

PFC-Contaminated Soil and Its Remediation Strategies: A Review

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Abstract

This literature review summarizes the current state of knowledge on soil contamination with perfluorinated compounds (PFCs) along with information on remediation strategies. The paper discusses PFC presence, levels, sources, and fate in soil and emphasizes the current lack of feasible technologies available for PFC-contaminated soil remediation. The bulk of research into PFC remediation focuses on treatment in aqueous systems, which does not generally translate well to soil- or sediment-based environmental decontamination. Although evidence suggests that aqueous film-forming foams (AFFFs) are composed of hundreds of diverse fluorinated surfactants, perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) seem to dominate the vast majority of studies concerning remediation techniques. Possible soil remediation technologies including excavation and landfilling, soil flushing, soil washing, chemical immobilization, encapsulation, vitrification, incineration, and in-situ chemical oxidation have been assessed and their performances and costs have been compared. Most of the technologies, especially emerging technologies such as in-situ persulfate oxidation, need further testing to evaluate their effectiveness for PFC treatment and determine whether their full-scale application is feasible. It is believed that a complete destruction of PFCs would be the best long-term strategy and would facilitate future reclamation of contaminated land for agricultural and residential use.

1 Introduction

Fluorinated surfactants are a class of synthetic organofluorine chemical compounds. They can be polyfluorinated or perfluorinated. An important application area for fluorinated surfactants is their use in aqueous film forming foams (AFFFs) against fires fueled by hydrocarbons. Fluorinated surfactants have surface-tension lowering properties allowing them to prevent re-ignition of hydrocarbon-based fires by spreading over the flammable liquid and sealing in vapours during firefighting applications. Owing to the strength of the C-F bond, perfluorinated compounds (PFCs) are particularly useful because they will not be easily broken down by the high levels of heat from the fire. For example, perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) are two of the most common PFCs. These compounds, their salts and their precursors have a wide variety of applications as water, oil, soil and grease repellents, as well as firefighting foams.

However, due to their unique physiochemical properties, PFCs have been found to be environmentally persistent and bioaccumulative. In particular, PFOS and PFOA have been detected globally in the hydrosphere, atmosphere and biosphere. Currently, PFOS has been categorized as a persistent organic pollutant under the Stockholm Convention, due to its high persistence, bioaccumulation, long-range transport potential and toxic effects.

In Canada, the historical use of PFCs including PFOS and PFOA has impacted some federal contaminated sites, particularly those with firefighting training centres. Since PFCs are resistant to most conventional treatment technologies, these contaminants present a series of tough remediation challenges. In order to support the Federal Contaminated Sites Action Plan

(FCSAP) program for addressing the PFC-contaminated site issues, Environment Canada's Emergencies Science and Technology Section (ESTS) conducted a literature review to summarize the remediation strategies for PFC-contaminated soil. The chemical composition of AFFFs and occurrence and fate of PFCs in soil are also discussed.

2 Literature Reviewed

2.1 AFFF Composition

Commercial AFFFs are complex mixtures. They are proprietary in nature and typically contain fluorinated and nonfluorinated surfactants. Due to the proprietary nature of AFFF formulations, the chemical structures of the actual perfluorinated surfactants used in commercial AFFFs are not known.

Place and Field (2012) used fast atom bombardment mass spectrometry (FAB-MS) and high resolution quadruple-time-of-flight mass spectrometry (QTOF-MS) to identify chemical formulas for the fluorochemicals present in military-grade AFFF mixtures. Samples were collected from 21 US Navy and Air force bases with specifications that the AFFFs come from their original product container. The researchers were able to identify anionic, cationic, and zwitterionic fluorinated surfactants with variable alkyl chain lengths from 4 to 12. An overview of the identified compounds is provided in Table 1.

D'Agostino and Mabury (2013) also performed a compositional analysis of AFFFs using a combination of high resolution mass spectrometry and collision induced dissociation (CID) spectra to deduce the molecular formulas and structures of the unknown perfluoroalkyl compounds contained in the foam. The researchers identified 12 novel perfluoroalkyl classes and 10 more uncommonly reported classes totalling 103 unique fluorinated surfactant compounds also summarized in Table 1.

Studies have shown the potential for many complex PFCs to exist as precursors for PFOS and PFOA even under normal environmental or biological conditions. Xie et al. (2009) documented the biotransformation of *N*-EtFOSE to PFOS in rats, while Rhoads et al. (2008) reported the transformation of *N*-EtFOSE to *N*-EtFOSAA and its subsequent transformation to PFASs in activated sludge from wastewater treatment plants (WWTPs). Since 2002, 3M has voluntarily ceased production of fluorinated compounds based on the C₈ structure, including PFOS and PFOA (Lindstrom et al., 2011). The implementation of the EPA Stewardship Program has also helped to reduce production of AFFFs containing PFOS and PFOA but regulations set for potential precursors are limited.

Houtz et al. (2013) investigated the fate of perfluoroalkyl acid (PFAA) precursors in soil and groundwater impacted by AFFFs. Comparisons were made between fluorinated compounds originally present in AFFFs (i.e., 3M, National Foam, and Ansul) and the fluorinated compounds detected in soil and groundwater samples at sites where the foams were released. The concentrations of precursors in the soil were significantly less than what would be expected based on the ratios present in the foam formulations, indicating that transformation of the precursors may have occurred in the environment. Of the five C₆ precursors specifically identified in the AFFFs, only perfluorohexane sulfonamide amine (PFHxSaAm) was detected in the soil samples, suggesting complete degeneration of the other precursor compounds. Known precursors, 6:2 FtS, 8:2 FtS, FHxSA, and FOSA, were not detected in the original AFFF samples but were detected in the soil samples. The presence of these compounds could be the result of intermediate precursor formation due to biological or chemical transformation of the original precursors present in the foam after contact with the soil.

Table 1: Identities and Structures of Several PFCs Found in AFFFs.

