFBA after the first day was ~14 times higher than at the beginning of the tests, while only an 18% increase in PFBA concentration was observed in the following 6 days. The observed trend for PFDoA was similar to that for PFBA. PFTA showed an unusual apparent decrease in concentration between 6 and 24 h, followed by a significant increase between 1 and 7 days.

Table 4.7: Mean PFC concentrations and their standard deviations in leachate samples after contacting with composite carpet samples at pH=6, temperature=15°C, rotation speed=8 rpm and certain contacting times. Underlined numbers show that corresponding PFC concentration was below MDL, and a value of 0.5 MDL was assigned.

Time (h)	Parameter	PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTA	PFBS	PFHxS	PFOS	PFDS	FOSA
1	Mean (ng/ml)	<u>0.009</u>	0.475	0.846	0.773	<u>0.044</u>	0.455	0.321	0.078	0.161	0.182	0.009	0.051	0.070	<u>0.002</u>	<u>0.000</u>
	¹ S.Dev	0.000	0.124	0.029	0.030	0.011	0.036	0.004	0.003	0.012	0.006	0.003	0.004	0.006	0.000	0.000
2	Mean (ng/mL)	0.068	0.754	1.191	1.379	0.425	0.729	0.360	0.111	0.213	0.330	<u>0.001</u>	0.075	0.092	<u>0.002</u>	0.001
	¹ S.Dev	0.011	0.291	0.141	0.100	0.029	0.050	0.009	0.026	0.049	0.066	0.000	0.004	0.007	0.000	0.000
6	Mean (ng/mL)	0.133	0.713	1.682	1.476	0.485	0.754	0.364	0.104	0.274	0.511	<u>0.001</u>	0.056	0.082	<u>0.002</u>	0.001
	¹ S.Dev	0.001	0.039	0.456	0.220	0.111	0.106	0.057	0.026	0.077	0.141	0.000	0.009	0.031	0.000	0.000
24	Mean (ng/mL)	0.136	1.267	1.988	2.016	0.588	0.924	0.424	0.180	0.288	0.450	0.005	0.057	0.061	<u>0.002</u>	0.003
	¹ S.Dev	0.016	0.028	0.133	0.087	0.043	0.009	0.042	0.007	0.012	0.041	0.006	0.003	0.008	0.000	0.000
168	Mean (ng/mL)	0.161	0.871	2.152	2.234	0.633	0.921	0.431	0.191	0.410	0.848	<u>0.001</u>	0.051	0.042	<u>0.002</u>	0.002
	S.Dev	0.012	0.091	0.041	0.199	0.027	0.050	0.041	0.026	0.098	0.202	0.000	0.005	0.003	0.000	0.000

¹ Standard deviation, also in ng/mL.

Table 4.8: Concentrations of remaining PFCs in composite carpet samples after 6 and 168 h contact with landfill leachate at pH=6, temperature=15°C and rotation speed=8 rpm.

Time (h)	PFBA (ng/g)	PFPA (ng/g)	PFHxA (ng/g)	PFHpA (ng/g)	PFOA (ng/g)	PFNA (ng/g)	PFDA (ng/g)	PFUnA (ng/g)	PFDoA (ng/g)	PFTA (ng/g)	PFBS (ng/g)	PFHxS (ng/g)	PFOS (ng/g)	PFDS (ng/g)	FOSA (ng/g)
6	1.63	22.38	39.72	58.12	23.08	56.47	55.99	16.37	29.59	44.07	0.11	0.87	10.24	0.11	2.95
168	0.79	3.34	11.23	25.20	10.81	28.89	33.98	9.20	12.79	18.65	0.09	2.92	12.26	0.09	2.22

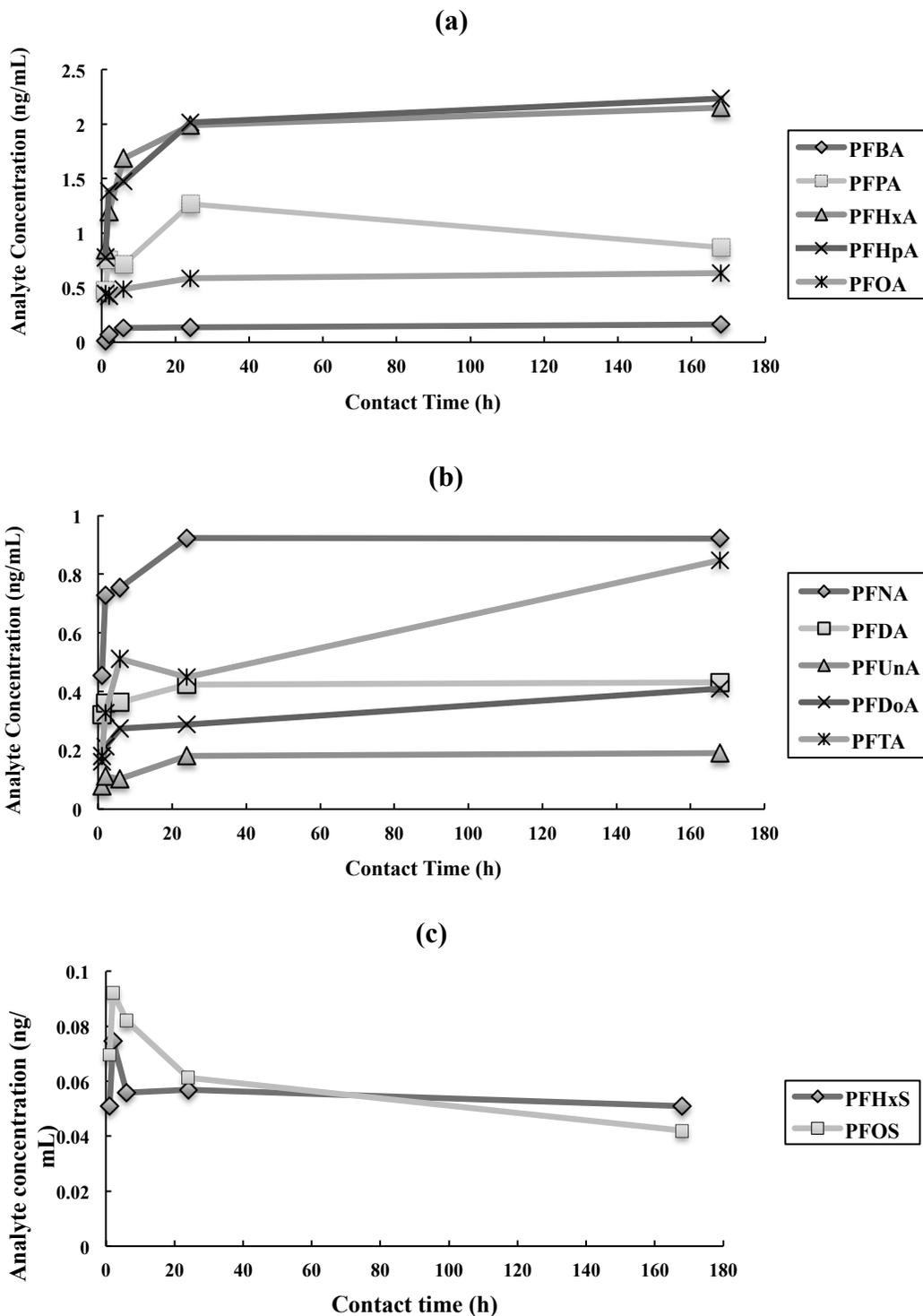


Figure 4.4: Concentrations of (a) PFBA, PFPA, PFHxA, PFHpA, PFOA (b) PFNA, PFDA, PFUnA, PFDoA, PFTA, (c) PFHxS, and PFOS in leachate samples after contacting with composite carpet samples at pH=6, temperature=15°C, rotation speed=8 rpm versus contact time. PFBS, PFDS, and FOSA are not included because their concentrations were below or slightly above MDLs.

A different trend was witnessed for all perfluorinated sulfonates and FOSA, as well as PFPA; the concentration decreased between 2 and 168 h for PFHxS and PFOS, and between 6 and 24 h for PFPA. For PFHxS and PFOS, this concentration decrease appears to have been due to reverse mass transfer of analytes i.e. from leachate to carpet. Table 4.8 displays changes in concentrations of PFCs in carpet samples between 6 and 168 h at 15°C. The table indicates that concentrations of all PFCAs in carpet decreased significantly from 6 to 168 h as a result of mass transfer to the leachate, while PFHxS and PFOS in carpet samples experienced an increase in concentration during this period, consistent with possible migration of PFHxS and PFOS from carpets to leachate.

Figure 4.5 shows the overall changes of total PFC concentrations in the 1-168 h period. The total amounts of PFCs are equal to the summations of leached PFC concentrations shown in Figure 4.4 (a), (b) and (c), which are mostly controlled by the PFCs shown in Figure 4.4 (a) and (b), since PFCAs were the dominant PFCs in the leachate. The best fitted line in this plot (i.e. $y = 0.95 \ln(x) + 4.67$) is very close to a logarithmic equation line.

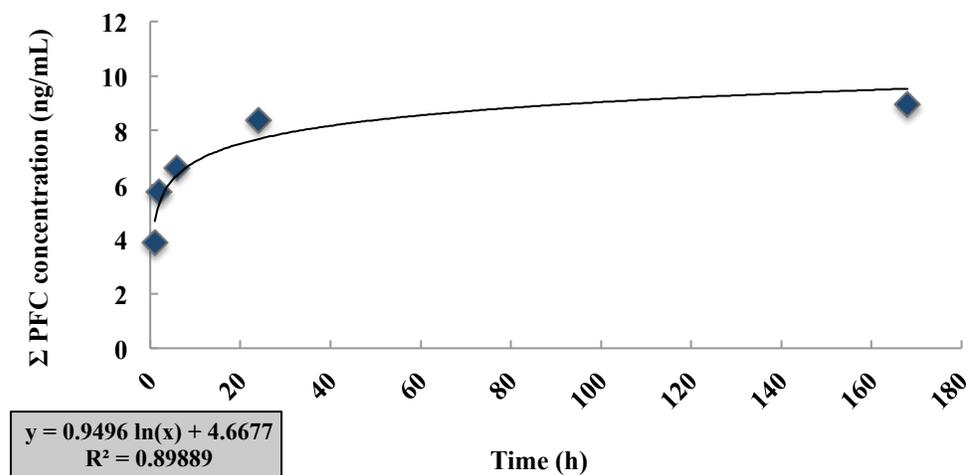


Figure 4.5: Total PFC concentrations in leachate samples after contacting with composite carpet samples at pH=6, temperature=15°C and rotation speed=8 rpm, versus contact time.

4.5.3 Effect of rotation speed on leaching rates

Table 4.9 summarizes leaching rates of different PFCs to landfill leachate for identical pH, temperature, and contact times, with rotational speed of the pilot-scale “end-over-end contactor” varying between 0 – 8 revolutions per minute (rpm). With the experiments were carried out in duplicate, the mean and standard deviations are displayed in Table 4.9.

It appears that except for PFTA, varying the rotation speed, i.e. the extent of mixing the contents of vessels, did not affect the leaching rates significantly. The slopes of linear regression lines which best fit the leaching rates at “8 rpm versus 0 rpm”, and “4 rpm versus 0 rpm”, shown in Figure 4.6 (a) and 4.6 (b) respectively, are close to 1, implying that the leaching rates were not significantly dependent on rotation.

There are two principal mechanisms of mass transfer between subsystems: diffusion and convection. For no rotation, only diffusion occurs, whereas convective transport augments external mass transport when there is rotation. For all species tested except PFTA, rotation appears to have had little or no effect on the leaching rate, showing that the leaching rates were dependent on some factor (e.g. adsorption or desorption) other than external mass transfer.

For PFTA, as labelled in Figure 4.6, a significant increase was observed due to rotation, whether at 4 rpm or 8 rpm. The leached PFTA concentrations in the leachate with rotation were almost 5 times higher than without rotation, suggesting that external mass transfer played a dominant role in determining the overall mass exchange of PFTA between carpets and leachate. Note that PFTA leaching rates were almost equal at 4 rpm and 8 rpm, suggesting that external mass transfer was favorable enough at either rotation speed, for the overall rate to be no longer external mass transfer controlled.

Table 4.9: Mean PFC concentrations and their standard deviations in leachate samples after contacting with composite carpet samples for 6 h at pH=6, temperature=15°C and varying rotation speeds (0, 4 and 8 rpm). Underlined numbers show that corresponding PFC concentration was below MDL, and a value of 0.5 MDL was assigned.

Rate	Parameter	PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTA	PFBS	PFHxS	PFOS	PFDS	FOSA
0 rpm	Mean (ng/ml)	0.194	0.594	1.229	1.376	0.445	0.650	0.494	0.113	0.150	0.116	0.012	0.064	0.105	<u>0.002</u>	0.001
	¹ S.Dev	0.013	0.022	0.233	0.016	0.034	0.033	0.030	0.002	0.012	0.013	0.016	0.002	0.008	0.000	0.000
4 rpm	Mean (ng/mL)	0.271	0.723	1.690	1.822	0.535	0.855	0.439	0.161	0.289	0.637	<u>0.001</u>	0.067	0.110	<u>0.002</u>	0.002
	¹ S.Dev	0.014	0.053	0.049	0.164	0.055	0.037	0.028	0.021	0.069	0.097	0.000	0.000	0.000	0.000	0.000
8 rpm	Mean (ng/mL)	0.145	0.661	1.386	1.551	0.430	0.750	0.367	0.104	0.269	0.585	0.007	0.059	0.077	<u>0.002</u>	0.001
	¹ S.Dev	0.000	0.007	0.176	0.002	0.006	0.034	0.007	0.007	0.038	0.030	0.009	0.010	0.000	0.000	0.000

¹ Standard deviation, also in ng/mL.

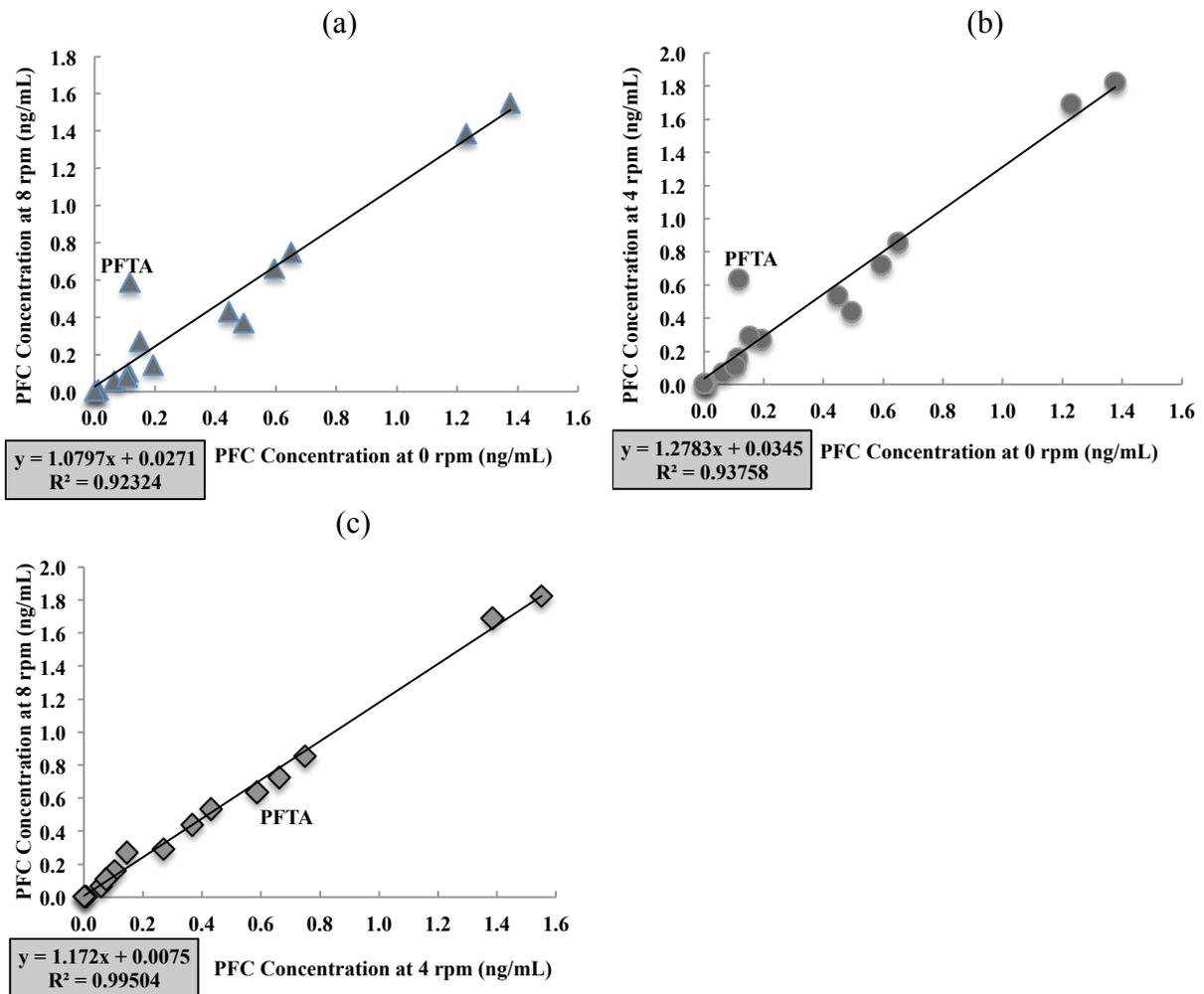


Figure 4.6: PFC concentrations in leachate samples after contacting with composite carpet samples for 6 h at pH=6, temperature=15°C and rotation speed of (a) 8 vs. 0 rpm, (b) 4 vs. 8 rpm and (c) 8 vs. 4 rpm.

