

REMEDICATION OF PERFLUORINATED ALKYL CHEMICALS AT A FORMER FIRE-FIGHTING TRAINING AREA – Lindsay Paterson, MSc, PAg, Tara Siemens Kennedy, MET, AAg and Douglas Sweeney, MSc, PEng

Introduction

Fire-fighting training areas (FFTAs) at airports, military bases and refineries have historically been contaminated by training activities. These exercises typically consisted of flooding an area or an aircraft fuselage mock-up with hydrocarbon fuels or waste solvents, igniting the flammable liquids and then completing fire suppression procedures. At some FFTAs, little or no containment of the applied fuel occurred, resulting in significant subsurface contamination.

SLR Consulting (Canada) Ltd (SLR) was retained in 2005 to oversee the installation of an in situ remediation system at a former FFTA in the British Columbia Interior (the Site). The system was installed to address subsurface hydrocarbon contamination related to the former fire-fighting exercises. In conjunction with remediation activities at the Site, a risk assessment approach was adopted in 2006 to address residual dissolved phase hydrocarbon contamination. A literature review conducted by SLR's risk assessors highlighted perfluorinated alkyl chemicals (PFCs) as potential contaminants of concern (PCOCs) as the result of the historical use of aqueous film forming foam (AFFF) during fire-fighting exercises (Moody and Field, 1999; Moody and Field, 2000; Moody et al, 2003).

This paper presents a summary of the chemical characterization of PFCs, development of risk-based criteria for PFCs at the Site and remediation efforts to date associated with PFC removal.

Perfluorinated Alkyl Chemicals and AFFF

PFCs are a group of man-made chemicals which consist of carbon chains saturated with fluorine atoms. The carbon-chains terminate in an end group such as a sulfonate or carboxylate group (Figure 1). PFCs have been used in a variety of consumer and industrial products, including use as surfactants in fire-fighting foams for Class B or flammable liquid fires. The PFCs used in AFFF reduce the surface tension of water, allowing an aqueous film to spread over the flammable liquid and further act as vapour sealants during fire-fighting (Schultz et al., 2003).

In recent years, research has focused on the environmental fate and impact of the eight-carbon chain carboxylate and sulfonate compounds, perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS).

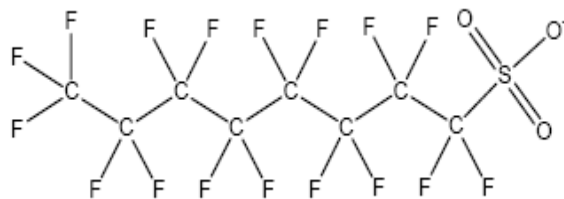


Figure 1: Chemical structure of PFOS anion (Health Canada, 2006).

The concern surrounding these compounds relates to the ubiquitous detection of these chemicals in the global environment, including in areas far-removed from manufacturing or major population centres. In 1999-2000 and again in 2003-2004, the US Centre for Disease Control surveyed over 1500 human serum samples for perfluorinated compounds and found detectable concentrations in 98% of the samples (Calafat et al, 2007). The carbon-fluorine bond is a very strong chemical bond, which lends to these compounds longevity in consumer and industrial applications, but also makes PFCs highly persistent in the environment. In particular, the eight-carbon compound, PFOS, is reportedly “resistant to hydrolysis, photolysis, microbial degradation and metabolism by vertebrates” (Environment Canada, 2006).

The eight-carbon PFCs have also been shown in various studies to be both toxic and bioaccumulative. Because of the oleophobic nature of PFCs, the compounds do not partition to lipids in the human body; rather, the compounds bind to proteins in blood serum. It has been reported that the elimination half-life of the eight-carbon PFCs in humans is approximately four years or more (MDH, 2008a). The most common health effects reported from animal studies are liver, thyroid and gastrointestinal effects. Although there is some evidence to suggest that these compounds may be carcinogenic, the link has yet to be shown conclusively.

It is not known how much AFFF may have been applied at the Site over the 20 years that the FFTAs operated. However, it is estimated that up to 2,000 to 2,700 L of AFFF may have been used annually in training exercises. Assuming a 1% PFC content in the AFFF (Hekster et al, 2002), nearly 500 L of PFCs may have been applied over the years of operation.

Site Features

The Site is relatively level and underlain by a glacial till primarily comprised of sand and silt materials. A seasonally confined aquifer is located at approximately 8.0 metres below ground surface. Hydraulic conductivities (as measured by single well response tests) vary from 10^{-5} to 10^{-7} m/s with hydraulic gradients ranging from 0.01 m/m to 0.04 m/m.

Previous Investigations

Site assessment activities completed by SLR and others identified significant subsurface hydrocarbon contamination, including the presence of light non aqueous phase liquid (LNAPL) in several locations across the Site.

Following the identification of PFCs as PCOCs, SLR began investigating soil and groundwater PFC concentrations in November 2006. All soil and groundwater samples were submitted to Axys Analytical Services in Sidney, BC for analysis. A variety of compounds, including perfluorobutanoate (PFBA), perfluoropentanoate (PFPeA), perfluorohexanoate (PFHxA), perfluoroheptanoate (PFHpA), PFOA, perfluorononanoate (PFNA), perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS) and PFOS, were detected at the Site.

As no soil or groundwater quality guidelines currently exist provincially or federally for PFCs, SLR developed risk-based remedial targets for soil and groundwater to assist in the evaluation of the PFC concentrations observed at the Site.