Group	Basic Structure	Examples
Perfluoroalkyl Sulfonates ^a		PFBS PFHxS PFOS PFDS
Perfluoroalkyl Carboxylates ^a		PFBA PFHxA PFOA PFUdA
Perfluoroalkyl Sulfonamide ^b		FOSA
Perfluoroalkyl Sulfonamido Ethanol ^c		FOSE N-EtFOSE
Fluorotelomer Thioamido Sulfonates ^a		4:2 FtTAoS 6:2 FtTAoS 8:2 FtTAoS
Fluorotelomer Thiohydroxyl Ammonium ^c		4:2 FtSHA 6:2 FtSHA 8:2 FtSHA 10:2 FtSHA
Fluorotelomer Betaines ^a		5:3 FtB 7:3 FtB 9:3 FtB
Fluorotelomer Sulfonamido Betaines ^a		6:2 FtSaB 8:2 FtSaB 10:2 FtSaB 12:2 FtSaB
Fluorotelomer Sulfonamido Amines ^a		6:2 FtSaAm 8:2 FtSaAm

Fluorotelomer Sulfonates ^a		4:2 FtS 6:2 FtS 8:2 FtS
Fluorotelomer Thioamido Amino Carboxylates ^d		
Perfluoroalkyl Sulfonamido Amines ^a		PFBSaAm PFHxSaAm PFOSaAm
Perfluoroalkyl Sulfonamide Amino Carboxylates ^d		PFBSaAmA PFPeSaAmA PFHxSaAmA PFOSaAmA
Perfluoroalkylamido Betaine ^c		PFAAB
Fluorotelomer Sulfonamide Alkyl Betaine ^a		FtSaB
Perfluoroalkyl Sulfonamido Amine Oxide ^c		PFASNO

^a Backe et al. (2013); ^b Houtz et al. (2013); ^c D'Agostino et al. (2013); ^d Place & Field (2012).

In addition to fluorinated surfactants, AFFFs also contain a variety of other chemicals:

- Solvents such as diethylene glycol monobutyl ether (MSDS 3M Light Water Brand AFFF, 1995; MSDS Tyco Fire Protection Products Ansulite AFFF, 2011), or 2-methoxymethylethoxy propanol (MSDS Badger Fire Protection AFFF, 2002).

- Thickeners such as the polysaccharide Xanthan gum (MSDS Badger Fire Protection Universal Ultra AFFF, 2002).
- Buffers or stabilizers including triethanolamine (TEA) and tolyl triazole (MSDS 3M Light Water Brand AFFF, 1995).

Considering the prevalence of applications at oil refineries and airports, the pre-existing condition of the soils to which AFFFs are applied is also an important factor (Moody et al., 2000; Nunes et al., 2011). Common contaminants at these sites include:

- Halogenated solvents and hydrocarbons including trichloroethylene (TCE), and carbon tetrachloride (CCl₄)
- Chlorinated surfactants
- Jet fuel components and other oils
- Hydrocarbon surfactants

2.2 Fate of PFCs in Soil

The two main paths of PFC entry into soil are industrial waste sites, and the application of AFFFs at military bases, airports, and municipal firefighting training areas (Houtz et al., 2013), therefore the highest concentrations of PFCs are expected to be found at these sites. Although PFC presence in soil may not pose an immediate threat, soil treatment is essential for long-term remediation. The dangers associated with PFCs in soil include the potential for leaching into water systems, and entry into the food chain through bioaccumulation in plants or soil-dwelling animals such as worms or insects.

Leaching of PFCs from soil to groundwater is of particular concern. Once PFCs have become dissolved in water, their potential for migration greatly increases (Nunes et al., 2011). PFCs may even seep into sources of drinking water. Wilhelm et al. (2008) performed a case study following the accidental application of PFCs to nearly 1000 agricultural land sites in Europe. PFCs were able to leach into nearby rivers leading to PFOA and PFOS levels of up to 150 µg L⁻¹. The contaminated water has subsequently been restored to suitable PFC levels through GAC filtration.

Higgins and Luthy (2006) analyzed the sorption of perfluorinated surfactants on sediments and were able to observe several trends. Firstly, the main property affecting the strength of PFC sorption is the organic content of the soil. Higher organic content generally favours sorption of PFCs. Other parameters which were observed to lead to lower perfluorinated surfactant mobility were higher [Ca²⁺], and decreased pH. They reported that Ca²⁺ ions may act to reduce the charge present on organic matter which would decrease the repulsion of anionic surfactants such as perfluoroalkyl sulfonates (PFAS) and perfluoroalkyl carboxylates (PFCA). You et al. (2010) also observed increased sorption due to greater salinity however they justified this trend using the salting-out effect, which would increase order between water molecules and reduce the solubility of PFOS in aqueous media. Higgins and Luthy (2006) observed that sorption is affected by PFC chain length and the presence of the sulfate moiety. Sorption is increased with each additional CF₂ moiety but the interaction is consistently stronger in PFASs compared to their PFCA analogs.

Gellrich et al. (2012) examined the behaviour of PFCs in soils during leaching experiments. The 2-year laboratory study simulated the effect that precipitation would have on the transport of PFCs from soil to groundwater using flow-through columns 60 cm in length. It

was observed that short chain PFCs with alkyl chains less than 7 carbons were much more mobile than PFCs with greater alkyl chain lengths. The leaching behaviour was dependent on the organic content of the soil sample. With an organic content of 2%, PFOS was eluted after 70 weeks, compared to PFBA and PFBS which began to elute after just 7 weeks. When the organic content was increased to 7% and 14%, PFOS was not observed to elute at all within the 2 year period. These results indicate that soil is a significant environmental sink for PFOS. Without remediation the soil may continue to be a gradual source of PFOS leachate to other environmental systems.

The sludge effluent from WWTPs is also referred to as biosolids and can be composed of anything that enters the processing plant. The makeup of sewage sludge is dependent on the location of the WWTP and its proximity to communities or industry. Approximately 50% of biosolids generated in the US are subsequently applied to agricultural land as fertilizer (Lindstrom et al., 2014). The land application of biosolids is controlled by Part 503 of the US Code of Federal Regulations (US GPO, 2014), “Standards for the Use and Disposal of Sewage Sludge”. The regulations control the level of metals and pathogens present in sludge destined for land application, but organic pollutants such as PFCs remain unmeasured and unregulated. Direct application of biosolids to agricultural fields may be a significant source of PFC soil pollution.