4.5.4 Effect of temperature on leaching rates

PFC leaching rates at two temperatures, $5 \pm 1^\circ\text{C}$ and $35 \pm 1^\circ\text{C}$, were obtained for contact times of 2, 6 and 24 h between composite carpet and leachate samples. The results are shown in Table 4.10. PFC leaching rates at 15°C are also included in Table 4.10.

Table 4.10: Concentrations of PFCs leached from composite carpet samples to leachate at 5±1, 15±3 and 35±1°C, pH 6 and rotation speed 8 rpm for 2, 6 and 24 h contact time. PFC concentrations of blank leachate are also included in the last line. Underlined numbers show that corresponding PFC concentration was below MDL, and a value of 0.5 MDL was assigned.

Temp. (°C)	Time (h)	PFBA (ng/ml)	PFPA (ng/ml)	PFHxA (ng/ml)	PFHpA (ng/ml)	PFOA (ng/ml)	PFNA (ng/ml)	PFDA (ng/ml)	PFUnA (ng/ml)	PFDoA (ng/ml)	PFTA (ng/ml)	PFBS (ng/ml)	PFHxS (ng/ml)	PFOS (ng/ml)	PFDS (ng/ml)	FOSA (ng/ml)
(5±1)°C	2	0.126	0.570	0.923	1.011	0.349	0.561	0.372	0.163	0.299	0.548	<u>0.001</u>	0.075	0.091	<u>0.002</u>	0.001
	6	0.127	0.793	1.073	1.372	0.393	0.573	0.322	0.090	0.323	0.798	<u>0.001</u>	0.068	0.093	<u>0.002</u>	<u>0.000</u>
	24	0.128	0.790	1.197	1.587	0.457	0.755	0.289	0.106	0.341	0.858	0.007	0.067	0.066	0.005	<u>0.000</u>
(15±3)°C	2	0.068	0.754	1.191	1.380	0.425	0.729	0.361	0.112	0.213	0.330	<u>0.001</u>	0.075	0.092	<u>0.002</u>	0.001
	6	0.133	0.713	1.682	1.476	0.485	0.754	0.364	0.104	0.274	0.511	<u>0.001</u>	0.056	0.082	<u>0.002</u>	0.001
	24	0.136	1.109	1.988	2.016	0.588	0.924	0.424	0.180	0.288	0.450	0.005	0.057	0.061	<u>0.002</u>	0.004
(35±1)°C	2	0.135	2.088	1.546	1.892	0.562	0.956	0.560	0.168	0.345	0.708	<u>0.001</u>	0.073	0.097	<u>0.002</u>	<u>0.000</u>
	6	0.123	1.199	1.600	1.899	0.511	0.923	0.457	0.128	0.241	0.556	0.006	0.050	0.075	<u>0.002</u>	0.001
	24	0.244	1.020	2.330	2.910	0.742	1.143	0.529	0.222	0.334	0.910	<u>0.001</u>	0.048	0.050	<u>0.002</u>	0.002
Raw Leachate	0	<u>0.009</u>	<u>0.038</u>	0.324	0.079	<u>0.044</u>	<u>0.191</u>	0.013	<u>0.004</u>	<u>0.005</u>	<u>0.004</u>	<u>0.001</u>	0.057	0.081	<u>0.002</u>	<u>0.000</u>

As noted in Section 4.5.3, except for PFTA, leaching rates of PFCs are not mass transfer controlled, but are likely adsorption/desorption controlled, in which case it is expected that the PFC adsorption/desorption rate constants are proportional to $e^{-E_a/RT}$ according to the “Arrhenius law”:

$$k = k_o e^{-E_a/RT} \quad (4.1)$$

The Arrhenius equation, in brief, gives the dependence of k (rate constant) on T (absolute temperature, i.e. in Kelvin) and E_A (activation energy), where R is the gas constant. In addition, assuming a first order reaction for species A , one can expect:

$$(r_A) = k (C_{A, \text{equilibrium}} - C_A) \quad (4.2)$$

where for species A , (r_A) is the leaching rate, k is a rate constant, $C_{A, \text{equilibrium}}$ is the equilibrium concentration and C_A is the concentration in the leachate. Substituting for k from Equation (4.1) in Equation (4.2) and taking natural logarithm of both sides results in:

$$\ln [r_A / k_o (C_{A, \text{equilibrium}} - C_A)] = - (E_A / RT) \quad (4.3)$$

Therefore, the results for $\ln (C_A / C_{A, \text{equilibrium}})$ could be plotted against $(1/T)$ in an Arrhenius plot, with the slope being equal to $- (E_A / R)$. However, the equilibrium concentration of species A (i.e. $C_{A, \text{equilibrium}}$) is very likely temperature dependent, but the data for this are not available in this study. Experiments should be conducted in the future to determine the equilibrium concentrations of PFCs in different temperatures.

In plots similar to Arrhenius plot, the PFCA concentrations in landfill leachate after contact with composite carpet samples for 2, 6 and 24 h are plotted versus $(1/T)$, where T is the absolute temperature (i.e. in Kelvin), as shown in Figure 4.7. Note that for each contact time, PFCAs of 4-8 carbon atoms and 9-13 carbon atoms are plotted separately.

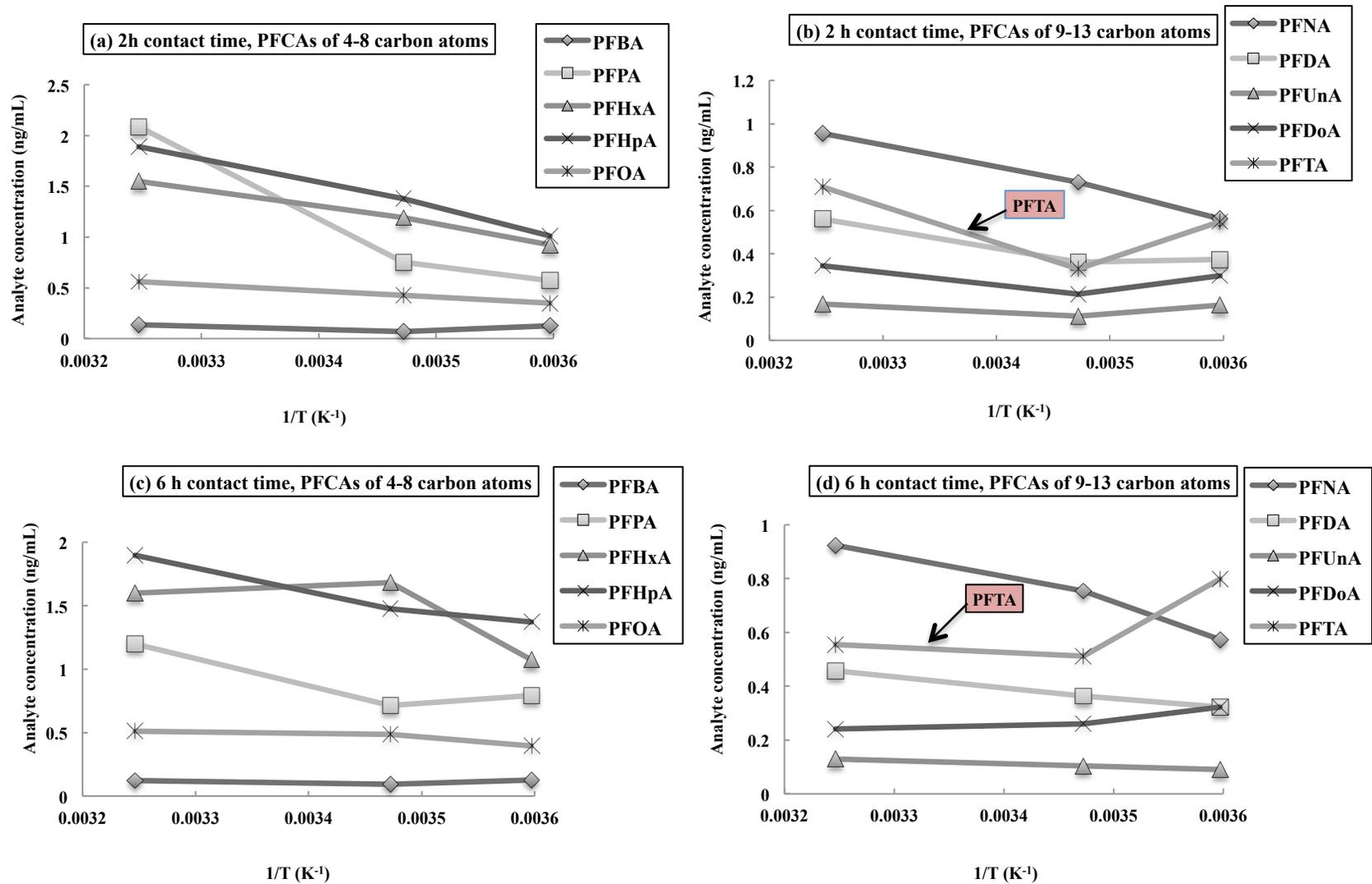


Figure 4.7: Concentrations of PFCAs in landfill leachate after contact with composite carpet for (a), (b) 2 h and (c), (d) 6 h vs. (1/T), where T is absolute temperature. Leaching experiments were conducted at pH 6, rotation speed 8 rpm and temperature 5, 15 and 35°C (Figure continued on next page).

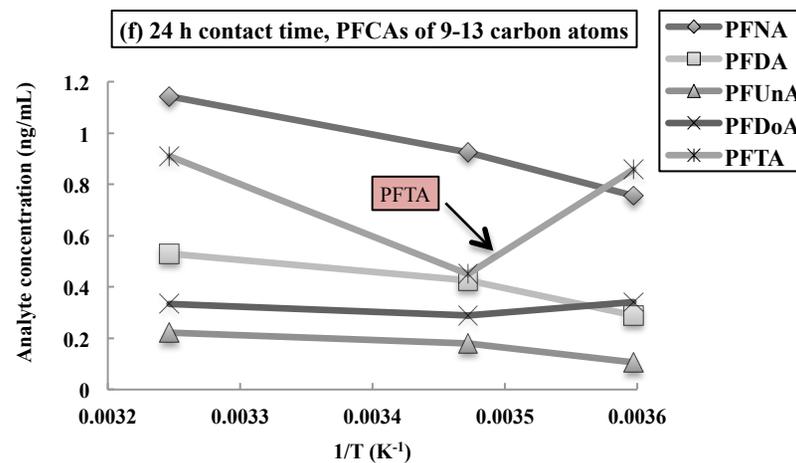
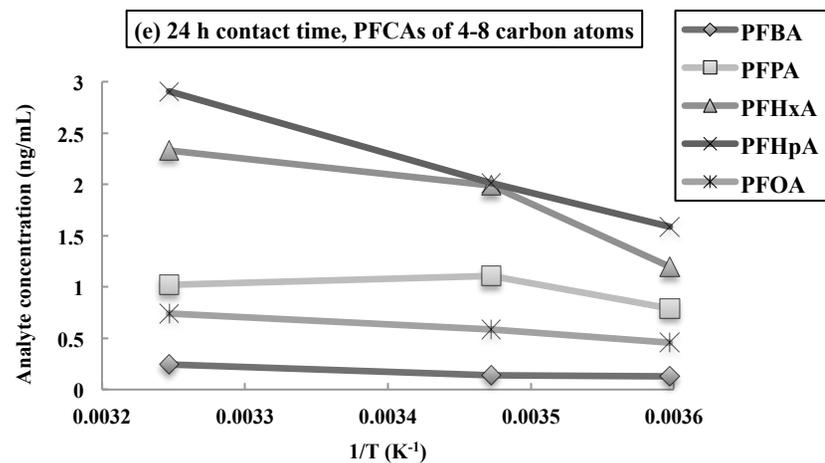


Figure 4.7 (continued): Concentrations of PFCAs in landfill leachate after 24 h contact with composite carpet vs. $(1/T)$, where T is absolute temperature. Leaching experiments were conducted at pH 6, rotation speed 8 rpm and temperature 5, 15 and 35°C.

From Figure 4.7, it appears that the leaching rates of PFPA, PFHxA, PFHpA, PFNA and PFDA underwent a decrease with increasing $(1/T)$; in other words, the leaching rates of these PFCAs increased with temperature, as expected for adsorption- /desorption-controlled transfer. On the other hand, PFBA, PFOA, PFUnA and PFDoA experienced little concentration changes with temperature, suggesting that temperature did not significantly affect the transfer rates of these compounds. For PFTA, however, a totally different trend was observed, as seen in Figure 4.7. Since PFTA was the only analyte for which the transport was externally mass transfer controlled, the effect of temperature on leaching rates of PFTA is discussed separately in this section. Figure 4.8 shows the concentrations of PFTA in landfill leachate after 2, 6 and 24 h contact with composite carpet at pH 6, rotation speed 8 rpm and temperature 5, 15 and 35°C. From Figure 4.8, it appears that PFTA increased from 0 to 2 h at all temperatures (i.e. 5, 15 and 35°C), with the highest concentration observed at 35°C. At 5°C a slight increase in PFTA concentration was observed from 2 to 24 h. At 15°C after a minor decrease in PFTA levels between 2 and 6 h, a slight increase was observed from 6 to 24 h. However at 35°C not only the observed decrease in PFTA level after 2 h was more significant than the decrease observed at 15°C, but also this drop in concentration occurred earlier compared to 15°C (at which the smaller decrease occurred after 6 h), implying higher transfer rates at 35°C. Note that this trend could not be confirmed unless more data at various times from 0 to 168 h were available.

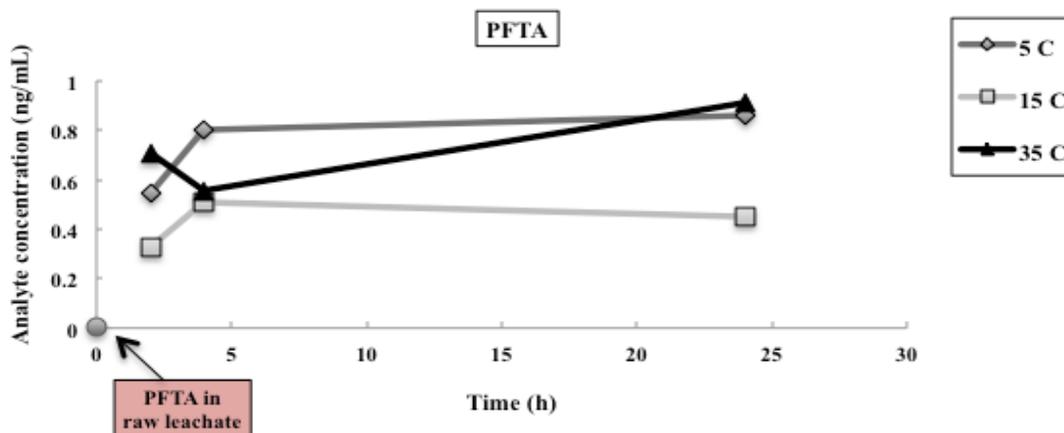


Figure 4.8: Leaching rates of PFTA from composite carpet samples to leachate at 5, 15 and 35°C after 2, 6 and 24 h contact time. These leaching experiments were conducted at pH 6 and rotation speed 8 rpm.

Trends for variation of PFSA leaching rates differed from those observed in PFCAs. Since concentrations of PFBS, PFDS, and FOSA were close to or below the MDLs, only leaching rates of PFHxS and PFOS are discussed in this section. Concentrations of PFHxS in leachate were similar after 2 h of contact with carpet samples at 5, 15 and 35°C, but decreased abruptly from 2 to 6 h, as shown in Figure 4.9 (a). The greatest rate of PFHxS concentration decrease from 2 to 6 h was observed at 35°C, followed by 15 and 5°C respectively. From 6 to 24 h, the concentration of PFHxS at all temperatures remained almost constant. The higher rate of PFHxS loss in leachate at the higher temperatures suggests that temperature speeds up the partitioning of PFHxS from leachate to carpet (i.e. reverse direction transfer). For PFOS, shown in Figure 4.9 (b), a steep concentration decrease was observed from 2 to 24 h, with the greatest rate of analyte decline at 35°C, followed by 15 and 5°C respectively. Similar to PFHxS in the range of 5 to 35°C, higher temperatures accelerated PFOS transfer.

