



Transport of Perfluorochemicals to Surface and Subsurface Soils

Final Report

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CTS 13-17

**CENTER FOR
TRANSPORTATION STUDIES**

UNIVERSITY OF MINNESOTA

Technical Report Documentation Page

1. Report No. CTS 13-17	2.	3. Recipients Accession No.	
4. Title and Subtitle Transport of Perfluorochemicals to Surface and Subsurface Soils		5. Report Date March 2013	
		6.	
7. Author(s) Feng Xiao, John S. Gulliver, and Matt Simcik		8. Performing Organization Report No.	
9. Performing Organization Name and Address St. Anthony Falls Laboratory University of Minnesota 2 Third Ave. SE. Minneapolis, MN 55455		10. Project/Task/Work Unit No. CTS Project #2013003	
		11. Contract (C) or Grant (G) No.	
12. Sponsoring Organization Name and Address Center for Transportation Studies University of Minnesota 200 Transportation and Safety Building 511 Washington Ave. SE Minneapolis, MN 55455		13. Type of Report and Period Covered Final Report	
		14. Sponsoring Agency Code	
15. Supplementary Notes http://www.cts.umn.edu/Publications/ResearchReports/			
16. Abstract (Limit: 250 words) Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA), as persistent organic pollutants, are ubiquitously present in the environment, and have been detected in human blood and breast milk at concentrations of concern to health and environmental regulators. This project aims to identify the PFOS/PFOA contamination sources, contaminant release mechanisms, and migration pathways from contaminated soils. Soil samples at different depths along and perpendicular to a U.S. highway were collected, and both compounds were regularly quantified in all of our surface soils samples (0.2–125.7 ng/g dry soil weight). The results of the surveying and sampling program and subsequently geo-statistical modeling with the aid of a Geographic Information System (GIS) identified two hot spots, and supported wind as the primary transport carrier causing the mitigation of contaminated soils from the hot spots to off-site soils. The observations indicate that PFOS and PFOA contamination is not contained to a few hot spots, but is migrating with wind and traffic to other locations. This proposed soil-to-soil migration pathway appears to be an important and heretofore overlooked migration mechanism of PFOS and PFOA from contaminated spots. We also studied their occurrence and fate in subsurface soil samples, and found a general increase in concentrations with the depth at which soil samples were collected, indicating that the contamination is also migrating toward the groundwater table.			
17. Document Analysis/Descriptors Perfluorinated compounds, Organic compounds, Perfluoroalkyl substances, Highway transportation, Wind transport, Hot spots, Groundwater, Soil pollution, Pollution		18. Availability Statement No restrictions. Document available from: National Technical Information Services, Alexandria, Virginia 22312	
19. Security Class (this report) Unclassified	20. Security Class (this page) Unclassified	21. No. of Pages 32	22. Price

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March 2013

Published by:

Center for Transportation Studies
University of Minnesota
200 Transportation and Safety Building
511 Washington Avenue SE
Minneapolis, Minnesota 55455

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The authors and the University of Minnesota do not endorse products or manufacturers. Any trade or manufacturers' names that may appear herein do so solely because they are considered essential to this report.

Acknowledgments

We, the authors, would like to thank the Center for Transportation Studies for sponsoring this research.

We would also like to thank Drs. Brock Matter and Peter Villalta at the Masonic Cancer Center of the University of Minnesota for the use of a liquid chromatograph and a tandem mass spectrometer. We would like to thank Lanre Adekola and Aaron Ketchmark from the St. Anthony Falls Laboratory for help with the field collection of samples.

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Executive Summary

Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) are persistent organic pollutants that are ubiquitously present in the environment. They are important perfluorochemicals (PFCs), or more precisely, perfluoroalkyl substances (PFASs), that were manufactured by a variety of companies around the world and suspected to have chronic effects in humans. These chemicals are resistant to degradation by physical or chemical mechanisms, and have been detected in human blood and breast milk at concentrations of concern to health and environmental regulators.

This project aims to determine the extent of PFOS and PFOA migration and how elevated levels of PFOS and PFOA in soils migrated from known hot spots to other locations. The suspected hot spot of interest is the 3M manufacturing plant in Cottage Grove, and the possible migration pathways are due to vehicle traffic, by air and by water.