PFCAs can enter the sewage system through a variety of industrial sources. Direct sources include: PFC manufacturing, fluoropolymer manufacturing, and AFFF manufacturing. Addition indirect sources include the breakdown of fluorotelomer-based products, and perfluorooctyl sulfonyl (POSF)-based products in the environment (Prevedouros et al., 2006). Several studies have attempted to quantify the degree of PFC pollution in wastewater sludge. Higgins et al. (2005) sampled digested sludge from 8 WWTPs scattered around the US receiving at least 50% domestic waste. The concentration of total PFCs in the domestic sludge ranged from 73 to 3390 ng g⁻¹, with total PFCAs between 5 and 152 ng g⁻¹, and total PFASs between 55 and 3370 ng g⁻¹. The highest concentration of PFOS was measured at 2610 ng g⁻¹ and isolated from a WWTP receiving 90% domestic waste and only 10% light industrial waste. This sample was however the only sample taken from 1998, before the PFOS production phase-out in 2002. A more recent sample taken from the same WWTP had a total PFC concentration of 335 ng g⁻¹, and a PFOS concentration of only 167 ng g⁻¹. If the average concentration is adjusted to exclude the sample from 1998, the total PFC concentration drops to 436 ng g⁻¹, and 124 ng g⁻¹ for PFOS alone. This evidence suggests a trend of decreasing PFOS levels entering the environment through WWTP sludge following the production phase-out.

Sun et al. (2011) conducted a similar study with digested sewage sludge from 20 WWTPs in Switzerland, where biosolids application to agricultural fields is currently forbidden. The total concentration of PFCs in the sludge ranged from 28 to 637 ng g⁻¹, while the total concentration of PFOS ranged from 15 to 600 ng g⁻¹. The predominant PFC in every sample was PFOS, and higher levels of PFOS had no correlation with higher levels of PFCAs within the same sample. Archived sludge samples were also screened from 1993 and 2002 accompanying the samples taken in 2008 to assess the effect of the 2002 production phase-out. No clear pattern of decline was observed for PFOS or PFOA concentrations over the years, with some WWTPs even measuring their highest concentrations in 2008.

A review by Jensen et al. (2012) compiled additional PFC concentrations in sewage sludge from Europe. Nordic countries had relatively low concentrations, in the range of 0.6 to 15.2 ng g⁻¹ total PFCs (Kallenborn et al., 2004). Levels of PFC contamination in Swedish sludge

ranged from 0.6 to 23.9 ng g⁻¹ and 1.6 to 54.8 ng g⁻¹ for PFOA and PFOS respectively (Haglund and Olofsson, 2009).

Sepulvado et al. (2011) analyzed PFC concentration in agricultural fields which had received applications of municipal biosolids. The amount of PFCs in biosolids amended fields was measurably higher than background fields which had never received biosolids application. PFCs were found to within a depth of 120 cm below the soil surface. The concentration of PFOS was up to 483 ng g⁻¹ in fields which had experienced long term biosolids application.

Washington et al. (2010) investigated sludge-applied soils in proximity to a WWTP handling sewage waste from industries known to work with perfluoroalkylates and their precursors. Sludge from this WWTP was measured to contain PFOA concentrations up to 1875 ng g⁻¹; however, since 2007 the application of biosolids from this WWTP has been discontinued and the concentration of PFCs in its sludge has decreased dramatically. The measured PFC of highest concentration in the sludge-applied fields was PFDA (C₁₀) at 989 ng g⁻¹. The highest concentrations of PFOS and PFOA were 408 ng g⁻¹ and 312 ng g⁻¹ respectively. The concentrations observed in the sludge-applied soils were compared to background fields which had never received biosolids application. The concentrations for all measured PFCs in the background fields were either below the limit of quantification, or in the pg g⁻¹ range. Evidence from the background fields suggests that PFC contamination in agricultural soil is likely a direct result of biosolids application.

In addition to the direct sources of PFAAs into WWTPs, a significant amount of precursors exist that can indirectly contribute to the final concentration of PFAAs in digested sludge. The Organisation for Economic Co-operation and Development (OECD) has listed 875 chemicals with the potential to degrade to PFAAs. For PFOS these precursors include derivatives and polymers of perfluoroalkyl sulfonyl or sulfonamide compounds, while PFOA precursors have even more diversity, including derivatives and polymers of perfluoroalkyl alcohols, amines, carboxylic acids, esters, ethers and iodides (OECD, 2007).

Several studies have reported that in addition to WWTPs being inefficient at general PFC removal, they may actually cause an increase in PFAAs, as evidenced by increased concentrations of PFAAs in wastewater effluents versus influents (Loganathan et al., 2007; Murakami et al., 2009; Sinclair and Kannan, 2006). Oil, fuel and AFFF components, common co-contaminants in PFC wastewater, have also been shown to have a negative effect on the activated sludge process (Moody et al., 2000). The increase of PFAAs in effluents is theorized to be attributed to the degradation of more complex PFAA precursors during activated sludge treatment. Schultz et al. (2006) sampled 10 WWTP, and in 7 of these plants PFOA was increased by a factor between 9% and 352%. Although PFOS often exhibited a decrease in concentration via sludge treatment, it should also be taken into account that the K_d value for PFOS on sludge is over 3 times higher than PFOA, indicating a higher affinity for PFOS to become adsorbed to the sludge causing final PFOS concentrations to appear lower in effluents (Yu et al., 2009). Becker et al. (2008) observed a 20-fold increase in PFOA from influents to effluents. Analysis of the sludge revealed that an additional 10% of PFOA was adsorbed to the sludge. PFOS was observed to increase 3-fold in effluents compared to influents, with almost 50% additional PFOS adsorbed to the sludge.