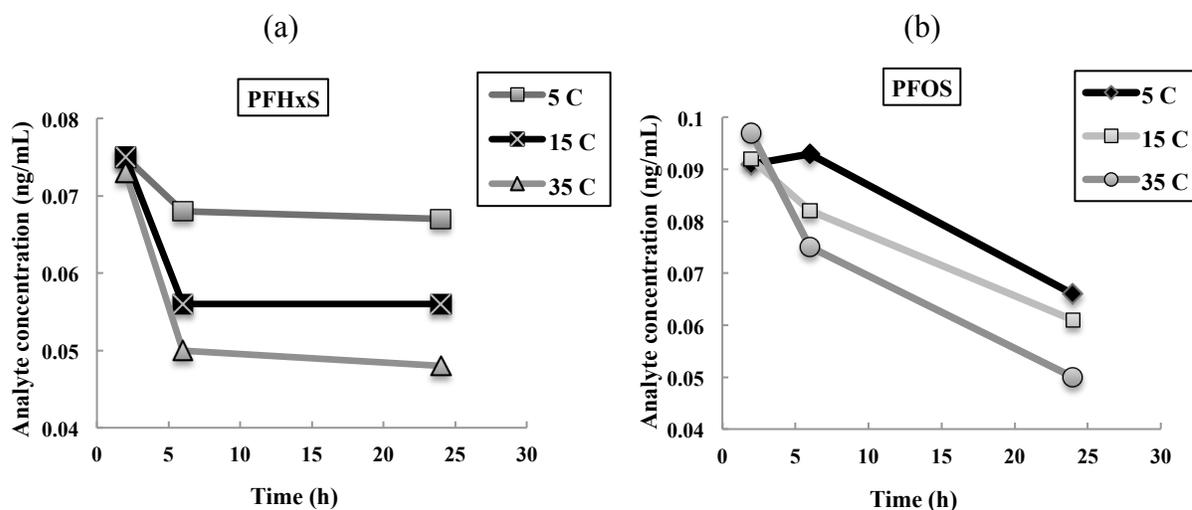


Figure 4.9: Leaching rates of (a) PFHxS and (b) PFOS from composite carpet to landfill leachate at 5, 15 and 35°C for 2, 6 and 24 h contact time. The leaching experiments were conducted at pH 6 and rotation speed 8 rpm.

4.5.5 Effect of pH on leaching rates

A series of tests was carried out to determine the effect of pH on leaching rates of different PFCs. Table 4.11 summarizes the concentrations of PFCs in leachate samples after contact with composite carpet samples for 6 h at a rotational speed of 8 rpm in the pilot-scale “end-over-end contactor” at varying pH values of 5, 6, 7 and 8. With the experiments were conducted in duplicate, the mean and standard deviation values are included in the Table 4.11. Generally, increasing the leachate pH from 5 to 6 and 6 to 7 resulted in an increase in total concentrations of PFCs, as well as total PFCAs, as shown in Figure 4.10. However, further increasing the pH from 7 to 8 caused a decline in the total concentrations of PFCs and PFCAs. This trend is very similar to that observed by Warner and Solomon (1990) for leaching rates of metals into solutions of varying pH (see Section 3.4.4.4).

Table 4.11: Mean and standard deviation of PFC concentrations (in ng/mL) in leachate after contacting with composite carpet samples at pH=6, temperature=15°C, rotation speed=8 rpm and solution pH of 5, 6, 7, and 8. Underlined numbers show that the corresponding PFC concentrations were below MDL, and values of 0.5 MDL were assigned in these cases.

pH	Parameter	PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTA	PFBS	PFHxS	PFOS	PFDS	FOSA
5	Mean	0.143	0.725	1.331	1.544	0.461	0.717	0.396	0.136	0.369	0.712	<u>0.001</u>	0.066	0.078	<u>0.002</u>	0.002
	¹ S.Dev	0.015	0.037	0.017	0.055	0.035	0.095	0.013	0.024	0.048	0.077	0.000	0.001	0.004	0.000	0.000
6	Mean	0.130	0.700	1.781	1.652	0.535	0.875	0.483	0.128	0.361	0.709	<u>0.001</u>	0.066	0.103	<u>0.002</u>	0.002
	¹ S.Dev	0.005	0.021	0.317	0.028	0.040	0.065	0.110	0.037	0.047	0.139	0.000	0.006	0.001	0.000	0.001
7	Mean	0.222	0.628	1.656	1.893	0.540	0.937	0.514	0.181	0.313	0.727	0.005	0.080	0.092	<u>0.002</u>	0.002
	¹ S.Dev	0.012	0.031	0.094	0.160	0.040	0.086	0.074	0.030	0.044	0.018	0.005	0.001	0.004	0.000	0.000
8	Mean	0.171	0.543	1.290	1.458	0.431	0.840	0.474	0.173	0.244	0.487	0.008	0.063	0.087	<u>0.002</u>	0.004
	¹ S.Dev	0.016	0.027	0.099	0.105	0.011	0.032	0.015	0.013	0.008	0.025	0.010	0.006	0.000	0.000	0.001

¹ Standard deviation, also in ng/mL.

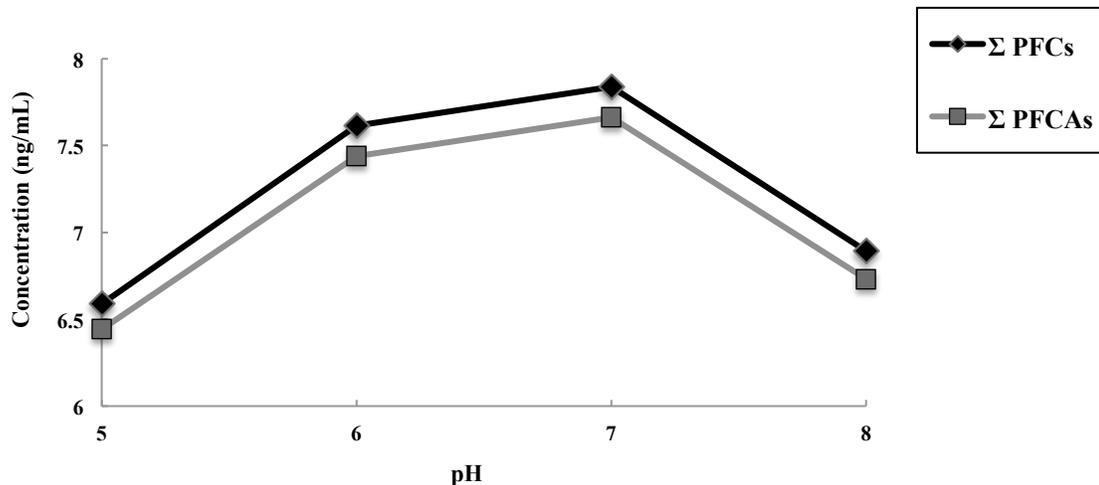


Figure 4.10: Total concentrations of PFCAs and PFCs in leachate after contacting with composite carpet samples at pH=6, temperature=15°C, rotation speed=8 rpm and solution pH of 5, 6, 7, and 8.

As shown in Figure 4.10, total concentrations of leached PFCAs were very close to total concentrations of PFCs. Perfluorinated sulfonates (PFSAs) comprised ~2.5% of total PFC concentrations in leachate in this study.

Concentrations of different PFCs in leachate after 6 h of contact between composite carpet samples and leachate at 15°C and varying pH are displayed in Figure 4.11. Compounds along the x-axis have been arranged in order of increasing number of carbon atoms in the fluorinated chain. Except for a few PFCs, the highest leaching rates were observed for a pH of 7, and in a few cases, at pH 6. Concentrations of PFHpA, PFNA, PFDA, PFUnA, PFTA, and PFHxS reached their highest levels at pH of 7, while the greatest concentrations of PFBA, PFHxA, and PFOS were detected at a pH of 6. PFPA and PFDoA followed a different trend, as more acidic solutions resulted in greater leaching rates for these two PFCAs. The leaching behaviour of PFBS, PFDS, and FOSA are not discussed here because of their concentrations being below or slightly above MDL levels so that these data are not sufficiently accurate to draw valid conclusions.

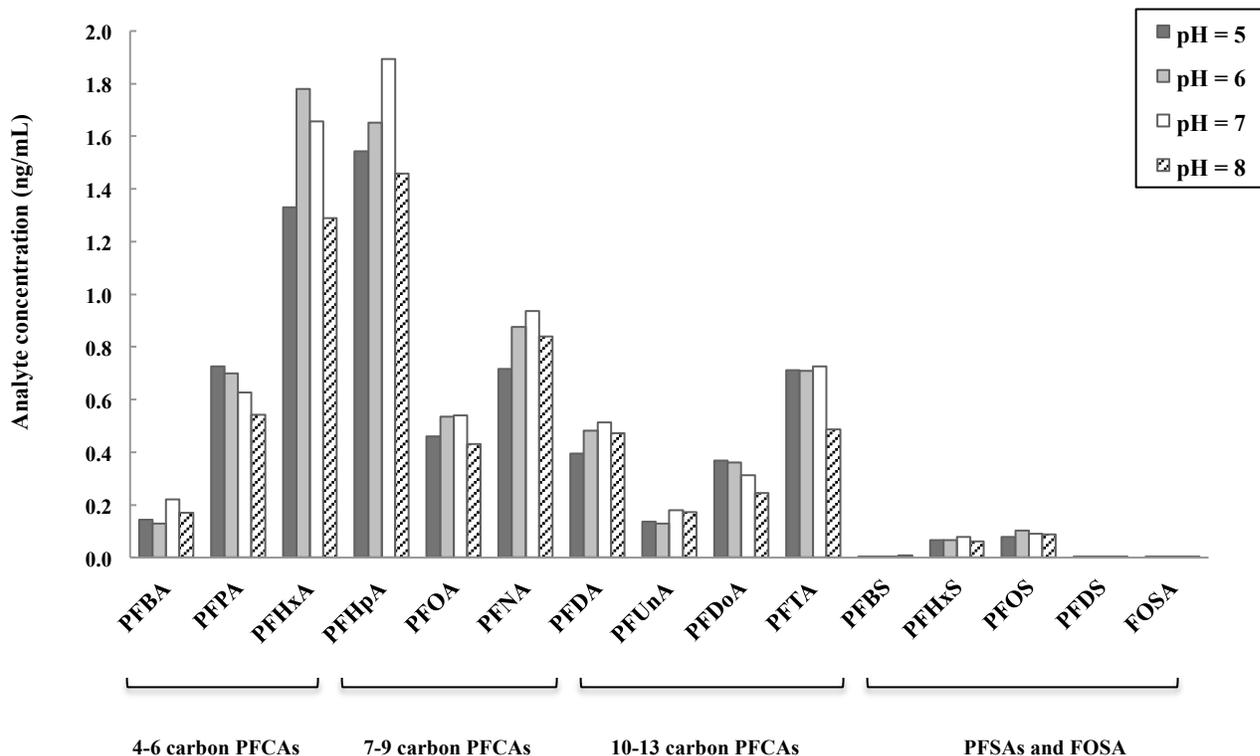


Figure 4.11: Concentrations of different PFCs leached from composite carpet samples to leachate after 6 h contact time at temperature=15°C, rotation speed=8 rpm and pH of 5, 6, 7, and 8.

4.5.6 Leaching rates of PFCs from samples of individual carpet compared to the composite samples

Some experimental runs were designed to compare leaching from composite and individual carpets (N₄, N₅, N₆, N₇ and N₈) with landfill leachate, to determine the leaching rates of different PFCs (See Section 3.4.4.5). Because observed PFC concentrations in the leachate included both PFCs leached from carpet samples and PFCs present in the background leachate, the results were corrected with leachate blanks and are summarized in Table 4.12.

The procedure for blank-correction was as follows:

$$\text{[PFC concentration leached from carpet to leachate]} = \text{[Final PFC concentration in the leachate after contact with carpet]} - \text{[Concentration of PFCs in the leachate without any carpet present after the same time (6 h) at the same temperature]}$$

Through this method, comparison between PFC leaching rates from individual and composite carpets was made feasible. For leachate blank samples, see Section 4.1.1.

Since composite carpet samples were composed of N₄, N₅, N₆, N₇ (22.5 wt. % each), and N₈ (10 wt. %), it is expected that if there are no synergistic effects, the PFC leaching rates from composite carpet samples would match that from a weighted average, i.e. from:

$$\text{[PFC concentration leached from composite carpet]} = 0.225 \times \text{[Summation of PFC concentrations leached from carpets N}_4\text{, N}_5\text{, N}_6\text{ and N}_7\text{]} + 0.1 \times \text{[PFC concentrations leached from carpet N}_8\text{]}$$

The “Expected PFCA leaching rates from composite carpets” based on this equation are plotted against the “Experimental PFCA leaching rates from composite carpets” in Figure 4.12. The results for perfluorinated sulfonates are not included because most concentrations were below the MDL. There are significant differences between the measured and expected data. Except for PFPA, highlighted in Figure 4.12, the discrepancy appears to be greater with increasing concentration. The expected concentration for PFPA was ~4 times greater than the experimental concentration.

Table 4.12: PFC concentrations in leachate after contact with composite and individual carpets (N₄, N₅, N₆, N₇ and N₈) at 15°C, pH 6 and rotation speed 8 rpm. Tabulated concentrations are final concentrations in leachate after correcting for concentration of PFCs in leachate with no carpet and identical time, temperature and rotation speed.

Carpet No.	Parameter	PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTA	PFBS	PFHxS	PFOS	PFDS	FOSA
N ₄	Mean (ng/ml)	0.261	1.162	3.332	5.620	1.008	2.303	0.482	0.047	0.094	0.161	0.000	0.029	0.018	0.000	0.000
	¹ S.Dev	0.051	0.034	0.375	0.079	0.042	0.133	0.039	0.000	0.008	0.006	0.000	0.003	0.007	0.000	0.000
N ₅	Mean (ng/mL)	0.381	1.003	1.213	0.768	0.286	0.299	0.190	0.057	0.168	0.052	0.000	0.002	0.000	0.000	0.000
	¹ S.Dev	0.080	0.267	0.559	0.148	0.036	0.121	0.039	0.018	0.162	0.012	0.000	0.012	0.011	0.000	0.000
N ₆	Mean (ng/mL)	0.210	0.499	1.196	0.601	0.575	0.414	0.942	0.313	1.312	2.612	0.013	0.012	0.088	0.000	0.010
	¹ S.Dev	0.071	0.132	0.172	0.052	0.026	0.016	0.002	0.016	0.062	0.308	0.021	0.005	0.002	0.000	0.001
N ₇	Mean (ng/mL)	0.235	0.679	0.390	0.672	0.186	0.100	0.101	0.039	0.034	0.071	0.003	0.026	0.017	0.000	0.000
	¹ S.Dev	0.041	0.200	0.077	0.230	0.044	0.052	0.017	0.000	0.000	0.004	0.006	0.006	0.007	0.000	0.000
N ₈	Mean (ng/mL)	0.034	0.259	0.000	0.087	0.035	0.000	0.000	0.000	0.041	0.134	0.032	0.051	0.297	0.000	0.000
	¹ S.Dev	0.050	0.067	0.061	0.062	0.022	0.000	0.007	0.000	0.022	0.083	0.049	0.012	0.060	0.000	0.000
Mixed	Mean (ng/mL)	0.061	0.216	0.908	1.436	0.390	0.559	0.342	0.092	0.253	0.537	0.005	0.006	0.012	0.000	0.001
	¹ S.Dev	0.004	0.054	0.254	0.332	0.012	0.034	0.023	0.017	0.051	0.021	0.009	0.015	0.003	0.000	0.000

¹ Standard deviation, also in ng/mL.

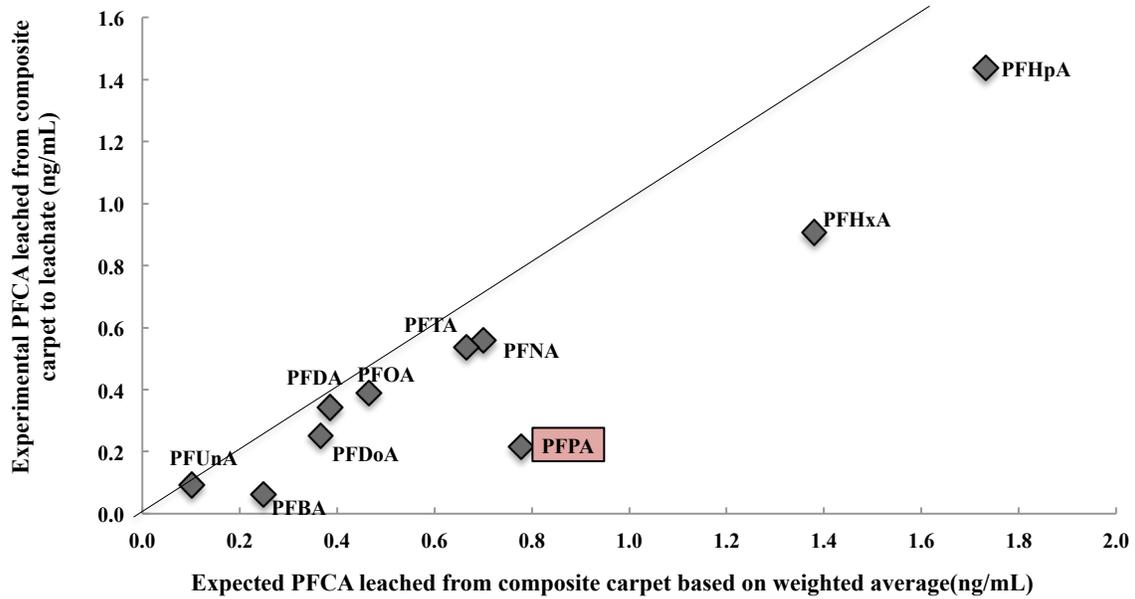


Figure 4.12: “Experimental” vs. “Expected” PFCA leaching rates from composite carpet samples to landfill leachate at temperature 15°C, pH 6 and rotation speed 8 rpm. Parity line is shown to facilitate comparison.