U.S. Highway 10 runs close to the 3M plant where PFOS and PFOA were manufactured before 2002. Soil samples at different depths along and perpendicular to U.S. Highway 10 were collected from Cottage Grove to Big Lake. PFOS and PFOA were regularly quantified in all of our surface soils samples (Σ PFCs = 6.0–135.0 ng/g dw; median, 20.4 ng/g dw. The term dw here and below stands for dry weight soil). The results of the surveying and sampling program and subsequently geo-statistical modeling with the aid of a Geographic Information System identified two hot spots, and supported wind as the primary transport carrier causing the migration of contaminated soils from the hot spots to off-site soils. Circumstantial evidence also suggests vehicular traffic as an important source or pollutant carrier. This newly proposed and confirmed soil-to-soil transport pathway appears to be an important and heretofore overlooked migration mechanism of PFOS and PFOA from contaminated soils.

We also studied the occurrence of PFOS and PFOA in subsurface soil samples, and found a general increase in concentrations with the depth at which soil sample was collected. Since neither PFOS nor PFOA adsorb strongly to soils, we hypothesize that the compounds are contained in particles that are transported by wind and vehicular traffic to other locations or by water infiltrating into the soil.

Overall, the results of this study indicate soil-to-soil pathways through wind and vehicular traffic and a soil-to-groundwater migration pathways of PFOS and PFOA. The observations indicate that PFOS and PFOA contamination is not contained to a few hot spots, but is migrating with wind and traffic to other locations. In addition, PFOS and PFOA contamination is migrating toward the groundwater table. We believe that the source of this contamination is PFOS and PFOA containing particles that can be picked up by wind and traffic, and by water infiltrating towards the groundwater table.

Chapter 1. Introduction

1.1 Perfluorochemicals

The scientific community and the public have become increasingly concerned about a group of emerging persistent organic pollutants called perfluorochemicals (PFCs) or perfluoroalkyl substances. PFCs are industrially produced compounds that contain a perfluorinated alkyl moiety of varying chain length and varying functional groups attached to that moiety. They have been produced for both industrial and commercial applications including aqueous fire fighting foam and polymers to repel water and oil (see Figure 1.1) (Xiao, 2012). Because of the strong carbon-fluorine bonds, PFCs are not easily degraded by physical or chemical mechanisms once in the environment.

At present the pollution of long-chain PFCs is a worldwide concern due to their persistency, toxicity and tendency to bioaccumulate (Xiao, 2012). Two long-chain PFCs, perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) have been found in surface runoff (Xiao et al., 2012b), wastewater treatment plant influents and effluents (Xiao et al., 2012a), the biosphere (Houde et al., 2011), and human blood at high concentrations relative to suspected chronic effects (several to tens of $\mu\text{g/L}$) (Kato et al., 2011). The presence of PFOS/PFOA in human blood has been linked to attention deficit/hyperactivity disorders in children (Hoffman et al., 2010), hyperuricemia (Steenland et al., 2010) and lowered immune response to vaccinations in children (Grandjean et al., 2012).

Despite the phase-out of the PFOS and PFOA production by a 3M in 2002, there is a potential reservoir of PFC-containing substances/products still in use in a wide range of industrial/commercial applications. In fact, the use of some PFC-containing products has been exempted from the most recent (2007) USEPA Significant New Use Rule regarding PFCs (Kelly and Solem, 2008). In addition, transportation activities can also contribute nonpoint source pollution of PFCs (Xiao et al., 2012b).

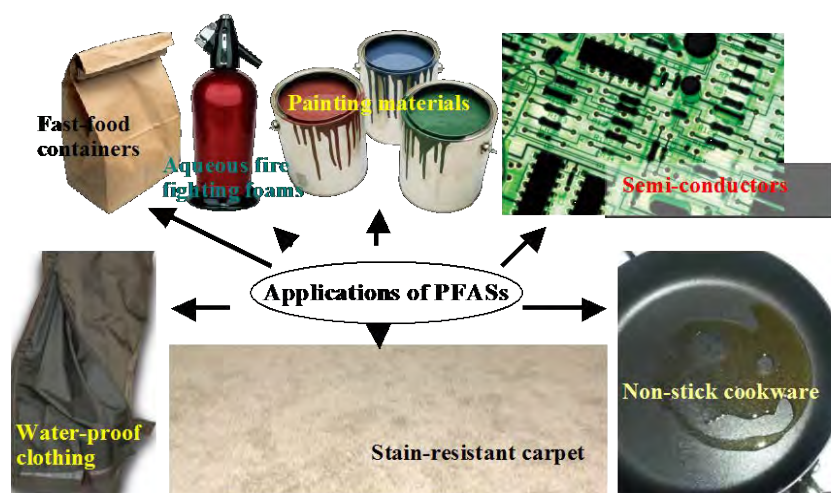


Figure 1.1: Applications of PFCs, also identified as PFASs (images are from Word 2011 Microsoft™ Cooperation or personal belongings) (adopted from (Xiao, 2012)).