Liu and Mejia (2013) compiled a list of biodegradability studies for PFAA precursors conducted in conditions including microbial cultures, activated sludge, soil, and sediment. The degradation of 8:2 FTOH caused an increase of PFOA by 6% in mixed bacterial culture (Wang et al., 2005a), 2.1% in activated sludge (Wang et al., 2005b), and up to ~40% in aerobic soils

(Wang et al., 2009). The degradation of EtFOSE caused an increase of PFOS by 7% in activated sludge (Lange, 2000), and 12% in marine sediment (Benskin et al., 2013). Liu and Mejia (2013) conclude by proposing that a knowledge gap exists for several important classes of precursors such as:

- Perfluorooctane sulfonamide-based side-chain polymers
- Zwitterionic, cationic, and anionic fluoroalkyl surfactants (from AFFFs)
- Fluorotelomer iodides (FTIs)

While the microbial degradation of fluorotelomer and perfluoroalkyl sulfonamide compounds has been well documented (Frömel and Knepper, 2010; Lange, 2000; Rhoads et al., 2008), the subsequent degradation of PFOS and PFOA is likely minimal or non-existent in sludge and soils under normal environmental conditions (Sáez et al., 2008; Schröder et al., 2003).

2.3 PFC Bioaccumulation Factors in Soil

PFCs left in soil have the potential to enter the food chain through plants and animals. Several studies exist which quantify the bioaccumulation factors (BAF) of PFCs in soil. This is calculated as a ratio of the PFC concentration in biota to the concentration in the soil from which it was extracted.

Stahl et al. (2009) studied the transfer of PFOA and PFOS from artificially contaminated soil to wheat, oat, maize, potato, and grass plants. The amount of PFOS and PFOA uptake was dependent on their original concentration in the soil. Concentrations were greater in the vegetative portion of the plant compared to the storage organs. Yoo et al. (2011) conducted a similar study using grass grown in fields contaminated with PFCs via biosolids application. As well as calculating their own grass-soil accumulation factors (GSAF), they used the previous research by Stahl et al. (2009) to generate GSAFs for comparison. The PFC with the highest GSAF was PFHxA, and accumulation decreased with increasing chain length. The GSAF for PFOA was calculated to be around 0.25, while PFOS was lower at around 0.07 to 0.16.

Beach et al. (2006) conducted an ecotoxicological evaluation of PFOS including the results of a study by Brignole et al. (2003) to determine the BAFs of 7 plant species under varying soil PFOS concentrations between 3.61 and 278 $\mu\text{g g}^{-1}$. The soybean plant had the highest measured BAF at 4.3 within its vegetative tissue. The vegetative tissue extracted from the 6 other plants averaged BAFs between 2 and 3, and the highest BAFs were measured from the soil with the lowest PFOS concentration (Brignole et al. 2003).

Lasier et al. (2011) studied the transfer of PFCs from soil to an aquatic worm *Lumbriculus variegatus* and calculated BAFs. The researchers found that the tendency to bioaccumulate increased with increasing chain length and the presence of the sulfate group. The BAFs for PFOS and PFOA respectively were 0.49 and 0.07, with the highest BAF belonging to PFHpS at 2.6.

Das et al. (2013a) calculated BAFs based on PFOS for earthworms (*Eisenia fetida*) in soil that had been impacted by AFFFs. The values they calculated ranged from 1.23 to 13.9, and the highest bioaccumulation was observed in soil that contained just 0.8 $\mu\text{g g}^{-1}$ PFOS, indicating that bioaccumulation can occur even in soils with less heavy pollution. It was observed that bioaccumulation was more pronounced in soils with lower organic content, perhaps due to weaker sorption of PFOS to the soil.

A similar study on earthworms conducted by the Norwegian Pollution Control Authority (SFT) (SFT, 2008) found the BAF for PFOS to be 2.6, while PFOA was 5.9. Yoo et al. (2011) hypothesized that BAFs tend to be higher in worms compared to plants because the worms directly ingest PFCs from organic matter while the plants depend on uptake of dissolved PFCs from soil-water. Once PFCs enter the food chain, they will continue to magnify in larger organisms.

2.4 Current Strategies for PFC Remediation in Soil

Many of the strategies effective for water decontamination cannot be translated to solid matrices such as soil, because the PFC molecules are much less accessible. As yet, there are no techniques available which allow total desorption of PFCs from soil. Presently, the cost of PFC remediation from soil is too high so that the remediation of PFC-contaminated sites is rarely performed (Eschauzier et al., 2012). In situ technologies for soil remediation which have already been proven ineffective include: air sparging, soil-vapour extraction, biodegradation, and hydrolysis (Pancras et al., 2013). This section will examine the current and developing technologies available for soil remediation as well as their limitations, most notably the lack of field studies available for emerging technologies. An overview of PFC treatment technology effectiveness is provided in Table 2 and some available cost estimates are summarized in Table 3.

2.4.1 Excavation and Specialized Landfills/Encapsulation

Contaminated soils can be excavated and moved to areas designed for long-term containment. These areas can be constructed to be surrounded by low-permeability barriers built of materials such as clay caps or synthetic textiles to reduce or eliminate migration of contaminants (Khan et al., 2004). Similarly, treatment walls can be set up at the original area of contamination or at the designated long-term storage area. Treatment walls can be constructed by digging a trench around the contaminated area and filling it with materials that will treat contaminated groundwater as it passes through the barrier. There are three main types of treatment walls: sorption barriers, precipitation barriers, and degradation barriers. Since PFCs are very non-reactive chemicals, it is hard to expect their precipitation or degradation from groundwater, however filling the barrier with a sorbent to capture and hold PFCs could be feasible.

With assistance from the Minnesota Pollution Control Agency (MPCA), 3M (2010) developed an action plan for the treatment of their PFC contaminated industrial waste sites. Strategies for soil remediation included removal of PFC contaminated soils in the cove leading to the Mississippi River and capping the area with soils heavy in clay content. The plan also included excavation of all soils on site which exceeded the Industrial Soil Reference Values for PFOS and PFOA followed by back-filling of the site with uncontaminated soil. The contaminated soil was transported to a long-term containment facility, engineered specifically to hold PFCs. All leachate from the containment site was continuously pumped out and treated with activated carbon. Remediation of the sites was completed in 2010, but soil and groundwater sampling procedures are still periodically implemented. The initial estimated cost for cleanup of one contaminated site including soil and groundwater was around \$20 million.

2.4.2 Groundwater Pump-and-Treat

Groundwater treatment for contaminated soil leachate is generally a reactionary measure which has been proven effective for preventing PFC release to sources of drinking water (Wilhelm, 2008; 3M, 2010). The theory could however be adapted as a precautionary measure to pump contaminated water from the soil before it has a chance to leach into surrounding areas, thereby facilitating direct site remediation.