In addition to the differences observed between “expected” and “experimental” PFC leaching rates from composite carpets to landfill leachate, which were probably due to synergistic effects between individual carpets in composite samples, the percentage of initial PFCs in the individual and composite carpets appearing in the landfill leachate after 6 h contact at pH 6, temperature 15°C and a rotation speed 8 rpm apparently differed, as shown in Figure 4.13. Since PFCA levels in carpet N₈ were close to or below their MDL, their corresponding percentages are excluded from Figure 4.13. The percentages were determined from the following procedure:

$$\frac{[\text{Blank-corrected PFCA concentration in leachate after contacting with the carpet for 6 h}] \times \text{leachate vol.}}{[\text{Initial concentration of PFCA in carpet}] \times \text{carpet weight}} \times 100(\%)$$

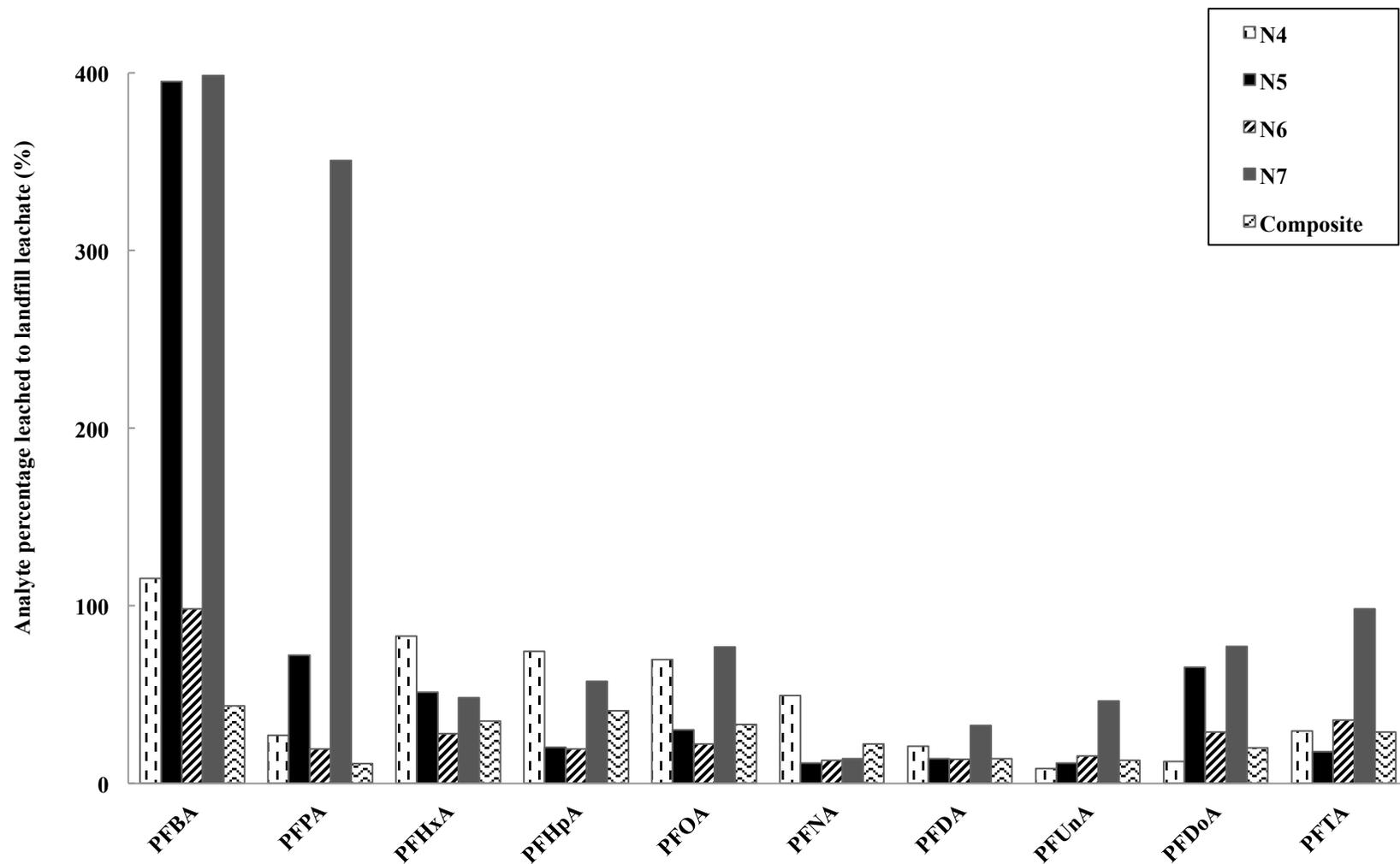


Figure 4.13: Percentage of initial PFCAs on different carpets appearing in landfill leachate after 6 h contact at pH 6, temperature 15°C and rotation speed 8 rpm.

Percentages observed for PFBA in N₄, N₅ and N₇, and for PFPA in N₇ in Figure 4.13 exceed 100%. These unusual percentages are probably due to low initial concentrations of PFBA in N₄, N₅ and N₇, and PFPA in N₇, making the denominator of the above equation low compared to the numerator and resulting in high percentages. These close-to-MDL concentrations are not sufficiently accurate to draw valid conclusions. For other PFCAs, the observed percentages for N₇ and N₄ were greater than for N₅ and N₆. Furthermore, the percentages for composite carpet samples were low enough to confirm the observed trend of lower “experimental” concentrations than “expected” concentrations for composite carpets (See Figure 4.12). Various methods of PFC treatment application on carpet surface could be a possible reason for the observed differences. In addition, dust may be a significant source of PFCs (Liu et al. 2011), especially for carpets N₆ and N₇, which were very dusty. The observed leaching rates in these carpets could indicate partitioning from the dust particles into the leachate, in addition to leaching from fibres. Moreover, since adsorption/desorption appear to have played a dominant role in determining the overall mass exchange between carpets and leachate except for PFTA, occupation of the adsorption sites on carpet samples by dust particles might have affected the leaching rates.

4.5.7 Leaching rates of PFCs to leachate compared to distilled water

PFC leaching rates from composite carpets to landfill leachate and distilled water at pH of 5, 6, 7 and 8 at 15°C are summarized in Table 4.13 for a rotation speed of 8 rpm and contact time of 6 h. Note that PFC concentrations for landfill leachate are corrected by concentrations of corresponding PFCs in the original leachate (with no carpet present) after 6 h at 15°C. Concentrations displayed in Table 4.13 are the mean values of tests conducted in duplicate.

Table 4.13: PFC concentrations leached from composite carpet samples to both leachate and distilled water with pH of 5, 6, 7 and 8 after 6 h contact at temperature of 15°C and rotation speed of 8 rpm. Tabulated concentrations are final concentrations in leachate after correcting for concentration of PFCs in leachate with no carpet and identical time, temperature and rotation speed, displayed in the last row.

pH	Parameter	PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTA	PFBS	PFHxS	PFOS	PFDS	FOSA
5	Leachate (ng/mL)	0.061	0.323	1.025	1.442	0.416	0.526	0.382	0.132	0.363	0.700	0.000	0.009	0.015	0.000	0.002
	Water (ng/mL)	0.081	0.857	1.316	2.197	0.500	1.000	0.586	0.103	0.250	0.606	0.000	0.017	0.089	0.003	0.001
6	Leachate (ng/mL)	0.054	0.288	1.227	1.509	0.426	0.656	0.447	0.123	0.312	0.695	0.000	0.011	0.027	0.000	0.003
	Water (ng/mL)	0.071	0.989	1.316	1.973	0.468	1.037	0.632	0.130	0.217	0.474	0.011	0.012	0.077	0.002	0.002
7	Leachate (ng/mL)	0.140	0.226	1.349	1.791	0.496	0.746	0.501	0.177	0.307	0.715	0.001	0.023	0.028	0.000	0.002
	Water (ng/mL)	0.087	0.853	1.263	1.929	0.429	1.013	0.603	0.129	0.204	0.551	0.000	0.013	0.071	0.002	0.001
8	Leachate (ng/mL)	0.089	0.141	0.984	1.356	0.387	0.648	0.460	0.169	0.238	0.475	0.005	0.006	0.024	0.000	0.089
	Water (ng/mL)	0.076	0.865	1.438	2.107	0.469	1.121	0.636	0.161	0.142	0.345	0.000	0.020	0.078	0.002	0.002
Blank leachate after 6 h (ng/mL)		0.087	0.434	0.273	0.106	0.044	0.191	0.015	0.004	0.006	0.011	0.001	0.055	0.063	0.002	0.000

Two approaches are taken in this section to compare the leaching rates into landfill leachate and into distilled water: First, leaching rates in both media are compared to determine the overall correlation between leaching into leachate and distilled water and to determine whether or not the relationship is pH-dependent. Second, leaching rates of different PFCs are compared one-by-one at different pH values to rule out species-specific correlations between leaching rates into landfill leachate and into distilled water.

Since the PFC concentrations in the original landfill leachate (with no carpet present) changed with time, it is essential to use blank-corrected PFC concentrations in order to compare the leaching rates into landfill leachate and distilled water (See Section 4.5.6 for blank-correction procedure). Figure 4.14 displays concentrations of different PFCAs in distilled water after 6 h contact with composite carpet samples at temperature of 15°C, rotation speed of 8 rpm and different values of pH plotted against the blank-corrected PFCA concentrations in landfill leachate under identical contacting conditions. Leaching data for perfluorinated sulfonates are excluded in Figure 4.14 because of their very low concentrations. Parity lines are shown to aid the comparison. Distilled water appears to have a higher tendency to leach the PFCs than landfill leachate at pH 5 and pH 8. On the other hand, for a pH of 6 and 7, the leaching rates to landfill leachate tended to be higher.

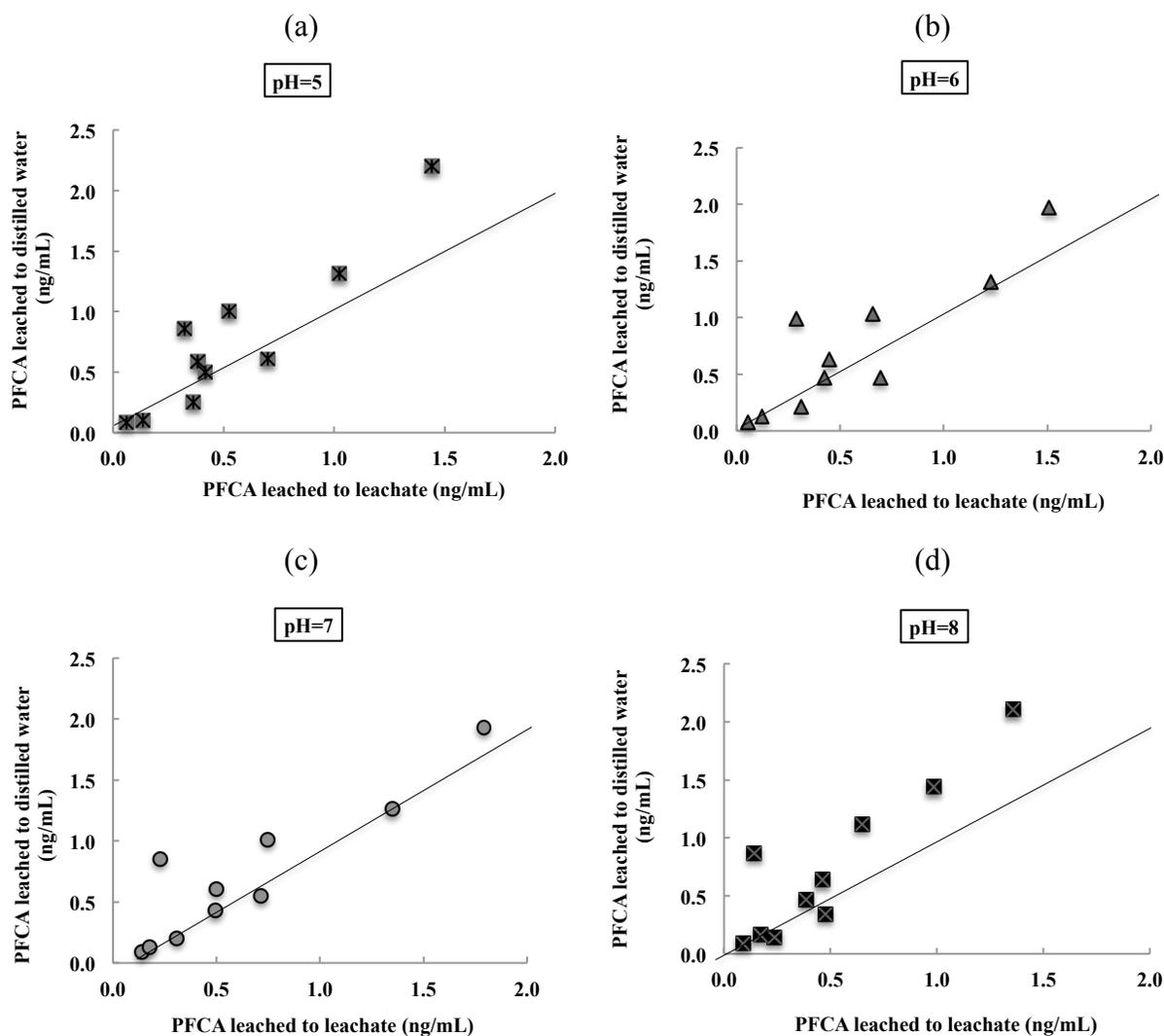


Figure 4.14: PFCA concentrations in distilled water versus blank-corrected PFCA concentrations in landfill leachate after 6 h contact with composite carpet samples at 15°C, rotation speed of 8 rpm and (a) pH=5, (b) pH=6, (c) pH=7, (d) pH=8. Parity lines are shown to aid comparison.

Figure 4.15, displays blank-corrected PFCA concentrations in landfill leachate and distilled water for different solution pHs. Compounds are again arranged along the x-axis in order of increasing number of carbon atoms in the fluorinated chain. In most cases, more lower-molecular-weight PFCAs (i.e. PFBA, PFPA, PFH_xA, PFHpA, PFOA, PFNA, and PFDA) transferred to distilled water than to landfill leachate. This trend appeared to be reversed for

the higher-molecular-weight compounds, with PFUnA being the transition compound where concentrations were similar. Since the concentrations of PFCAs of lower molecular weight in blank leachate were greater than those of the PFCAs of higher molecular weight (see Table 4.13), the concentration driving force for analyte transfer in landfill leachate was lower for low-molecular-weight compounds in this study, resulting in less transfer into landfill leachate than into distilled water for lower-molecular-weight PFCAs. This might be the reason for the witnessed trend change for PFCAs of higher molecular weight than PFUnA. Note that the trend discussed above was clear for solution pH of 5, 6 and 8. For pH 7, however, no specific trend was observed, as shown in Figure 4.15 (c). Another reason for the difference in PFC leaching rates to landfill leachate and distilled water might be due to leachate impurities. Organic and inorganic matter, humic substances, surfactants and solvents, which are known to be present in landfill leachate, might influence the leaching of PFCs.

Among perfluorinated sulfonates, PFHxS and PFOS are discussed. Like PFCAs, the maximum blank-corrected PFHxS concentration in landfill leachate was observed at pH 7, as shown in Figure 4.16 (a); at pH 5 and 8, levels of PFHxS in distilled water were significantly higher than in blank-corrected leachate, and at pH 6, these levels were almost equal. For PFOS, displayed in Figure 4.16 (b), analyte concentrations in distilled water were higher than blank-corrected concentrations in landfill leachate at all pHs examined.