Development of Risk-Based Remedial Targets

As toxicity data is limited for many of the PFCs detected at the Site and based on the relative concentrations of the various compounds in soil and groundwater at the Site, SLR’s efforts were focused on the development of remedial targets for PFOS.

Soil and groundwater remedial targets were developed for the human receptors of concern (ROC) identified at the Site (Siemens Kennedy and Paterson, 2008) and are summarized in Tables 1 and 2.

Limited ecotoxicological data is available for PFOS. Using US EPA methodologies, Beach et al. (2006) compiled the available data to derive ecological benchmarks. SLR reviewed the ecological benchmarks to determine appropriate soil remedial targets for the protection of terrestrial ecological ROC. A remedial target of 1.3 mg PFOS/kg soil (dry weight) was adopted which was derived from a NOAEC of <3.9 mg PFOS/kg soil (dw) for lettuce with the application of an uncertainty factor of 3.

A groundwater target of 50 ug/L was adopted for the protection of freshwater aquatic life. The target was derived from a NOEC of 50 ug/L for *Chironomus tentans* (freshwater midge). A safety factor of 0.1 was applied to obtain a surface water target of 5 ug/L. Derivation of an acceptable groundwater concentration, based on an acceptable surface water concentration, was accomplished by multiplying the surface water target by a factor of ten to account for groundwater dilution during discharge to a surface water body.

Table 1. Risk based soil remedial targets.

Receptor	Soil Remedial Target (mg/kg)
Commercial Worker	23 mg/kg
Construction Worker	4 mg/kg
Terrestrial Ecological Receptors	1.3 mg/kg

Table 2. Risk-based groundwater remedial targets.

Receptor	Groundwater Remedial Target (ug/L)
Residential Drinking Water Consumer	0.4 ug/L
Freshwater Ecological Receptor	50 ug/L

Source zone soil and groundwater concentrations measured at the Site exceed the risk-based targets developed.

In Situ Remediation

The remedial options available to address PFC contamination are limited by the unique properties of the compounds. Many remediation methods utilized to address hydrocarbon contamination at FFTAs, such as sparging, soil vapour extraction and bioremediation, are ineffective on PFCs due to the low volatility of the compounds and their resistance to microbial degradation. However, sorption of PFCs to granular activated carbon (GAC) and anionic resins has been demonstrated to successfully remove PFCs from contaminated groundwater (MDH, 2008b). It is noted that GAC and anionic resins will only remove PFCs from contaminated water. For destruction of the PFCs to occur, a tremendous amount of energy is required. Spent activated carbon from water treatment units must be incinerated at temperatures in excess of 1000 degrees Celsius (Schultz et al., 2003; UDR, 2003).

An in situ vacuum-enhanced multiphase extraction (VEMPE) system was installed at the Site in 2005. The system, including the extraction well layout, was designed for hydrocarbon removal and remediation. Four rotary claw pumps remove LNAPL, groundwater and vapours from the subsurface. Recovered groundwater is treated through an integrated treatment system (combined oil/water separator and air stripping unit) and then through GAC vessels prior to discharge to the ground surface. The system configuration in 2005 included two 110 kg GAC vessels, which was expanded to include an additional three 225 kg GAC vessels in the spring of 2008.

Remediation Results

Based on Influent and Effluent testing, a PFC removal rate of more than 99% was generally measured through the GAC units in 2008. Removal of two carboxylate compounds, PFBA and PFPeA, had been noted to decrease with continued operation in 2007, but a similar trend was not observed in 2008.

Table 3. 2008 GAC Influent and Effluent Concentrations (ug/L).

Date	Influent	Effluent	Influent	Effluent	Influent	Effluent
	22-May-08		8-Jul-08		27-Aug-08	
PFBA	13	< 0.001	16	0.004	1	0.002
PFPeA	38	< 0.003	46	0.004	2	< 0.001
PFHxA	141	< 0.001	162	0.004	6	< 0.001
PFHpA	10	< 0.001	14	< 0.001	0.7	< 0.001
PFOA	16	< 0.001	22	< 0.001	0.6	< 0.001
PFNA	< 0.2	< 0.001	< 0.2	< 0.001	< 0.03	< 0.001
PFBS	24	< 0.002	23	< 0.002	2	< 0.002
PFHxS	4	< 0.002	105	0.004	1	< 0.002
PFOS	< 0.3	< 0.002	28	< 0.002	< 0.06	< 0.002

The reduction in influent concentrations between July and August 2008 corresponds to a change in the configuration of the active extraction wells to areas of the Site where in situ PFC concentrations have been observed to be lower.

Despite demonstrating removal of PFCs with GAC, the remediation results to-date are less than encouraging from a site closure perspective. Based on the groundwater extraction rates at the Site, it is estimated that only 100 g of PFCs (or less than 0.1% of the estimated 500 L present at the Site) have been recovered over a two-year period. Consequently, the results suggest that alternatives to active remediation be evaluated. These alternatives include groundwater fate and transport modelling, implementation of administrative controls such as restrictive covenants on the use of groundwater and application of controls at the receptor exposure point such as point-of-use (or under-the-counter) water treatment devices.

Conclusions

The remedial options available to address PFC contamination are limited by the unique characteristics of these compounds. Many remediation methods utilized to address hydrocarbon contamination at FFTAs, such as sparging, soil vapour extraction and bioremediation, are ineffective on PFCs. Consequently, such sites may require development of a separate strategy for PFCs in order to successfully obtain environmental closure.

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