The only known field study investigating the effectiveness of groundwater extraction as a remediation technique for PFC contaminated soil at AFFF-impacted sites was conducted by Paterson et al. (2008) and involved the installation of an in situ vacuum-enhanced multiphase extraction (VEMPE) system at a former firefighting training area (FFTA) in British Columbia. Four rotary claw pumps removed groundwater and vapour from the subsurface. The extracted groundwater was first pumped through an oil/water separator and air stripping unit, and then treated in tanks via GAC filtration and released back to the soil. Although the GAC filtration had an efficiency of > 99% PFC removal from the groundwater, it was estimated that only 0.1% of the total PFCs in the soil were removed over a period of two years. This demonstration emphasizes the affinity that PFCs have for soil and the lack of feasibility this technique would have in a real remediation scenario under time constraints.

2.4.3 Soil Flushing

Although groundwater extraction by itself may be an ineffective remediation strategy, release of PFCs from soil may be enhanced if coupled with a flushing agent. Soil flushing is an in-situ process that involves injection of a flushing solution into the ground for extracting contaminants. Soil flushing has been used for the removal of POPs from soil in the past with apparent success, the main advantage being that large quantities of soil can be treated in-situ, meaning excavation and transport are not needed (Jawitz et al, 2000; Svab et al., 2009; Zheng et al., 2012). The efficiency of this technique was evaluated at CFB Borden for the removal of TCE from soil (Mulligan et al., 2001). It was estimated that with the addition of 1% surfactant to water, the remediation of the site would take approximately 21 pore volumes of solution over 4 years, as opposed to simple pumping and treatment of groundwater which was estimated to require 2000 pore volumes and over 100 times longer for decontamination.

Surfactants contain both hydrophobic and hydrophilic portions, making them particularly effective soil flushing additives for the mobilization of organic contaminants. Many PFCs, including PFOS and PFOA, are themselves surfactants which can make their behaviour more difficult to predict. Other common soil flushing additives include: organic/inorganic acids/bases, solvents such as methanol or ethanol, oxidizing/reducing agents, and chelating agents. In order for the process to remain cost effective, the flushing solution should be recyclable and non-toxic. In an ideal scenario, once the contaminant has been flushed out of the soil and collected, the solution could be decontaminated using water treatment technologies such as adsorption, ion-exchangers, or filtration, and then reused for subsequent flushes.

Analysis of PFCs in soil requires an extraction step before liquid chromatography and mass spectroscopy can be performed. Several separation methods exist involving organic solvent extraction. In a method used by Sun et al. (2011) and Powely et al. (2005), sewage or soil samples are flushed three times with methanol, with shaking, sonication, and centrifugation between each flush. In the pressurized solvent extraction (PSE) procedure used by Llorca et al. (2011), sewage samples were treated to two cycles of methanol at 70 °C, and 100 bar of pressure. Schröder et al. (2003) experimented with several organic solvents to determine the solvent or

combination of solvents with the greatest PFC extraction potential. Sludge samples were subjected to PSE at 150 °C and 143 bar using solvents: ethyl acetate (EtOAc), dimethylformamide (DMF), pyridine, tert-butyl methyl ether (MTBE), 1,4-dioxane, or tetrahydrofuran (THF). The most effective extraction procedure involved sequential flushing with a mixture of EtOAc and DMF, then methanol modified with phosphoric acid, although the extraction was almost as effective without DMF. The principles of small scale extraction have the potential for full scale-modification to soil flushing; however attention must be placed on the environmental impacts of introducing an organic solvent to the soil ecosystem.

Pan et al. (2009) investigated the effect of cationic and anionic surfactants on the sorption and desorption of PFOS on sediments. The cationic surfactant tested was cetyltrimethylammonium bromide (CTAB) while the anionic surfactant was sodium dodecylbenzene sulfonate (SDBS). Batch sorption and desorption tests were conducted with increasing concentrations of surfactant and the effect was observed as the changing concentration of PFOS in the water, measured through HPLC.

CTAB was found to significantly enhance the sorption of PFOS to sediments. This was observed as a linear increase in the Freundlich coefficient (K_F) with increasing concentrations of CTAB below its critical micelle concentration (CMC), after which a maximum was reached and increasing CTAB concentrations had a negligible effect. While the cationic surfactant seemed to effectively immobilize PFOS, the anionic surfactant SDBS had a concentration dependent effect. At concentrations of SDBS lower than 4.34 mg L^{-1} , sorption of PFOS to sediments was increased, however at the measured concentrations of 21.7 and 43.4 mg L^{-1} , sorption of PFOS was significantly decreased with inhibition becoming more pronounced with increasing concentrations of SDBS. The researchers justified the observed effect of the cationic surfactant by postulating that CTAB may become adsorbed to the sediment first, thus exposing its hydrophobic tails which can act as a sink for PFOS. In a separate experiment, the anionic surfactant was observed to enhance the solubility of PFOS in water which would account for the observed decrease in sorption to sediments.

In terms of soil flushing strategies, SDBS can act as an effective surfactant for the increased mobilization of PFOS from sediments. The results by Pan et al. (2009) should encourage further study into a variety of surfactants and their interactions with a larger suite of PFCs. For example, in a study by Guelfo and Higgins (2013) on the interactions between PFCs and co-contaminants in AFFFs, it was found that although sorption was decreased in the presence of anionic surfactant sodium dodecyl sulfate (SDS) for low concentrations of PFOS, PFNA, and PFDA, it appeared to have no effect on long chain PFAAs and actually increased sorption for PFBA, PFPeA, PFHxA, PFHpA and PFBS. Other co-contaminants tested were amphoteric surfactant N,N-dimethyldodecylamine N-oxide (AO), and non-aqueous phase liquid (NAPL) in the form of TCE. All PFAAs showed increased sorption or no effect in the presence of AO. Addition of NAPL caused decreased PFOS sorption to soil at low concentrations of PFOS ($1 \text{ } \mu\text{g/L}$) but increased sorption at a higher PFOS concentration ($500 \text{ } \mu\text{g L}^{-1}$). For their experiments with reverse osmosis (RO), Tang et al. (2006) found that an organic solvent, isopropyl alcohol, was capable of increasing the solubility of PFOS but also caused a decrease in membrane flux. This finding is important as RO may be used to treat the leachate generated in soil flushing. RO rejects the contaminants and some other dissolved compounds and collects them as a concentrate. AFFF-impacted sites may contain any number of co-contaminants, meaning the effectiveness of remediation via soil flushing would require analysis using a case-based approach.