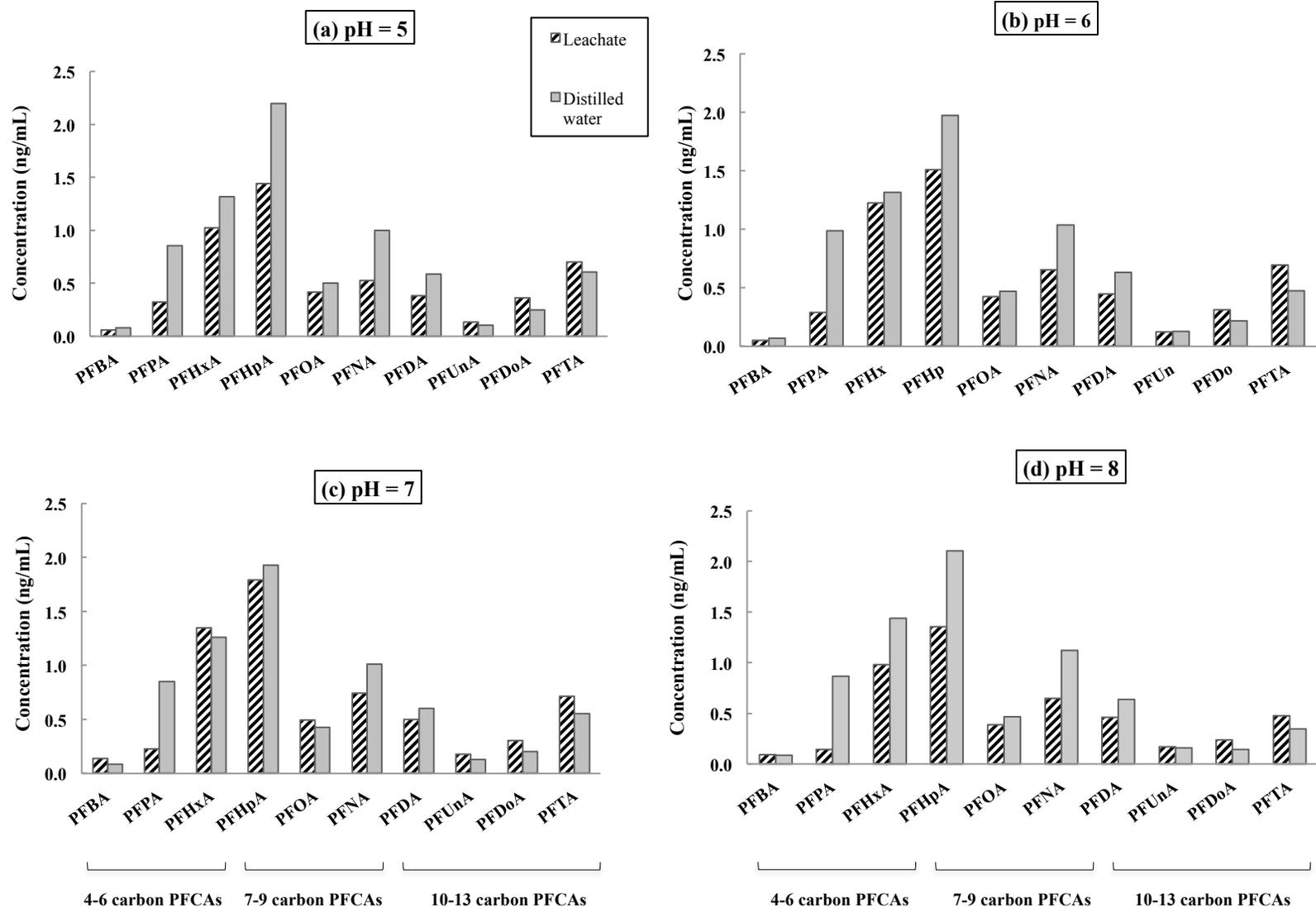


Figure 4.15: PFCAs concentrations in distilled water and blank-corrected landfill leachate after 6 h contact with composite carpet samples at 15°C, rotation speed of 8 rpm and (a) pH=5, (b) pH=6, (c) pH=7 and (d) pH=8.

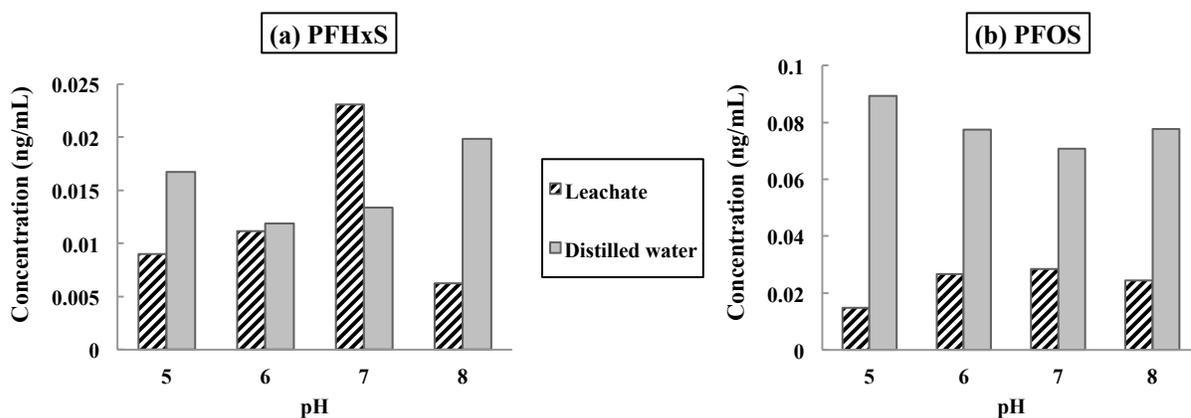


Figure 4.16: (a) PFHxS and (b) PFOS concentrations in distilled water and blank-corrected landfill leachate after 6 h contact with composite carpet samples at 15°C, rotation speed of 8 rpm and solution pH of 5, 6, 7 and 8.

Chapter 5: Conclusions and Recommendations

5.1 Conclusions

The major findings from the analysis of perfluorinated compounds in carpet and landfill leachate/distilled water samples before and after contacting experiments may be summarized as follows:

- Used and unused carpet samples manufactured in 2005 and before contained significant amounts of PFCs. Carpet samples manufactured in 2005, five years after the voluntary phase-out of PFOS manufacturing by the 3M Company in 2000 and three years after discontinuing PFOS manufacture in Canada in 2002, contained negligible PFOS. However carpets manufactured in 2000 and before (prior to PFOS ban) contained substantial amounts of both perfluorinated carboxylic acids and sulfonates.
- PFHxA was the dominant PFC in raw landfill leachate, comprising ~38.0% of the total. PFNA and PFOS were also strongly present, representing ~22.4% and ~9.5% of the total PFCs in leachate respectively.
- A notable increase in concentration of PFCAs in leachate samples was observed from 1 to 168 h of contact between composite carpet samples and leachate. Differences between 1 and 24 h were much greater than between 24 and 168 h of contact time. Concentrations of several PFCAs in this study stayed nearly constant between 24 and 168 h, suggesting that an equilibrium was reached between PFCs in carpets and landfill leachate.
- Perfluorinated sulfonates underwent a decrease in leaching from 2 to 168 h contacting time due to reverse mass transfer, i.e. analyte transfer from leachate to carpet samples. An increase in concentrations of these compounds in carpet samples between 6 and 168 h of contacting with landfill leachate confirmed this finding.

- Increasing the temperature from 5 to 35°C notably increased the transfer rates of most PFCs between carpet samples and landfill leachate.
- The leaching rates of most PFCs increased, followed by a decrease, with leachate pH increasing from 5 to 8. The maximum leaching rates were detected at pH of 7 for most PFCs, while a few reached maxima at a pH of 6.
- Except for PFTA, rotation had little or no effect on leaching rates, suggesting that the leaching rates were dependent on some factor (e.g. adsorption or desorption) other than external mass transfer.
- The leaching rates of PFTA increased significantly due to rotation, suggesting that external mass transfer was the major contributor to the overall mass exchange of PFTA between carpets and leachate.
- The overall leaching rates of PFCs into distilled water were somewhat higher than into landfill leachate.
- Transfer of PFCAs with molecular weights lower than PFUnA (i.e. from PFBA with molecular weight of 214 g/mol to PFUnA with molecular weight of 564 g/mol) to distilled water was greater than to landfill leachate. For higher-molecular-weight PFCAs (i.e. PFDoA and PFTA with molecular weight of 714 g/mol) the trend reversed. Assuming that the major mass transfer mechanism for PFCAs leaching was based on the concentration driving force, greater concentrations of lower-molecular-weight PFCAs in blank leachate resulted in lower concentration driving forces, explaining why the leaching rates of these PFCAs to distilled water was higher than for landfill leachate.
- Mass balances applied to six leaching tests displayed net PFC outputs of 12 to 32% lower than net inputs in the leaching experiments. This could be due to dislodgement of dust

particles from carpets, especially from carpets N₆ and N₇ (old and dusty carpets), which might settle in the leachate sampling tubes or separate from leachate samples through filtration, and result in under-estimation of the final PFC concentrations in landfill leachate or distilled water samples.

5.2 Recommendations

Key recommendations for future work are as follows:

- The data provided in this study were preliminary. In addition, no information was available in the literature for comparison. These gaps should be filled by future work in order to obtain a better understanding of PFCs leaching from consumer products to landfill leachates and ultimately to groundwater.
- In order to obtain better consistency in the results, more standardized methodologies for the analysis of PFCs as well as sample extraction and clean-up should be utilized in the future. Also it would be useful to include PFC precursors, especially fluorotelomer alcohols, in the analysis in order to keep track of generation or consumption of different PFCs through degradation pathways.
- In this study, the number of tests was limited. Obtaining further data for effect of different factors on PFC leaching rates in future would be useful to derive more reliable conclusions.
- Extending the time range for contact between carpets and leachate in future would be beneficial, as it would help to estimate the time required for each PFC to reach equilibrium. Also extending the contact time would be helpful in estimating long-term PFC leaching rates in landfills.
- Further analysis of other landfill leachate constituents that possibly affect the PFC leaching

rates into aqueous media would help to shed light on the agents contributing to different leaching rates into leachate and distilled water.

- Experiments should be designed to measure the equilibrium concentrations of PFCs in landfill leachate at different temperatures, in order to facilitate the application of Arrhenius law on leaching rates to determine the temperature-dependence of PFC leaching.
- Dust particles might be a significant source of PFCs. Analysing the dust from old carpets might shed light on the mechanism of PFC transfer from different carpets into landfill aqueous media.
- Leaching experiments should be conducted where other PFC-containing consumer products e.g. textiles, paper and packaging products and food wraps are exposed to landfill leachate and distilled water in order to gain a better understanding of how PFCs enter landfills.
- The data from this study should be used to develop mass transfer models for landfills.

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Appendix A: Heat transfer between liquid in vessels and air

In this appendix, the required time for changes in the liquid temperature when the air temperature undergoes a step change from T_{liq} to T_{atm} is calculated. In other words, the time lag for changes in liquid temperature after a step change in air temperature is determined.

To figure out whether the dominant resistance is on the outside or inside of the vessel, the Biot modulus is calculated as follows:

$$\text{Biot modulus} = \text{Bi} = \frac{hs}{k} \quad (\text{A.1})$$

h : Natural convection heat transfer coefficient for air, $\sim 25 \text{ W/m}^2\cdot\text{°C}$ (Holman 1976)

s : Characteristic dimension of the body, which is equal to half-thickness for a plate. Since the vessel could be assumed as a plate with thickness of 34 mm, $s = 34/2 = 17 \text{ mm} = 0.017 \text{ m}$.

k : Thermal conductivity of the vessel. According to AK Steel Corporation (2007), for stainless steel 316, k is $\sim 16.2 \text{ W/m}\cdot\text{°C}$.

The Biot modulus from Equation (A.1) is:

$$\text{Bi} = \frac{250 \times 0.017}{16.2} = 0.026 \quad (\text{A.2})$$

Very low values for Biot number (i.e. less than 0.1) indicate negligible internal-conduction resistance in comparison with surface-convection resistance (Holman 1976). With this assumption, Equation (A.3) represents heat transfer between liquid and its surrounding air, based on the “lumped capacitance” method. Note that this method is utilized when the temperature changes uniformly under a cooling or warming convective flow, i.e. temperature gradients are negligible inside the object.

$$h_{air} A (T_{atm} - T_{liq}) dt = (M_{vessel} C_{p,vessel} + M_{liq} C_{p,liq}) dT \quad (\text{A.3})$$

The constant values in the Equation (A.3) are discussed below. Note that the calculated numbers are based on one vessel.

Convection Heat Transfer Coefficient for Air: According to Holman (1976), the natural convection heat transfer coefficient for air (h_{air}) is 5-25 W/m².°C in case of free convection. Since there was air movement when the doors were opened, and it is a “worst-case value”, h_{air} has been assumed to be 25 W/m².°C.

Surface Area of Vessel: Each vessel is divided into three regions and the surface area for each region has been calculated separately. Figure A.1 shows a side-view of a single vessel.

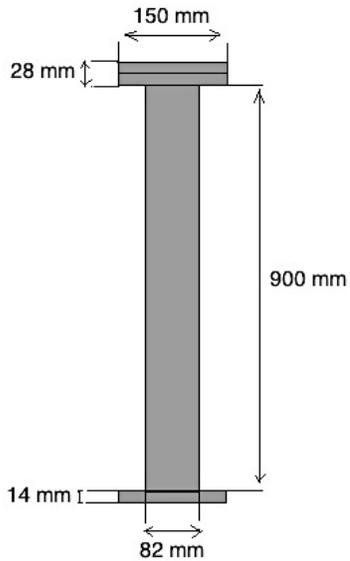


Figure A.1: Side-view of a single vessel

$$A_{\text{Main cylinder}}: \Pi \cdot 900 \cdot 82 \cdot 10^{-6} = 231.73 \times 10^{-3} \text{ (m}^2\text{)}$$

$$A_{\text{Top end}}: \{[\Pi \cdot (150)^2/4] + [\Pi \cdot 28 \cdot 150] + [\Pi \cdot (150^2 - 82^2)/4]\} \times 10^{-6} = 43.24 \times 10^{-3} \text{ (m}^2\text{)}$$

$$A_{\text{Bottom end}}: \{[\Pi \cdot (82)^2/4] + [\Pi \cdot 14 \cdot 150] + [\Pi \cdot (150^2 - 82^2)/4]\} \times 10^{-6} = 24.26 \times 10^{-3} \text{ (m}^2\text{)}$$

$$A_{\text{Total}}: (231.73 + 43.24 + 24.26) \times 10^{-3} = 299.23 \times 10^{-3} \text{ (m}^2\text{)}$$

Vessel Mass: The mass of a single vessel has been measured by a scale and equals to 18.1 kg. The vessel ends were included in measuring the weight.

C_p of Vessel: The specific heat capacity of Stainless Steel 316 in the range of 0-100°C is 0.50 kJ/kg.°C (AK Steel Corporation 2007).

Liquid Mass: Since the vessels were filled up to 80% of their capacity in all experiments, the $M_{liq} \approx 4$ kg.

C_p of Leachate: It is assumed that the specific heat capacity of leachate is similar to water ($C_{p_{liq}} = 4.2$ kJ/kg.K).

Substituting these numbers simplifies equation (A.3) to:

$$\int_{T_{liq\ 1}}^{T_{liq}} \frac{dT_{liq}}{(T_{atm} - T_{liq})} = 4.75 \times 10^{-4} \quad (A.4)$$

Finally differentiation from equation (A.4) results in:

$$\ln \frac{(T_{atm} - T_{liq})}{(T_{atm} - T_{liq\ 1})} = 4.75 \times 10^{-4} t \quad (A.5)$$

Note that the initial condition for temperature is as follows:

at $t_1 = 0$, $T_{liq} = T_{liq\ 1}$ (initial liquid temperature)

Solving Equation (A.5) for liquid temperature as a function of time:

$$T_{liq} = T_{atm} - [(T_{atm} - T_{liq\ 1}) (e^{-4.75 \times 10^{-4} t})] \quad (A.6)$$

The final liquid temperature after a sudden temperature change in room temperature at a specific time could be calculated through Equation (A.6).

In addition, the “thermal time constant”, which represents the time required for the system’s step response to reach ~63.2% of its final value in a lumped system is calculated as follows:

$$\text{Thermal time constant} = [(M_{vessel} C_{p_{vessel}} + M_{liq} C_{p_{liq}}) / (hA)] \quad (A.7)$$

Substituting for the M_{vessel} , $C_{p_{vessel}}$, M_{liq} , $C_{p_{liq}}$, h and A from the previous part results in:

Thermal time constant = $[(18.1 \times 500 + 4 \times 4200) / (25 \times 0.299)] = \sim 3458 \text{ s} = \sim 58 \text{ min}$

Therefore, almost one hour is required for the vessel contents to reach $\sim 63.2 \%$ of the final temperature. This time constant suggests that the apparatus will not show short-term temperature fluctuations due, for example, to opening of a window or door, but that the temperature will stabilize to a new room temperature after several hours.