1.2 Previous Studies

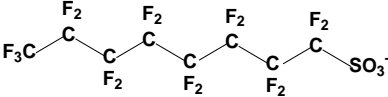
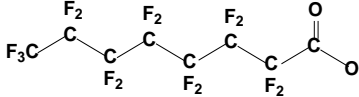
There are studies available in the literature about the PFC pollution in the Minnesota ambient environment (Simcik and Dorweiler, 2005, Xiao, 2012, Xiao et al., 2012a, Xiao et al., 2012b). By means of unsupervised pattern recognition techniques and a Geographic Information System (GIS), Xiao et al. modeled the PFC pollution trends in wastewater treatment plants across more than 40 cities (Xiao et al., 2012a) and fish caught from 28 urban lakes (unpublished results). Xiao et al. also analyzed PFCs in stormwater runoff from several storm events (2009–2011) at various outfall locations corresponding to different watershed land uses (Xiao et al., 2012b). Previous results indicate that elevated PFC levels are mostly observed in the Minneapolis–St. Paul metropolitan area (MSP) in Minnesota, a region concentrating the state’s industrial and commercial activities and generating ~74% of the state’s total GDP. MSP is the sixteenth largest metropolitan region in the U.S. and home to approximately 60% of the state’s pollution of 5.34 million (2010 census).

1.3 Research Gap – Soil Contamination of PFCs

Although PFOS and PFOA are believed to be ubiquitous in the environment, few studies are available about their occurrence in surface and subsurface soils, partially because these chemicals are known as hydrophilic and water-borne species, with moderate sorption potential (Xiao et al., 2011), relatively high solubility in water, and low volatility (see Table 1.1) (Xiao, 2012). When considering the aqueous concentrations of PFOS/PFOA in rainwater and surface runoff samples (several to a few tens of ng/L) (Xiao et al., 2012b) and the low solid–water partitioning coefficient (several L/kg) (Xiao et al., 2011), one may reasonably assume low levels of PFOS and PFOA present in soils (i.e., < 0.1 ng/g dw). However, elevated levels of PFOS up to 590 ng/g dw were found on the particulate matter in runoff collected from industrial and commercial areas (Xiao et al., 2012b). The levels were so high that they could not be explained by the solid–water distribution or adsorption (Xiao et al., 2012b). PFOS can also be inherent in the particles/debris, possibly including the debris of industrial polymers containing PFOS (Xiao et al., 2012b).

There are several public concerns about soil pollution of PFOS and PFOA: they can transfer from soils to crops (Felizeter et al., 2012, Lechner and Knapp, 2011), contaminated soil particles can migrate with wind from outdoors to indoors, and children are vulnerable to contaminated soils because of frequent hand-to-mouth contact. The literature on PFCs in Minnesota soils, however, is minimal, and the transport mechanisms of PFCs from contaminated soils to remote areas remain largely unknown.

Table 1.1: Physicochemical properties of PFOS and PFOA (adopted from (Xiao, 2012)).

Property	PFOS (Potassium salt)	PFOA
CAS No.	2795-39-3	335-67-1
Chemical structure		
Appearance at normal room temperature and pressure)	White powder	White powder/waxy white solid
Molecular weight (g/mol)	538 (potassium salt); 499 (anionic species)	414; 413 (anionic species)
Water solubility (mg/L at 25°C)	570 (purified), 370 (freshwater)	9500 (purified)
Melting point (°C)	> 400	40 to 50
Boiling point (°C)	Not measurable	188
Vapor pressure at 20°C (mm Hg)	2.48×10^{-6}	0.017
Air–water partition coefficient, K_{aw} (Pa m ³ /mol)	$< 2 \times 10^{-6}$	Not available
Octanol–water partition coefficient, K_{ow}	Not measurable	Not measurable
Organic carbon-normalized sorption coefficient, log K_{oc}	2.57	2.06
Half-life	Atmospheric: 114 days; Water: > 41 years (at 25°C)	Atmospheric: 90 days; Water: > 92 years (at 25°C)