2.4.4 Soil Washing

Soil washing involves the excavation of contaminated soils and their ex-situ treatment. Soil washing usually involves the separation of coarse components of the soil, such as sand and gravel, from the finer components such as clay and silt (Khan et al., 2004). Hydrophobic organic contaminants tend to stick to smaller soil particles, meaning it may be feasible to simply treat the clay and silt portions of the soil. This separation process reduces the amount of contaminated soil that requires treatment. Similar to soil flushing, the efficiency of soil washing can be enhanced by the addition of a solvent or surfactant to the wash water. Soil washing has been recognized as effective at removing hydrophobic organic compounds (HOCs) such as: aromatic compounds, polyaromatic hydrocarbons (PAH), polychlorinated biphenyls (PCBs), herbicides, and pesticides (Chu and Kwan, 2003; Chu and Chan, 2003).

The first stage of soil washing only concentrates the contaminated components of the soil so it must be combined with other treatment technologies for subsequent stages. Common second stage treatments include (Hasegawa et al., 1997; Khan et al., 2004):

- Incineration
- Landfill storage
- Liquid-liquid or solid phase extraction
- Membrane separation
- Advanced oxidation/reduction
- Bioremediation

2.4.5 Supercritical Fluid Extraction

Chen et al. (2012) developed a method for supercritical fluid extraction (SFE) of PFOS and PFOA from solid matrices, using supercritical CO₂ (Sc-CO₂), methanol and HNO₃. This method takes advantage of the readily achievable critical point of CO₂ (T_c= 31.1 °C, P_c= 74 bar). Concentrated HNO₃ is used to suppress the polarity of the PFOS and PFOA molecules, therefore increasing their solubility in Sc-CO₂. Methanol, as a highly polar solvent, was used to modify Sc-CO₂ by increasing its polarity, which also ultimately leads to increased solubility of PFOS and PFOA. The contaminated samples were treated in pressurized cells at 20.3 MPa (203 bar) and 50 °C with 16 M HNO₃ under dynamic and static extraction conditions. The extract was collected in vials filled with methanol and prepared for LC/MS analysis. Extraction took between 40 to 180 minutes and the expired gaseous CO₂ was released to the atmosphere. The extraction efficiency from sand (after double extraction) was 77% for PFOA and 59% for PFOS. The method was also tested against paper and fabric matrices, with efficiencies of 100% and 80% for PFOA and PFOS respectively. The researchers postulate that this method would be a rapid, low-cost, environmentally friendly solution to PFOA and PFOS remediation however no field tests are currently available for this technology.

2.4.6 Immobilization of PFCs in Soil

If removal of PFCs from soil is not feasible, an alternative method such as immobilization can be used. The immobilizing agent could be an adsorbent, similar or identical to those used in water treatment, or a liquid chemical solution. The idea behind this technique would be to prevent leaching of PFCs from the initial source of pollution, and evidence suggests that it could even reduce the bioavailability of the contaminants in the soil.

Pan et al. (2009) calculated the Thermodynamic Index of Irreversibility (TII) for PFOS to sediments in the presence of cationic surfactant CTAB to quantify the degree of sorption irreversibility caused by CTAB; with a value of 0 representing a highly reversible system and 1 representing irreversible sorption. A value of 1 was approached for concentrations of 18.1 and 36.1 mg L⁻¹ CTAB, indicating its potential use for site immobilization of PFOS. The cationic surfactant could be delivered to the source of pollution using *in situ* percolation or injection. Due to the possibility of biodegradation of the cationic surfactant, this solution may be temporary.

Brändli et al. (2008) tested whether AC could immobilize PAH in soil. Powdered activated carbon (PAC) and GAC were mixed into the soil and the dissolved PAH concentration was measured in a soil-water slurry system. It took six weeks for the GAC amended soils to reach equilibrium and 31 days for PAC amended soils. The PAC was found to be more effective than GAC at reducing the freely dissolved PAH concentration. It was observed that only 2% PAC was needed to reduce the aqueous PAH concentration by 99%.

A continuation of the study was conducted by Hale et al. (2012) in order to test the results in a field application. This was the first in-situ field study of AC amendment in soil. Three plots were constructed in the soil measuring 25 m³: one reference area, one mixed with 2% (wt) PAC, and another mixed with 2% (wt) GAC. After 17 months, the free aqueous PAH concentration from the soil was reduced by 93% with PAC and 84% with GAC. In another follow-up study by Jakob et al. (2012), the environmental implications of AC amendment were evaluated specifically observing the effects on plant growth and BAFs. PAC was found to inhibit the growth of plants and reduced their BAF by an average of 53% while GAC had a positive effect on plant growth and reduced their BAF by an average of 46%. PAC was toxic to earthworms as evidenced by their observed significant weight loss. The toxicity of GAC for earthworms was inconclusive. The BAF for earthworms was reduced by an average of 72% and 47% for PAC and GAC respectively.

Zimmerman et al. (2004) tested the efficiency of using AC in reducing the release of POPs from marine sediments. They found that upon addition of AC to the sediments, the available aqueous concentrations of PCB and PAH were reduced by 92% and 84% respectively. While AC has been shown to be effective at binding PFCs in water (Ochoa-Herrera and Sierra-Alvarez, 2008), no studies were found specifically testing whether AC can efficiently immobilize PFCs in soil. Other documented adsorbents for PFCs in water include: anion-exchange resins (Yu et al., 2009; Senevirathna et al., 2010), chars and ash (Chen et al., 2011), and carbon nanotubes (Li et al., 2011).