Appendix B: Preliminary test results

The results for preliminary tests are summarized in this section. As noted in Chapter 3, these leaching tests were conducted with carpet fibre at temperature of $21 \pm 2^\circ\text{C}$, pH of 7.1 and rotation speed of 8 rpm. The concentrations of different PFCs in leachate/distilled water after contacting with carpet fibre for 0.5, 1, 2, 4, 10, 24 and 72 h are summarized in Table B.2. Figure B.1 also shows the concentrations of different PFCs in leachate after contacting with carpet fibre for 0.5, 1, 2, 4, 10, 24 and 72 h. From Figure B.1, all PFCA concentrations underwent a rapid initial increase followed by a slower increase during the 72 h of contacting. Among the PFCAs of interest in this study, PFBA, PFHpA and PFOA appear to have approached an equilibrium, since minor concentration changes were observed between 1 and 3 days. PFPA and PFHxA were subject to notable concentration increases between 1 and 3 days, suggesting that they still need some more contact time to reach equilibrium. An unusual decrease in concentration was observed for PFNA between 1 to 3 days. Figure B.2 also shows the total concentrations of PFCAs in leachate after 0.5, 1, 2, 4, 10, 24 and 72 h contact with carpet fibre, suggesting that the total concentrations of PFCAs increased from 0.5 to 72 h.

Concentrations of different PFCs in blank leachate samples after 0, 0.5, 24, and 72 h, at temperature of $21 \pm 2^\circ\text{C}$, pH of 7.1 and rotation speed of 8 rpm, shown in Table B.2, suggest that concentrations of most PFCs underwent changes over time due to biodegradation of precursors present in landfill leachate.

Figure B.3 compares the PFCA concentrations in blank-corrected landfill leachate and distilled water after 3 days of contact with carpet fibre at temperature of $21 \pm 2^\circ\text{C}$, pH of 7.1 and rotation speed of 8 rpm.

Table B.1: Preliminary tests - concentrations of different PFCs in leachate/distilled water after contacting with carpet fibre for 0.5, 1, 2, 4, 10, 24 and 72 h. The experiments were conducted at temperature of 21± 2°C, pH of 7.1 and a rotation speed of 8 rpm.

Media	time (h)	PFBA (ng/L)	PFPA (ng/L)	PFHxA (ng/L)	PFHpA (ng/L)	PFOA (ng/L)	PFNA (ng/L)	PFDA (ng/L)	PFUnA (ng/L)	PFDoA (ng/L)	PFTA (ng/L)	PFBS (ng/L)	PFHxS (ng/L)	PFOS (ng/L)	PFDS (ng/L)	FOSA (ng/L)
Leachate/Fibre	0.5	645	1698	2192	1935	1292	1658	957	430	58	28	96	221	95	1	*BMDL
	1	422	1881	3176	3810	1953	2000	1114	281	60	21	92	164	96	*BMDL	*BMDL
	2	450	2130	3591	5129	2319	2743	1122	306	54	17	96	147	87	*BMDL	*BMDL
	4	635	2716	5674	7163	3702	3505	2050	475	111	30	78	140	96	*BMDL	*BMDL
	10	946	3802	6751	10445	4352	4874	1949	557	106	21	96	124	82	*BMDL	*BMDL
	24	1370	5970	10034	16674	5949	6891	2116	683	96	16	84	82	64	*BMDL	*BMDL
	72	1714	7589	13403	17294	5772	5900	1860	477	64	11	74	41	37	*BMDL	*BMDL
Water/Fibre	72	1173	6471	11401	16830	5711	7600	2649	1099	235	36	3	*BMDL	35	*BMDL	*BMDL

* Below Method Detection Limit.

Table B.2: Preliminary tests - concentrations of different PFCs in blank leachate samples after 0, 0.5, 24, and 72 h, at temperature of 21± 2°C, pH of 7.1 and a rotation speed of 8 rpm.

Media	time (h)	PFBA (ng/L)	PFPA (ng/L)	PFHxA (ng/L)	PFHpA (ng/L)	PFOA (ng/L)	PFNA (ng/L)	PFDA (ng/L)	PFUnA (ng/L)	PFDoA (ng/L)	PFTA (ng/L)	PFBS (ng/L)	PFHxS (ng/L)	PFOS (ng/L)	PFDS (ng/L)	FOSA (ng/L)
Leachate/Fibre	0	0	146	272	495	154	268	16	11	4	0.5	*BMDL	99	242	182	*BMDL
	0.5	1	220	312	539	148	274	17	14	1	*BMDL	*BMDL	123	237	175	*BMDL
	24	24	134	511	466	160	261	14	15	2	0.5	*BMDL	117	246	190	*BMDL
	72	72	263	1084	556	190	323	19	18	2	0.4	*BMDL	126	263	216	*BMDL

* Below Method Detection Limit.

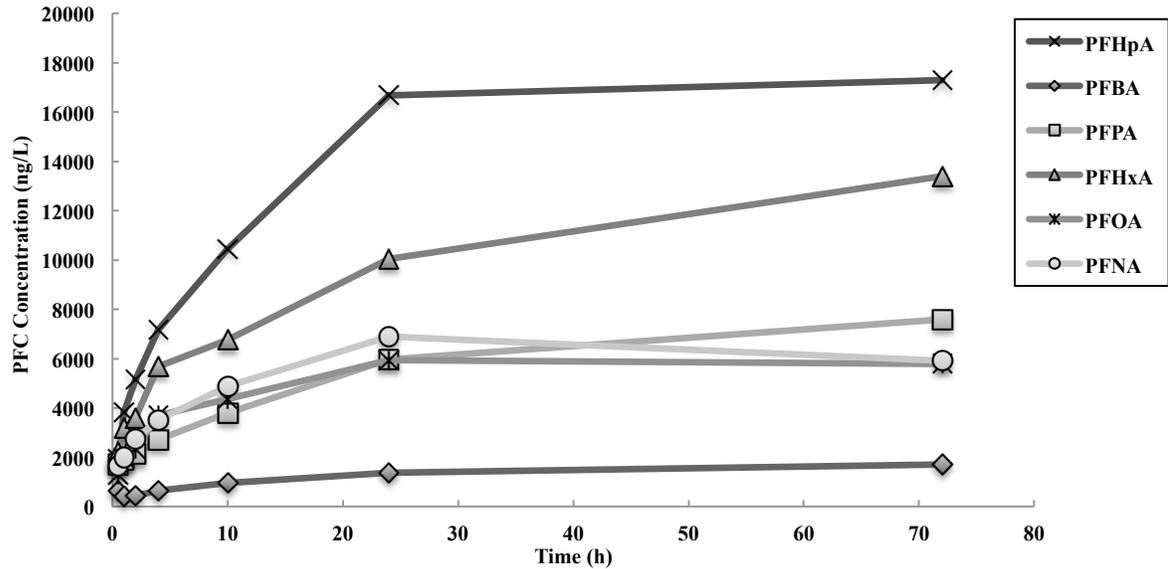


Figure B.1: Concentrations of different PFCAs in leachate after contacting with carpet fibre for 0.5, 1, 2, 4, 10, 24 and 72 h. The experiments were conducted at temperature of $21 \pm 2^\circ\text{C}$, pH of 7.1 and rotation speed of 8 rpm.

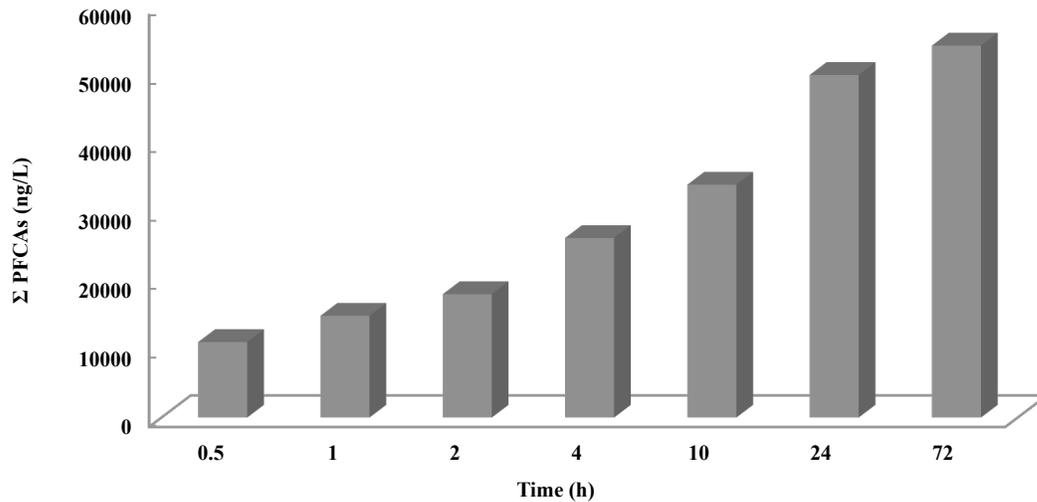


Figure B.2: Summation of PFCAs in leachate after contacting with carpet fibre for 0.5, 1, 2, 4, 10, 24 and 72 h. The experiments were conducted at temperature of $21 \pm 2^\circ\text{C}$, pH of 7.1 and rotation speed of 8 rpm.

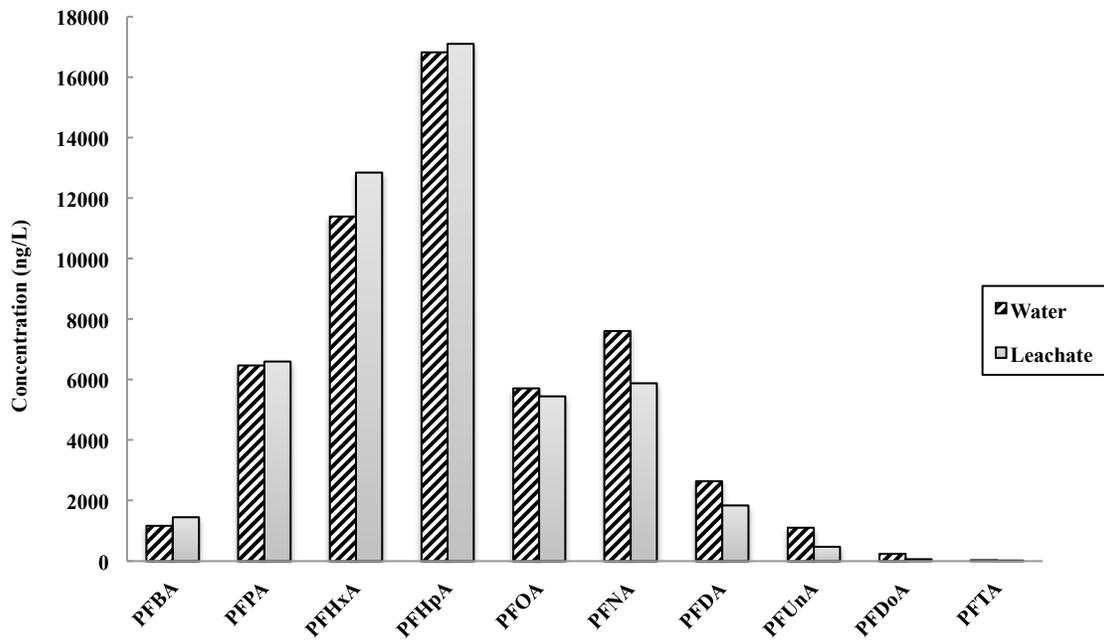


Figure B.3: Comparison of PFCA concentrations in blank-corrected landfill leachate and distilled water after 3 days of contact with carpet fibre at temperature of $21 \pm 2^\circ\text{C}$, pH of 7.1 and rotation speed of 8 rpm.

Appendix C: Raw data and recoveries for carpet samples

Table C.1: Raw data for carpet analysis for samples before and after contact with leachate or distilled water. Note that the experiments were conducted in triplicate, with tabulated values being the average of the three determinations.

Description	Weight (g)	PFBA (ng/g)	PFPA (ng/g)	PFHxA (ng/g)	PFHpA (ng/g)	PFOA (ng/g)	PFNA (ng/g)	PFDA (ng/g)	PFUnA (ng/g)	PFDoA (ng/g)	PFTA (ng/g)	PFBS (ng/g)	PFHxS (ng/g)	PFOS (ng/g)	PFDS (ng/g)	FOSA (ng/g)
Blank Carpet-1 (spiked)	1.00	75.21	74.37	83.98	89.38	87.69	84.32	104.55	101.18	71.92	86.85	61.97	72.43	81.62	75.13	96.96
Blk Carpet-2 (spiked)	1.00	113.37	93.00	90.35	80.96	78.92	90.35	100.97	106.29	73.52	89.46	72.81	79.36	87.95	70.95	115.15
Blk carpet-3 (spiked)	1.00	94.34	91.89	93.30	80.00	89.53	100.00	118.87	112.26	76.60	100.94	69.25	70.38	96.23	81.70	122.64
Blk carpet 1	1.14	7.10	23.27	3.30	3.58	0.73	1.52	0.70	0.62	0.32	0.63	0.46	0.72	0.69	0.46	0.15
Blk carpet 2	1.24	6.54	21.43	3.04	3.30	0.67	1.40	0.65	0.57	0.30	0.58	0.43	0.66	0.63	0.42	2.81
Blk carpet 3	1.08	7.54	24.70	3.50	3.80	0.77	1.61	0.75	0.65	0.34	0.67	0.49	0.76	0.73	0.49	2.36
N4	3.88	12.37	170.10	165.72	324.74	58.76	188.66	93.81	21.47	29.90	20.03	0.14	0.21	1.54	0.14	0.07
N4-A	3.87	6.72	173.60	153.97	297.08	55.80	186.00	91.45	23.77	30.74	22.78	0.14	0.21	2.16	0.14	0.07
N4-B	3.80	8.05	171.80	162.06	284.14	59.19	182.32	90.24	22.23	29.99	22.60	0.14	0.22	2.29	0.14	0.08
N5	3.70	3.95	56.52	89.78	151.70	35.69	108.98	50.30	18.85	9.73	9.73	0.14	3.79	3.70	0.14	0.08
N5-A	4.24	5.29	57.84	100.33	142.12	38.48	99.86	56.66	19.19	10.48	13.64	0.12	5.34	4.77	0.12	0.07
N5-B	3.48	2.33	52.62	94.02	158.71	39.97	104.08	57.22	21.51	10.67	11.56	0.15	5.09	5.15	0.15	0.08
N6	1.83	10.08	115.62	215.34	149.04	121.64	138.63	267.40	79.45	165.48	304.66	8.49	0.68	95.34	0.29	14.03
N6-A	2.18	7.02	109.22	146.40	99.59	98.67	131.71	312.53	90.87	251.03	370.81	0.24	0.38	67.92	0.74	13.63
N6-B	1.97	8.50	81.93	150.13	119.59	90.08	107.38	240.71	73.79	124.68	199.49	0.27	0.04	66.67	2.04	13.74
N7	3.10	2.62	16.88	34.86	83.93	12.88	34.54	15.56	4.33	2.56	3.36	0.17	0.27	28.83	0.17	0.09
N7-A	3.81	2.13	6.98	33.61	38.34	7.25	24.26	10.82	3.94	1.68	2.78	0.14	0.56	28.36	0.14	0.08
N7-B	3.46	2.34	6.33	28.43	50.27	8.99	27.74	10.78	1.74	1.08	2.55	0.15	0.24	22.22	0.15	0.08
N8	3.16	2.57	8.41	1.19	1.29	0.26	0.55	0.25	0.22	0.12	0.23	0.17	0.26	3.51	0.17	0.09

Table C.1 (Continued): Raw data for carpet analysis for samples before and after contact with leachate or distilled water.