1.4 Scope of Research

The overall goal of this project is to investigate the sources of PFCs in roadside soils and the role of wind and vehicular traffic in transporting PFCs from contaminated soils to other plots. The specific objectives are to:

- 1) Collect surface and subsurface soil samples from both MSP metropolitan area and rural areas along a national highway, and determine PFOS and POFA concentrations in soils associated with different land uses.
- 2) Identify pollution hotspots in urban soils for better environmental management and pollution control with the aid of a Geographic Information System (GIS) and exploratory spatial data analysis.
- 3) Examine major transport mechanisms of PFOS and PFOA from sources to other plots.

Chapter 2. Methods and Materials

2.1 Soil Sample Collection and Characterization

The sampling of soil samples from different layers was carried out at different sites along the U.S. Highway (Hwy) 10 from Cottage Grove to Big Lake (see Figure 2.1) running across the MSP. U.S. Hwy 10 is an east–west national highway originally formed in 1926 (Wikipedia, 2011). The eastern terminus of U.S. Hwy 10 is Bay City, Michigan and its western terminus is West Fargo, North Dakota. U.S. Hwy 10 is a major route in Minnesota, which enters St. Paul duplexed with interstate 35-E and exists St. Paul duplexed with Minnesota State Highway 61 (Wikipedia, 2011).

A combined stratified and judgmental sampling plan was performed. The target U.S. Hwy 10 section was separated into non-overlapping subsections, and roadside soil samples were collected from each subsection; intensive samples were collected at the suspended hot spots. Each sample was a composite sample, consisting of four sub-samples obtained in a 2 m × 2 m grid using a stainless steel auger after carefully removing stones and vegetation from the sampling surface. The approximate mass of each sample was 50 g. Samples were placed in pre-cleaned polythene bags and sent to the laboratory for drying at 50 °C for four days. Each sample was then sieved through a 2-mm stainless steel mesh to remove stones and other coarse materials, and mixed thoroughly to obtain a representative sample. After that, the sample was ground and homogenized with a solvent-rinsed mortar and pestle, and divided into three separate containers, which were treated as filed-triplicate samples. The mesh, mortar, and pestle were thoroughly cleaned after a sample was processed. Homogenized, dried samples were sent to the Soil Testing and Research Analytical Lab (RAL) at the University of Minnesota for analysis of the organic matter content in soils by a Loss on Ignition Method. A 5-g soil sample was weighted into a quartz crucible and dried for 2 h at 105 °C and weighted, and then ashed at 360 °C for another 2 h and reweighted. The resulting loss of weight was an estimate of the organic matter (<http://ral.cfans.umn.edu/soil-analysis-and-methods/#6>). RAL also determined the soil cation exchange capacity (CEC) by both the direct method and the summation method. In the direct method, CEC was determined when an amount of dry soil sample (5 g) was leached with 60 mL 1 M ammonium acetate at pH 7 to saturate exchange sites with ammonium ions. Excess free ammonium ions were rinsed from the soil sample with isopropyl alcohol. The remaining ammonium ions held on cation exchange sites were replaced by leaching the sample with successive aliquots of a solution of 10% KCl acidified to 0.005 N HCl. CEC was then calculated after the ammonium concentration was determined (<http://ral.cfans.umn.edu/soil-analysis-and-methods/#19>). In the summation method, CEC was determined by the summation of exchangeable Ca^+ , Mg^+ , Na^+ , K^+ , and H^+ . Base cations were extracted by leaching 3 g dry soil with successive aliquots of 1 M ammonium acetate at pH 7 to a total volume of 60 mL. The concentrations of these metal cations in the leachate were determined by inductively coupled plasma atomic emission spectroscopy (IPC-AES), and CEC was then calculated from the summation of the cations and exchanged hydrogen ions (<http://ral.cfans.umn.edu/soil-analysis-and-methods/#20>).