Das et al. (2013b) along with the Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE) developed a modified clay adsorbent for the immobilization of PFOS in contaminated soils. The material (a palygorskite-based clay modified with oleylamine) is in the advanced stages of commercialization under the trade name MatCARE™. Soils from four different sites impacted by AFFFs were measured for initial PFOS concentration then used for treatability studies, with 10 g of MatCARE™ being applied for every 100 g soil. Without treatment with MatCARE™, the average PFOS release from the control soils after 1 year at 25 °C was 8.14 %, and 9.48 % at 37 °C. With the application of MatCARE™, there was no detectable PFOS release after 1 year at 25 °C, and only 0.15 % at 37 °C. The experiment was also performed with spiked soils, with average PFOS release decreasing from around 18 % (control soil) to 0.5% (treated soil). It was found that for most soils, total immobilization of PFOS occurred with the application of 100 g MatCARE™ per kg of soil. Application of MatCARE™ has also been reported to be successful in field trials.

Cost comparisons between MatCARE™ and other common adsorbents were included in the paper. The cost of MatCARE™ is listed as \$26.0/kg, compared to \$14.6/kg for a commercial GAC (Hydrffin CC8*30) and \$88.0/kg for an anion-exchange resin (Amberlite IRA 400). Although MatCARE™ is more expensive than GAC, it should also be noted that MatCARE™ has a greater adsorption capacity at 0.09 mmol PFOS/g, compared to the adsorption capacity for Hydrffin GAC at 0.07 mmol PFOS/g. MatCARE™ has been successfully used for water remediation, with over 1 million litres of AFFF-contaminated water being reduced to PFOS concentrations of less than 5 ppb (CRC CARE, 2013). MatCARE™ has been advertised to reduce the cost of cleaning an AFFF-contaminated water site from \$300,000 to \$30,000. CRC CARE has also developed astkCARE™, an anionic-surfactant test kit, able to detect and measure anionic surfactants such as PFOS in the environment.

2.4.7 Vitrification or Incineration

Also referred to as molten glass process, vitrification involves using a powerful energy source to essentially melt soil, causing pyrolysis or immobilization of virtually all contaminants (Khan et al., 2004). Temperatures required for vitrification range between 1600°C to 2000°C. An advantage to this process in the context of PFCs is the lack of by-products generated because all organic contaminants are destroyed. There are several processes available to reach vitrification temperatures: electrical, thermal, and plasma. The electrical process is *in situ* and involves construction of a zone surrounded by graphite electrodes inserted in the ground which pass energy through the soil. The thermal process is *ex-situ* and is generally carried out in a rotary kiln. Plasma processes are only necessary when temperatures of up to 5000°C are required.

Electrical or thermal processes could be used to target the combustion of PFCs on site without using more extreme temperatures. Typical municipal incinerators operate at temperatures of around 600°C to 1000°C for approximately 2 seconds (Vecitis et al., 2009; Yamada et al., 2005). These temperatures are generally sufficient for the incineration of PFOS and PFOA. Yamada et al. (2005) tested whether fluorotelomer-treated textiles and paper, after being destroyed under municipal incinerator conditions, would form PFOA as a degradation product. There was no PFOA detected in the samples after incineration. Even if PFOA was formed during incineration, it must have also been destroyed in the process, meaning degradation of precursors during incineration would not be a significant source of PFOA to the environment.

2.4.8 In-Situ Chemical Oxidation

In-situ chemical oxidation (ISCO) using peroxydisulfate ($S_2O_8^{2-}$), often simply referred to as persulfate, is a promising technique for soil remediation. The process has previously been used for the remediation of pollutants such as chlorinated ethenes and benzenes, oxygenates, benzene, toluene, ethylbenzene, and xylenes (BTEXs), and PAHs from soil (Nadim et al., 2006; Tsitonaki et al., 2010). Forming the activated persulfate radical can be accomplished through UV exposure, heat, high pH (alkaline conditions), hydrogen peroxide, and a variety of transition metals (Watts and Teel, 2006). Persulfate can first be delivered to the soil subsurface in an inactive form, and then activated once contact with the contaminated zone has occurred. An example of a delivery system would be a network of high pressure injection points, followed by mixing of the soil with a backhoe (Tsitonaki et al., 2010). Activation by heat can be accomplished using steam injection. Heat can also be incorporated into the soil using six-phase soil heating, which involves the use of electricity to pass current through the soil resulting in thermal energy production (Heine et al., 1999). Six-phase soil heating can be used as a stand-

alone soil remediation technique for more volatile compounds as it encourages their release from the soil matrices. Nadim et al. (2006) used a complex of Fe (II) with EDTA to activate persulfate for the degradation of PAH because the addition of a chelating agent can effectively keep the Fe (II) in solution even at neutral pH.

Hori et al. (2008) found that persulfate oxidation, activated by hot water, was effective at degrading PFOA to below the detection limit after 6 hours of treatment at 80°C. Formation of CO₂, fluoride ions, and shorter chain PFCAs was indicative of the degradation. Lee et al. (2012) were able to degrade PFOA in aqueous solution with an efficiency of 80.5% at temperatures as low as 20°C by changing the persulfate dose and pH of the system. Complete degradation was observed at a pH of 2.5 after 72 hours at 40°C and 215 hours for 30°C.

In an ARCADIS paper by Hawley et al. (2012), it is reported that ARCADIS has conducted experiments along with the Imperial College of London to assess the best method for activation of persulfate oxidation with the goal of soil and groundwater treatment. Activators which were able to degrade PFOS by more than 97.5% included: Fenton's reagent, peroxide-activated persulfate, and heat-activated persulfate. Strong reducing agents such as sodium dithionite and sodium hypophosphate were also tested but only partial degradation of PFOS was observed. Follow-up tests were conducted to develop a mixture of common oxidants which could function under less-extreme conditions (such as a field setting) to efficiently degrade PFOS and PFOA in groundwater and soil. The exact reagent combination is currently patent pending under the name Smart Combination In-Situ Oxidation/Reduction (SCISOR). It was observed that SCISOR reduced the amount of PFOS in soil by 60% after one contact phase, however information on intermediate formation following destruction was notably lacking. Place and Field (2012) expressed concern regarding the use of ISCO for the remediation of AFFF-impacted sites, as advanced oxidation techniques have been known to encourage PFAS and PFCA formation from the more complex precursors present in AFFFs. The idea of using advanced soil washing in tandem with SCISOR was presented by Pancras et al. (2013) with the results of lab tests indicating that the technique was able to remove > 99% of PFOS from contaminated soil. Pilot tests are currently being conducted.