Description	Weight (g)	PFBA (ng/g)	PFPA (ng/g)	PFHxA (ng/g)	PFHpA (ng/g)	PFOA (ng/g)	PFNA (ng/g)	PFDA (ng/g)	PFUnA (ng/g)	PFDoA (ng/g)	PFTA (ng/g)	PFBS (ng/g)	PFHxS (ng/g)	PFOS (ng/g)	PFDS (ng/g)	FOSA (ng/g)
N8-A	3.87	2.09	6.86	0.97	1.06	0.21	0.45	0.21	0.18	0.10	0.19	0.14	0.21	2.71	0.14	0.07
N8-B	3.41	2.38	7.79	1.11	1.20	0.24	0.51	0.24	0.21	0.11	0.21	0.15	0.24	0.16	0.15	0.08
Rotation:0rpm Time: 6h	5.34	1.52	22.84	40.43	68.89	22.28	51.67	55.60	13.29	29.76	37.81	0.10	0.15	13.55	0.10	2.64
Rotation:0rpm Time: 6h (A)	4.79	1.49	12.61	23.18	23.18	14.95	23.39	43.23	18.36	26.94	34.67	0.11	0.17	13.95	0.11	3.15
Rotation:0rpm Time: 6h (B)	4.66	2.23	22.55	43.38	64.85	24.05	44.02	58.19	21.69	24.05	35.43	0.11	1.69	14.75	0.11	3.89
Time:168 h Rotation:0rpm	4.92	1.65	4.25	11.71	29.48	11.26	33.96	33.96	9.66	10.31	17.06	0.11	4.35	12.73	0.11	2.07
Time:168 h Rotation:0rpm(A)	6.58	0.38	2.96	10.09	19.61	9.32	23.71	33.14	7.96	16.26	20.06	0.08	0.82	11.28	0.08	2.46
Time:168 h Rotation:0rpm(B)	6.00	0.35	2.82	11.88	26.50	11.85	29.00	34.84	9.98	11.78	18.84	0.09	3.58	12.78	0.09	2.12
Time: 6h Temp: 5C	4.94	2.29	30.97	57.49	80.77	27.13	64.17	56.68	17.11	17.79	30.97	0.11	2.35	13.48	0.11	2.37
Time: 6h Temp: 5C (A)	4.73	1.72	12.44	39.13	63.24	20.60	44.84	49.92	9.96	28.13	34.90	0.11	0.17	13.87	0.11	2.58
Time: 6h Temp: 5C (B)	5.40	1.94	25.74	48.69	78.69	28.70	45.92	57.03	16.81	24.25	40.92	0.10	0.60	15.55	0.10	2.96
Carpet contacted w/ N62, 6hr, 20C	4.72	2.16	24.36	39.19	56.78	22.67	60.59	53.18	16.29	19.72	26.27	0.11	1.28	13.07	0.11	3.26
Distilled water pH:7	6.04	1.34	13.74	27.32	42.05	15.50	31.46	43.54	8.64	21.52	23.18	0.09	0.14	10.02	0.09	2.85
Distilled water pH:7 (A)	4.79	1.69	15.88	31.10	37.36	15.72	29.64	43.41	10.48	20.52	20.77	0.11	0.17	7.99	0.11	3.24
Distilled water pH:7 (B)	4.41	1.88	22.60	36.04	65.05	18.47	42.61	45.56	17.07	17.04	24.71	0.12	7.39	13.51	0.12	2.18
Carpet N8 Time:6h	4.79	1.70	5.55	0.79	0.85	0.17	0.36	0.17	0.15	0.87	0.15	0.11	0.17	2.11	0.11	0.06
Carpet N8 Time:6h (A)	5.08	1.60	5.24	0.32	0.81	0.16	0.34	0.16	0.14	0.65	0.14	0.10	0.16	2.34	0.10	0.06
Carpet N8 Time:6h (B)	4.50	1.19	5.91	0.84	0.73	0.18	0.38	0.18	0.16	0.90	0.16	0.12	0.18	1.98	0.12	0.06
Time: 24 h Temp: 35 C	7.83	1.04	6.41	12.41	15.84	6.32	22.22	23.88	8.40	9.53	17.37	0.07	1.27	4.96	0.07	0.67
Time: 24 h Temp: 35 C (A)	6.30	1.29	4.37	8.28	20.97	9.04	29.22	39.39	8.61	16.68	18.42	0.08	0.94	12.90	0.08	2.05

Table C.1 (Continued): Raw data for carpet analysis for samples before and after contact with leachate or distilled water.

Description	Weight (g)	PFBA (ng/g)	PFPA (ng/g)	PFHxA (ng/g)	PFHpA (ng/g)	PFOA (ng/g)	PFNA (ng/g)	PFDA (ng/g)	PFUnA (ng/g)	PFDoA (ng/g)	PFTA (ng/g)	PFBS (ng/g)	PFHxS (ng/g)	PFOS (ng/g)	PFDS (ng/g)	FOSA (ng/g)
Time: 24 h Temp: 35 C (B)	4.77	1.70	3.38	8.85	20.48	9.36	30.84	37.98	8.75	19.87	22.45	0.11	1.12	12.32	0.11	2.41
Time: 24 h Temp: 35 C (C)	5.50	1.48	4.11	9.21	21.11	8.79	24.93	35.30	8.30	18.09	20.01	0.10	0.67	9.39	0.10	1.97
Time: 24 h Temp: 35 C (D)	6.38	1.27	3.93	7.43	18.96	5.64	18.33	18.02	4.59	10.37	23.03	0.08	1.80	4.04	0.08	1.44
Reagent Blank	1.00	8.11	26.57	3.77	4.09	0.83	1.73	0.80	0.70	0.37	0.72	0.53	0.82	0.79	0.53	0.29
Reagent Blank A	1.00	8.11	26.57	3.77	4.09	0.83	1.73	0.80	0.70	0.37	0.72	0.53	0.82	0.79	0.53	0.29
Reagent Blank B	1.00	8.11	26.57	3.77	4.09	0.83	1.73	0.80	0.70	0.37	0.72	0.53	0.82	0.79	0.53	0.29
Reagent Blank	1.00	8.11	26.57	3.77	4.09	0.83	1.73	0.80	0.70	0.37	0.72	0.53	0.82	0.79	0.53	0.29
Time: 6 h Temp: 20C	5.25	1.57	18.55	46.14	59.29	23.64	54.91	57.39	19.45	35.65	67.30	0.10	1.14	12.53	0.10	2.23
Time: 6 h Temp: 20C (A)	4.58	1.17	24.23	33.84	58.28	22.92	53.92	57.41	13.38	33.40	38.64	0.12	0.18	17.11	0.11	3.36
Time: 6 h Temp: 20C (B)	4.72	1.72	5.63	0.80	0.89	0.18	1.00	1.06	0.51	0.48	0.76	0.11	0.17	0.14	0.11	0.06
Distilled water pH: 7	6.04	1.34	13.74	27.32	42.05	15.50	31.46	43.54	8.64	21.52	23.18	0.09	0.14	10.02	0.09	2.85
Distilled water pH: 7 (A)	4.79	1.69	15.88	31.10	37.36	15.72	29.64	43.41	10.48	20.52	20.77	0.11	0.17	7.99	0.11	3.24
Distilled water pH: 7 (B)	4.41	1.88	22.60	36.04	65.05	18.47	42.61	45.56	17.07	17.04	24.71	0.12	7.39	13.51	0.12	2.18

Table C.2: Recovery percentages for carpet samples before contact.

Sample Name	¹³ C-PFBA Accuracy (%)	¹³ C-PFHxA Accuracy (%)	¹³ C-PFOA Accuracy (%)	¹³ C-PFNA Accuracy (%)	¹³ C-PFDA Accuracy (%)	¹³ C PFOS Accuracy (%)
N4-A	68	142	243	157	152	173
N4-B	73	126	241	136	123	149
N4-C	87	152	264	161	156	154
Mean (N4)	76	140	249	151	144	159
S.Dev (N4)	10	13	13	13	18	13
N5-B	100	150	175	143	172	133
N5-A	126	166	218	169	186	165
N5-C	57	54	63	55	52	61
Mean (N5)	94	123	152	122	137	119
S.Dev (N5)	35	60	80	60	74	53
N6-A	138	142	159	159	162	155
N6-B	58	45	67	53	53	61
N6-C	130	120	152	189	144	154
Mean (N6)	109	102	126	134	120	123
S.Dev (N6)	44	51	52	71	58	54
N7-A	175	173	195	148	198	179
N7-B	183	152	212	167	195	242
N7-C	264	179	251	216	240	173
Mean (N7)	207	168	219	177	211	198
S.Dev (N7)	49	14	29	35	25	38
N8-A	158	200	145	88	64	132
N8-B	138	140	126	80	61	104
N8-C	64	53	66	64	63	64
Mean (N8)	120	131	112	77	63	100
S.Dev (N8)	50	74	41	12	2	34

Table C.3: Efficiencies for extraction of different PFCs from carpet samples.

Sample No.	PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTA	PFBS	PFHxS	PFOS	PFDS	FOSA
*E.E (%) N ₄	100	100	99	99	100	99	99	100	100	100	100	100	95	100	100
E.E (%) N ₅	100	100	100	99	100	98	98	98	100	100	100	100	94	100	100
E.E (%) N ₆	100	100	98	98	100	98	98	97	98	99	100	100	99	100	100
E.E (%) N ₇	100	100	100	96	100	98	100	100	100	100	100	100	99	100	100
E.E (%) N ₈	100	100	100	100	100	100	100	100	100	100	100	100	99	100	100

* Extraction Efficiency

Appendix D: Raw data, recoveries and characteristics of leachate samples

Table D.1: Recovery percentages for leachate samples.

Media/Carpet	Sample ID	Time (h)	pH	Temp (°C)	Rot. speed (rpm)	¹³ CPFBA Accuracy (%)	¹³ CPFHxA Accuracy (%)	¹³ CPFOA Accuracy (%)	¹³ CPFNA Accuracy (%)	¹³ CPFDA Accuracy (%)	¹³ CPFOS Accuracy (%)
Lab Blank 1	N/A	N/A	N/A	N/A	N/A	109	98	95.7	101	85.4	87.1
Lab Blank 2	N/A	N/A	N/A	N/A	N/A	130	99.4	99.5	122	125	109
Lab Blank 3	N/A	N/A	N/A	N/A	N/A	129	96.5	121	128	135	119
Leachate Blank 1	N/A	N/A	N/A	N/A	N/A	80.5	73.5	113	129	127	97
Leachate Blank 2	N/A	N/A	N/A	N/A	N/A	57.8	52.2	89.7	106	102	75.3
Leachate Blank 3	N/A	N/A	N/A	N/A	N/A	59.2	55.2	93.6	107	111	77.8
Leach Spike 1	N/A	N/A	N/A	N/A	N/A	60.4	57.7	86.2	99	106	68.6
Leach Spike 2	N/A	N/A	N/A	N/A	N/A	51.8	55.4	97.7	105	103	74.3
Leach Spike 3	N/A	N/A	N/A	N/A	N/A	51.1	54.6	93.2	107	118	77.9
Leachate/Composite	L1	2	6	15	8	55.2	67	85.9	96.1	81.8	84.2
Leachate/Composite	L2	1	6	15	8	90.6	97.3	121	130	133	102
Leachate/Composite	L3	1	6	15	8	98.5	103	133	150	151	120
Leachate/Composite	L6	24	6	15	8	44.3	56	74.4	72.6	102	62.2
Leachate/Composite	L7	24	6	15	8	49.2	60.4	82.8	87.1	98.7	69.9
Leachate/Composite	L8	6	6	15	8	57.2	76.9	99.3	104	102	72.4
Leachate/Composite	L9	6	6	15	8	70.7	83.2	113	126	115	122
Leachate/Composite	L10	2	6	15	8	55.3	79.9	97.7	97.8	106	61.3
MeOH	MeOH	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
MeOH	MeOH	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
1 ppb	1 ppb	N/A	N/A	N/A	N/A	84.8	93.4	91.8	94.9	84.8	89
MeOH	MeOH	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
MeOH	MeOH	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Leachate/Composite	L11	6	6	15	0	48.5	66.6	80.9	93	88.4	63
Leachate/Composite	L12	6	6	15	0	58.6	70.9	95.6	96.9	87.4	65.6
Blank Leachate	L13	168	6	15	8	58	57	81.4	89.6	77.3	61.7
Leachate/Composite	L14	168	6	15	8	32.4	57	80.4	86.7	81.6	50.7
Leachate/Composite	L15	168	6	15	8	52.5	80.2	100	107	101	67.5
Leachate/Composite	L16	6	7	15	8	48.4	74.4	90.7	104	90	67.4
Leachate/Composite	L17	6	7	15	8	27.2	52.3	70	66.9	59.7	50.3
Leachate/Composite	L18	6	5	15	8	53.4	71	122	111	98.7	67.7
Leachate/Composite	L19	6	5	15	8	64.6	64.4	86.6	80.1	63.2	48.3
Leachate/Composite	L20	6	6	15	8	40.6	92.8	128	130	120	81.7
Leachate/Composite	L21	6	5	15	8	120	128	132	125	96.7	92.9
Leachate/Composite	L22	6	6	15	8	54.1	76.7	93.8	100	95.8	62.5
Leachate/Composite	L23	6	8	15	8	54.7	84.8	104	106	102	93

Table D.1 (Continued): Recovery percentages for leachate samples.

Media/Carpet	Sample ID	Time (h)	pH	Temp (°C)	Rot. speed (rpm)	¹³ CPFBA Accuracy (%)	¹³ CPFHxA Accuracy (%)	¹³ CPFOA Accuracy (%)	¹³ CPFNA Accuracy (%)	¹³ CPFDA Accuracy (%)	¹³ CPFOS Accuracy (%)
Leachate/Composite	L24	6	8	15	8	60.6	75.6	123	127	112	101
Leachate Blank	L25	6	6	15	8	75.7	88	128	138	119	96.5
Water/Composite	L26	6	7	15	8	119	138	132	121	106	123
Water/Composite	L27	6	8	15	8	64.9	101	99.4	96.5	80.3	60.9
Water/Composite	L28	6	5	15	8	121	131	137	129	98.2	76.5
Water/Composite	L29	6	8	15	8	92.5	143	129	117	104	85.2
Leachate Blank	L30	6	6	15	8	45.2	55.5	96	98.6	94.2	71.1
MeOH	MeOH	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
MeOH	MeOH	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
1 ppb	1 ppb	N/A	N/A	N/A	N/A	77.9	104	124	117	105	105
MeOH	MeOH	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
MeOH	MeOH	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Water/Composite	L31	6	6	15	8	94.5	119	124	117	98.2	76.5
Water Blank	L32	6	N/A	15	8	66.8	97.5	96.5	103	83.7	79
Water/Composite	L33	6	6	15	8	113	139	134	127	106	77.6
Water/Composite	L34	6	7	15	8	88.2	158	142	130	105	77.6
Leachate Blank	L35	6	6	15	8	41.8	54.2	97.3	101	93.9	71.7
Leachate/Composite	L36	24	6	35	8	64.6	106	125	116	86.2	60.2
Leachate/Composite	L37	24	6	35	8	52.9	70.3	79.5	75.1	65.6	53.1
Leachate/Composite	L38	2	6	35	8	70.9	75.2	116	115	94	72.2
Leachate/Composite	L39	2	6	35	8	66.1	79.8	134	127	106	75.1
Leachate/Composite	L40	2	6	5	8	49.4	70.8	96.2	96	82.8	83
Leachate/Composite	L41	24	6	5	8	57.7	96.8	128	136	121	88.9
Leachate/Composite	L42	24	6	5	8	48.5	72.2	87.3	83.3	83.1	67.1
Leachate/Composite	L43	6	6	35	8	51.3	73.5	116	108	96.7	90.7
Leachate/Composite	L44	6	6	35	8	67.2	112	112	111	92.9	75.1
Leachate/Composite	L45	6	6	15	8	54	85.1	128	139	140	88.6
Leachate Blank	L46	6	6	15	8	46.5	64.8	100	113	105	80.5
Leachate/Composite	L47	6	6	5	8	74.6	90.5	135	128	99.7	88.5
Leachate/Composite	L48	6	6	5	8	80.9	72.3	124	114	84.2	82.1
Leachate/Composite	L49	2	6	5	8	53.2	71.8	94	96.2	96.8	74.3
Leachate/ N6	L50	6	6	15	8	69.4	64.6	89.2	94.1	87	71.8
Leachate/N7	L51	6	6	15	8	33.7	37	56.1	50.2	45.7	46.4
Leachate/N7	L52	6	6	15	8	43.5	47.2	57.2	56.5	50.7	47.2
Leachate/N8	L53	6	6	15	8	97.4	89.6	105	79.7	41.5	85
Leachate/N8	L54	6	6	15	8	122	119	141	91.6	57	51.6

Table D.1 (Continued): Recovery percentages for leachate samples.

Media/Carpet	Sample ID	Time (h)	pH	Temp (°C)	Rot. speed (rpm)	¹³ CPFBA Accuracy (%)	¹³ CPFHxA Accuracy (%)	¹³ CPFOA Accuracy (%)	¹³ CPFNA Accuracy (%)	¹³ CPFDA Accuracy (%)	¹³ CPFOS Accuracy (%)
Leachate/N4	L55	6	6	15	8	55.8	123	123	111	76.4	98.7
Leachate/N4	L56	6	6	15	8	81.5	132	146	137	106	114
Leachate/N5	L57	6	6	15	8	54	68.4	103	108	103	78.2
Leachate/N5	L58	6	6	15	8	17.3	24.7	42.1	38.2	32.4	27.6
Leachate/ N6	L59	6	6	15	8	49.4	56.6	84.9	83.1	79	82.2
Leachate/ Composite	L60	6	6	15	4	60.4	87.3	112	106	109	120
Leachate/ N6	L61	6	6	20	8	77.4	59.6	120	112	82.5	72.7
Blank Leachate	L62	6	6	15	8	67.4	76.7	125	140	123	90.6
Leachate/ Composite	L63	6	6	15	4	48.5	53.5	79	80.8	75.7	67.5

Table D.2: Raw data for PFC amounts (ng) in leachate samples. Note that the sample IDs correspond to those introduced in Table D.1 (N.D. stands for non-detectable).

Sample ID	PFBA (ng)	PFPA (ng)	PFHxA (ng)	PFHpA (ng)	PFOA (ng)	PFNA (ng)	PFDA (ng)	PFUnA (ng)	PFDoA (ng)	PFTA (ng)	PFBS (ng)	PFHxS (ng)	PFOS (ng)	PFDS (ng)	FOSA (ng)
L1	2.78	25.2	59.4	66.7	20.5	31.9	16.3	5.97	11.4	17.3	N.D.	3.56	5.41	N.D.	0.0241
L2	N.D.	26.2	40.4	37	12.9	22.4	15.1	3.76	7.12	8.26	0.494	2.5	4.12	N.D.	0.0194
L3	N.D.	17.9	38.2	34.8	12.1	19.9	14.7	3.53	7.86	8.6	0.31	2.25	5.83	N.D.	0.0251
L6	5.62	58	93.9	93.7	27.9	41.4	17.8	7.9	12.6	19	N.D.	2.66	5.1	N.D.	0.126
L7	6.63	56.3	85.5	88.2	25.2	42	20.5	8.36	13.4	21.6	0.418	2.48	5.6	N.D.	0.125
L8	6.22	32	93.6	76.2	26.3	38.7	18.9	4.74	15.3	28.5	N.D.	2.91	6.32	N.D.	0.0342
L9	6.03	33.8	62.1	60.3	18.6	31	14.8	5.57	10	18.8	N.D.	2.25	3.62	N.D.	0.0208
L10	3.45	43.7	49.7	59.6	18.4	34.8	16.7	4.23	8.11	12.9	N.D.	3.27	5.13	N.D.	0.0287
MeOH	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
MeOH	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
1 ppb	4.1	3.8	3.97	4.17	4.16	4.05	4.37	5.42	4.81	5.68	4.06	4.23	4.18	3.69	4.46
MeOH	N.D.	N.D.	194	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
MeOH	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
L11	8.59	28.3	64.7	64.4	21.8	29.1	21.9	5.17	6.59	4.93	1.09	3.03	7.12	N.D.	0.0677
L12	9.33	26.6	49	62.8	19.4	31	23.7	5.25	7.31	5.75	N.D.	2.85	6.32	N.D.	0.0621
L13	3.04	28.3	16.7	6.25	5.87	0.895	1.23	0.531	0.865	1	0.503	3	3.2	N.D.	0.0424
L14	7.25	44.5	101	113	31	45.5	21.9	9.96	22.8	47.1	N.D.	2.58	4.92	N.D.	0.111
L15	7.9	37.7	102	97.9	28.7	41.4	18.8	8.06	15.9	33	N.D.	2.23	4.55	N.D.	0.0989
L16	10.5	29.7	72.6	81.3	23.4	40	21.1	7.28	12.9	32.6	N.D.	3.66	6.5	N.D.	0.0696
L17	9.6	27.3	77.6	90.4	25.6	45	25.5	9.11	15.5	33.3	0.357	3.55	7.56	N.D.	0.0893
L18	5.85	31.1	59.7	66.9	19.4	28.9	17.2	5.31	14.9	29.2	N.D.	2.88	8.53	N.D.	0.0709
L19	7.05	34.5	60.6	72.7	22.3	36	18.6	7.02	18.5	35.2	N.D.	3.03	4.95	N.D.	0.0774
L20	6.72	30.8	69.9	71.7	20.1	35.8	16.7	4.6	11.2	28.1	N.D.	3.06	4.53	N.D.	0.0502

Table D.2 (Continued): Raw data for PFC amounts (ng) in leachate samples. Note that the sample IDs correspond to those introduced in Table D.1 (N.D. stands for non-detectable).

Sample ID	PFBA (ng)	PFPA (ng)	PFHxA (ng)	PFHpA (ng)	PFOA (ng)	PFNA (ng)	PFDA (ng)	PFUnA (ng)	PFDoA (ng)	PFTA (ng)	PFBS (ng)	PFHxS (ng)	PFOS (ng)	PFDS (ng)	FOSA (ng)
L21	3.18	38.9	60.8	101	22.9	45.5	26.5	4.3	11.4	27.3	N.D.	0.643	3.46	0.18	0.0161
L22	5.83	33	72	77.3	23.4	42.6	25.9	7.11	18.2	37.3	N.D.	3.17	7.66	N.D.	0.154
L23	8.34	24	62.3	70.2	20.1	39.5	21.2	8.35	10.9	23.1	N.D.	3.09	5.76	N.D.	0.155
L24	7.37	25.9	56.2	63.7	19.5	37.6	22.3	7.54	11.5	21.6	0.684	2.66	5.26	N.D.	0.17
L25	2.52	15.3	9.33	4.52	3.93	0.491	0.892	0.197	0.323	0.447	N.D.	2.14	2.78	N.D.	N.D.
L26	4.05	39.9	55.2	82.2	20.1	47	28.1	5.83	9.52	25.2	N.D.	0.649	4.53	N.D.	0.0693
L27	3.68	41.4	71.7	101	23	53.3	31.8	7.8	6.74	18.1	N.D.	0.972	5.37	N.D.	0.127
L28	4.19	39.9	60.2	101	23.1	46.4	27.4	5.2	11.6	28.4	N.D.	0.894	3.94	N.D.	0.0347
L29	3.29	38.4	61	93.3	20.2	50	26.9	7.05	6.35	13.7	N.D.	0.857	3.78	N.D.	0.118
L30	6.54	30.9	18.8	14.3	8.42	7.26	5.74	1.93	1.88	1.35	N.D.	2.27	3.02	N.D.	0.0245
MeOH	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
MeOH	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
1 ppb	3.93	4.03	3.94	4.02	4.19	3.92	4.05	4.45	N.D.	6.24	3.92	3.99	4.06	2.49	3.9
MeOH	N.D.	N.D.	N.D.	80.5	22.9	38.6	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
MeOH	N.D.	N.D.	41.7	130	37.7	60.2	23.9	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
L31	3.12	45.2	58.9	87.7	20.4	47.5	27.3	5.38	8.92	21.2	0.529	0.491	4.08	N.D.	0.0743
L32	N.D.	N.D.	N.D.	0.391	N.D.	0.174	0.02	0.01	0.183	0.335	N.D.	N.D.	N.D.	N.D.	N.D.
L33	3.5	47.3	61.7	96.8	23.4	49.5	31.8	6.75	11.4	23.1	0.47	0.618	4.63	N.D.	0.0997
L34	4.02	39	61.7	96.4	19.6	46.7	27.7	6.11	9.38	25.8	N.D.	0.589	3.59	N.D.	0.0537
L35	3.26	15.6	17.2	4.28	4.21	0.272	0.512	0.143	0.327	0.655	0.289	2.75	3.49	N.D.	N.D.
L36	12.7	45.9	111	137	32.5	49.1	23.8	8.92	13.9	37.2	N.D.	2.31	8.64	N.D.	0.0891
L37	9.99	49.1	106	134	36.6	57.4	25.5	11.5	17.2	47.6	N.D.	2.13	8.31	N.D.	0.124
L38	5.23	66.1	73	89.6	27.5	43.4	27	7.91	16.2	31.9	N.D.	3.28	6.04	N.D.	0.041
L39	4.29	67.1	71.9	87.7	25.2	46.2	25.5	7.79	16.1	34.5	N.D.	3.61	7.44	N.D.	0.0438

Table D.2 (Continued): Raw data for PFC amounts (ng) in leachate samples. Note that the sample IDs correspond to those introduced in Table D.1 (N.D. stands for non-detectable).

Sample ID	PFBA (ng)	PFPA (ng)	PFHxA (ng)	PFHpA (ng)	PFOA (ng)	PFNA (ng)	PFDA (ng)	PFUnA (ng)	PFDoA (ng)	PFTA (ng)	PFBS (ng)	PFHxS (ng)	PFOS (ng)	PFDS (ng)	FOSA (ng)
L40	3.1	22.5	36.8	47.6	15.7	26.4	19.6	8.39	15.9	27.2	N.D.	3.6	5.23	N.D.	
L41	1.11	34.8	51.7	69.3	20.5	31.7	11.5	4.35	12.2	36.4	0.585	2.78	3.27	0.373	0.00819
L42	3.34	38.7	59.6	78.3	22	38.5	15.4	5.5	19.5	43.4	N.D.	3.44	7.1	N.D.	0.0106
L43	6.4	48.5	74.1	82.8	23.6	43.7	20.9	6.44	12.8	28.6	0.542	2.04	7.13	N.D.	0.0362
L44	5.38	55.7	73.6	92.4	23.6	41.6	21.3	5.44	9.53	22.8	N.D.	2.54	5.67	N.D.	0.0249
L45	6.65	30	57.7	71	19.5	33.2	17	4.96	13.5	25.8	0.614	2.38	4.08	N.D.	0.0474
L46	5.61	25.1	16.1	5.32	4.55	0.792	0.477	0.196	0.251	0.577	N.D.	2.95	3.82	N.D.	N.D.
L47	1.54	31.3	39.3	54.5	16.4	23.2	14	3.85	12.8	32	N.D.	2.91	4.43	N.D.	0.016
L48	3.74	41	58.4	70.6	19.5	29.1	15.4	4.4	16.7	36.2	N.D.	3.26	6.36	N.D.	0.0109
L49	3.43	30.4	48.8	46.3	16.7	25.7	15	6.75	11.9	23.7	N.D.	3.37	5.08	N.D.	0.0423
L50	15.3	44.6	63.6	34.1	29.4	28.4	44.1	14.1	62.8	120	N.D.	3.32	10.2	N.D.	0.487
L51	13.2	44.7	34.4	42.9	12	15	5.77	1.95	1.87	3.93	N.D.	3.98	8.23	N.D.	N.D.
L52	16.2	44.4	30.1	28.6	9.34	11.9	4.79	2	1.88	3.77	N.D.	N.D.	6.65	N.D.	N.D.
L53	6.95	32.6	9.65	10.7	4.34	0.844	0.801	N.D.	2.89	9.45	N.D.	5.21	3.29	N.D.	N.D.
L54	3.69	28.2	13.6	6.66	2.93	0.479	0.224	N.D.	1.45	4.02	N.D.	4.87	2.2	N.D.	N.D.
L55	17	71.2	166	259	48.5	116	21	2.28	4.22	7.94	N.D.	3.91	1.99	N.D.	N.D.
L56	14.2	71.2	164	262	47.3	111	24.2	2.36	4.88	7.82	N.D.	3.87	2.33	N.D.	N.D.
L57	23.9	66.9	49.5	44.3	16.2	26.2	10.5	3.33	2.72	3.29	N.D.	2.43	2.14	N.D.	N.D.
L58	23.70	72.71	51.28	34.87	13.92	18.45	8.00	2.17	13.20	2.55	N.D.	2.27	1.58	N.D.	N.D.
L59	15.2	49.1	72.2	29.6	26.7	26.4	42.4	14.6	56.7	110	N.D.	2.9	9.01	N.D.	0.407
L60	13.2	32.2	77.7	80.1	23.3	38.9	19.7	6.87	11.3	26.7	N.D.	3.17	5.46	N.D.	0.0966
L61	6.48	105	72.8	72.8	20.8	37.4	18	5.63	16.2	41.1	N.D.	3.28	6.16	N.D.	0.00824
L62	5.89	5.45	7.55	5.56	4.32	1.3	1.58	0.88	0.752	0.857	N.D.	2.45	3.22	N.D.	0.00224
L63	11.9	34.6	78.5	88.2	26.1	40.1	20.9	8.03	15.4	32.1	N.D.	3.06	7.07	N.D.	0.102

Table D.3: Initial and final pH, Total Dissolved Solids (TDS) and electrical conductivity of leachate samples of different leaching experiments.

Media/Carpet	Time (h)	Mean Temp. (°C)	Rotation Speed (rpm)	¹ (pH) _i	² (pH) _f	³ (TDS) _i (mg/L)	⁴ (TDS) _f (mg/L)	⁵ (Cond) _i (µs/cm)	⁶ (Cond) _f (µs/cm)
Leachate/Composite	1	18	8	5.94	6.35	680	743	1403	1500
Leachate/Composite	1	18	8	5.95	6.34	679	752	1400	1517
Leachate/Composite	2	17	8	5.95	6.45	675	734	1385	1485
Leachate/Composite	2	17	8	5.98	6.48	674	745	1375	1502
Leachate/Composite	6	17	8	5.98	6.35	661	759	1366	1528
Leachate/Composite	6	17	8	6.01	6.39	663	774	1366	1557
Leachate/Composite	24	15	8	6.03	6.48	676	797	1389	1605
Leachate/Composite	24	15	8	6.03	6.47	675	801	1387	1612
Leachate/Composite	168	14	8	5.9	6.38	690	815	1402	1650
Leachate/Composite	168	14	8	5.89	6.42	689	806	1401	1632
Blank Leachate	168	14	8	5.91	6.1	675	673	1372	1370
Leachate/Composite	6	15	0	5.9	6.16	686	748	1414	1511
Leachate/Composite	6	15	0	5.91	6.15	684	746	1410	1506
Leachate/Composite	6	15	4	5.90	6.18	679	734	1400	1510
Leachate/Composite	6	15	4	5.93	6.21	683	753	1410	1528
Leachate/Composite	6	16	8	6.04	6.25	659	783	1348	1575
Leachate/Composite	5	16	8	5.08	5.73	658	936	1346	1871
Leachate/Composite	5	16	8	5.07	5.75	661	925	1352	1845
Leachate/Composite	7	16	8	7.01	7.04	676	734	1381	1480
Leachate/Composite	7	16	8	6.99	6.99	678	743	1382	1497
Blank Leachate	6	16	8	6.06	6.29	670	670	1379	1355
Leachate/Composite	8	16	8	7.95	7.53	766	816	1564	1640
Leachate/Composite	8	16	8	8.05	7.48	723	781	1479	1573
Leachate/Composite	6	14	8	6.04	6.46	674	771	1386	1554
Water/Composite	5	15	8	4.95	6.5	33.3	131	71.7	273
Water/Composite	5	15	8	4.92	6.35	35	161	76.5	333
Water/Composite	6	15	8	5.92	7.02	0.9	83.6	3	175.2
Water/Composite	6	15	8	5.94	7.1	0.7	81.2	2.53	170.1
Water/Composite	7	14	8	7.01	7.43	0.4	76	1.96	161
Water/Composite	7	14	8	7.05	7.5	0.2	88	0.74	184
Water/Composite	8	14	8	8.05	7.32	0	102.8	0.54	215
Water/Composite	8	14	8	8.08	7.45	0	81.6	0.53	172
Blank Leachate	6	15	8	6.04	6.38	672	685	1384	1406
Leachate/N ₄	6	14	8	5.9	6.32	671	717	1399	1450
Leachate/N ₄	6	14	8	5.91	6.33	673	709	1403	1434
Leachate/N ₅	6	14	8	5.9	6.28	674	703	1406	1424
Leachate/N ₅	6	14	8	5.9	6.26	674	696	1405	1410
Leachate/N ₆	6	14	8	5.92	6.4	668	826	1390	1658
Leachate/N ₆	6	14	8	5.94	6.42	667	831	1388	1670
Leachate/N ₇	6	14	8	5.91	6.31	669	816	1392	1642
Leachate/N ₈	6	15	8	5.9	6.32	680	723	1412	1459

Table D.3 (Continued): Initial and final pH, Total Dissolved Solids (TDS) and electrical conductivity of leachate samples of different leaching experiments.

Media/Carpet	Time (h)	Mean Temp. (°C)	Rotation Speed (rpm)	¹ (pH) _i	² (pH) _f	³ (TDS) _i (mg/L)	⁴ (TDS) _f (mg/L)	⁵ (Cond) _i (µs/cm)	⁶ (Cond) _f (µs/cm)
Leachate/N ₈	6	15	8	5.93	6.28	679	729	1410	1471
Leachate/Composite	6	15	8	6.03	6.47	677	766	1391	1544
Blank Leachate	6	15	8	5.92	6.2	679	678	1410	1371
Leachate/Composite	6	5	8	5.92	6.27	676	746	1410	1544
Leachate/Composite	6	5	8	5.93	6.3	679	723	1416	1488
Leachate/Composite	2	5	8	5.91	6.13	676	735	1410	1532
Leachate/Composite	2	5	8	5.92	6.12	675	739	1406	1541
Leachate/Composite	24	5	8	5.91	6.24	677	793	1411	1650
Leachate/Composite	24	35	8	5.93	6.26	677	792	1411	1649
Leachate/Composite	6	35	8	5.94	6.36	691	796	1427	1607
Leachate/Composite	6	35	8	5.92	6.34	680	791	1402	1596
Leachate/Composite	2	35	8	5.91	6.25	667	765	1356	1542
Leachate/Composite	2	35	8	5.94	6.3	683	774	1386	1561
Leachate/Composite	24	35	8	5.93	6.37	679	792	1385	1601
Leachate/Composite	24	35	8	5.92	6.38	682	781	1392	1579
Blank Leachate	6	20	8	6.01	6.22	685	678	1420	1369
Blank Leachate	6	35	8	5.94	6.19	686	690	1417	1411

¹ Initial pH measured before starting the experiment.

² Final pH measured at the end of the experiment.

³ Initial Total Dissolved Solids (TDS) measured before starting the experiment.

⁴ Final Total Dissolved Solids (TDS) measured at the end of the experiment.

⁵ Electrical Conductivity measured before starting the experiment.

⁶ Electrical Conductivity measured at the end of the experiment.