Table 2: Summary of PFC Treatment Technology Effectiveness

Technology Type	Summary of Technology Effectiveness	Relevant Papers
Excavation and Specialized Landfills	<ul style="list-style-type: none"> • Temporary solution—landfills becoming increasingly unwilling to accept PFOS and PFOA. • Potential still exists for soil leaching. • Sorption barrier treatment walls have the potential to effectively inhibit the migration of PFC contaminated groundwater. 	Khan et al. (2004) MPCA (2009)
Groundwater Pumping	<ul style="list-style-type: none"> • GAC treatment of collected groundwater is highly effective (>99%). • Separation of PFCs from soil is slow or does not occur. 	Paterson et al. (2008) Wilhem et al. (2008) 3M (2010)
Soil Flushing	<ul style="list-style-type: none"> • SDBS (anionic surfactant) could potentially mobilize PFOS from 	Mulligan et al. (2001) Sun et al. (2011)

	<p>sediments.</p> <ul style="list-style-type: none"> • Possible adaptation of organic solvent extraction techniques. • Requires more study into possible interactions with AFFF co-contaminants. • Sc-CO₂ flushing with methanol and HNO₃ demonstrated possible success as a low-cost, environmentally friendly method for PFOS decontamination from solid matrices. 	<p>Powely et al. (2005) Llorca et al. (2011) Schröder et al. (2003) Pan et al. (2009) Guelfo and Higgins (2013) Tang et al. (2006) Chen et al. (2012)</p>
Soil Washing	<ul style="list-style-type: none"> • Reduces the volume of contaminated soil requiring decontamination. • Exhibited past success with a variety of HOCs. • Must be combined with another treatment technology. 	<p>Khan et al. (2004) Chu and Kwan (2003) Chu and Chan (2003) Hasegawa et al. (1997) Pancras et al. (2013)</p>
Immobilization	<ul style="list-style-type: none"> • CTAB (cationic surfactant) showed effective immobilization of PFOS to sediments. • Evidence suggests AC may be able to immobilize PFCs in soil as well as water. • Clay-based adsorbent, MatCARE™, is in late commercial stages as a remediation technology involving PFOS immobilization in soil. 	<p>Pan et al. (2009) Brändli et al. (2008) Hale et al. (2012) Jakob et al. (2012) Zimmerman et al. (2004) Das et al. (2013b)</p>
Vitrification and Incineration	<ul style="list-style-type: none"> • Extreme temperatures (1600 to 2000 °C) destroy all organic pollutants causing very few by-products. • Requires powerful thermal or electrical energy source. • Could be adapted for temperatures suitable for PFC incineration (>600 °C) 	<p>Khan et al. (2004) Vecitis et al. (2009) Yamada et al. (2005)</p>
Persulfate Oxidation	<ul style="list-style-type: none"> • Exhibited past success with other POPs for <i>in situ</i> remediation of soil. • SCISOR technology currently in development by ARCADIS to be combined with advanced soil washing. Lab tests indicate >99.9% removal of PFOS from soil. • Implications of PFOS and PFOA precursors and intermediate formation via oxidation are not addressed. 	<p>Nadim et al. (2006) Tsitonaki et al. (2010) Watts and Teel (2006) Hori et al. (2008) Lee et al. (2012) Hawley et al. (2012) Pancras et al. (2013)</p>

Table 3: Cost data for Presented Soil Remediation Technologies

Technology	Relevant Cost Data
Encapsulation	Dependent on depth of contamination and physical characteristics of site ^a .
Groundwater Pump-and-Treat	\$200,000 to \$900,000 US for design and installation cost. \$1 to \$100 US per 1,000 gal (3,785 L) of groundwater ^a .
Soil Flushing	\$25 to \$250 US per cubic yard (\$33 to \$327 US per cubic meter) ^a .
Soil Washing (Including Excavation)	\$75 to \$170 US per ton (1000 kg) of soil ^a .
Immobilization	Dependent on choice of adsorbent ^b : <ul style="list-style-type: none"> • \$5.77/kg Filtrasorb 400 GAC with 0.002 mmol PFOS/g adsorption capacity. • \$14.60/kg Hydrffin CC8*30 GAC with 0.07 mmol PFOS/g adsorption capacity. • \$26.0/kg MatCARE™ with 0.09 mmol PFOS/g adsorption capacity. • \$88.00/kg Amberlite IRA 400 Resin with 0.42 mmol PFOS/g adsorption capacity. • \$218.00/kg Amberlite XAD4 Resin with 1.59 mmol PFOS/g adsorption capacity.
Vitrification	\$270 US per cubic yard treated (electrical) (\$353 US per cubic meter) ^a .
Persulfate Oxidation	\$1.65 US per lb (\$3.64 US per kg) of sodium persulfate ^c . Average total cost (capital plus operating) for one site is around \$450,000 US ^c .

^a Khan et al. (2004); ^b Das et al., (2013b); ^c Rosansky and Dindal (2010).

3 Conclusions

This literature review highlights the current lack of off-the-shelf commercial technologies available for PFC contaminated soil remediation. The bulk of research into PFC remediation focuses on treatment in aqueous systems, which does not generally translate well to soil or sediment based environmental decontamination. It should also be noted that while evidence suggests that AFFFs are composed of hundreds of diverse fluorinated surfactants, PFOS and PFOA seem to dominate the vast majority of studies concerning remediation technologies. Based on this literature review, the emerging technologies which possess potential for a large-scale remedial application include: immobilization via MatCARE™ (a clay-based adsorbent), and in-situ destruction by persulfate oxidation (SCISOR). Further work is required in regards to identification of effective soil flushing and washing solutions. A complete mineralization of PFCs would be desirable to prevent further bioaccumulation or leaching into water systems, and would also allow future reclamation of contaminated land for agricultural and residential use.

4 Acknowledgments

This study was funded by the Environment Canada's Compliance Promotion and Contaminated Sites Division (CPCSD) under the Federal Contaminated Sites Action Plan (FCSAP) program. The authors thank Kathy Kitagawa and Jeremy Anglesey of CPCSD for valuable discussions and organizational support.

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