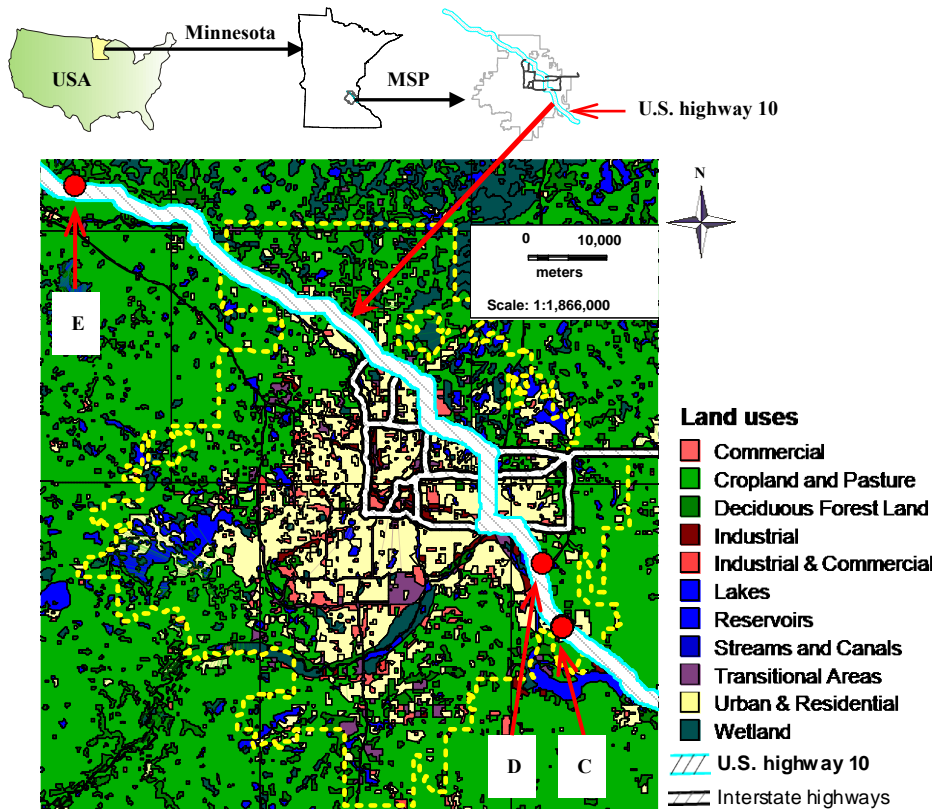


Figure 2.1: Land-use information around sampling sites shown in a GIS map. The sampling sites C, D, and E (Big Lake) are identified in the map to illustrate the sources of PFOS outside the MSP region (see Section 3.2 in Chapter 3).

2.2 Chemicals

PFOS (CAS 2795-39-3) and PFOA (CAS 375-95-1) standards for calibration were purchased from Sigma-Aldrich (Milwaukee, WI, USA & Steinheim, Switzerland). Isotopically labeled standards $^{13}\text{C}_4$ -PFOA, $^{13}\text{C}_4$ -PFOS, $^{18}\text{O}_2$ -PFOS, and $^{13}\text{C}^8$ -PFOA, were purchased from Cambridge Isotope Laboratories (MA, USA). Methanol and R.O. water were used to clean the containers and equipment.

2.3 Sample Extraction and Cleanup

Sample extraction and cleanup were conducted by following a previously developed approach (Higgins et al., 2005) with a slight modification. Homogenized, dried soil (20 g) was transferred to a 50-mL pre-cleaned polystyrene vial, to which 10 mL R.O. water containing 1% acetic acid and a pre-determined amount of $^{13}\text{C}_4$ -PFOA and $^{13}\text{C}_4$ -PFOS (surrogate standards) were added. R.O. water refers to as deionized water purified further by reverse osmosis. Each vial was mixed vigorously, placed in the preheated sonication bath, and sonicated for 30 min. After sonication, the vials were removed from the bath, centrifuged for 2 min, and the acetic acid solution was decanted into a pre-cleaned high-density polyethylene container. An aliquot of Optima-grade methanol (25 mL) was then added to the original vial, which was again mixed vigorously and sonicated for 20 min before centrifuging and decanting the extract. The whole process was

repeated once again, and a final 10-mL acetic acid wash was performed. To remove the acetic acid, salts, and potential matrix interferences, the soil extract was pumped through an Amberlite XAD-7HP cartridge at a volumetric flow rate of 2 mL/min, approximately two drops per three seconds. Each cartridge was first conditioned with 10 mL of methanol followed by 10 mL of 1% acetic acid. After loading, the cartridge was washed with 10 mL of R.O. water and air-dried. PFCs retained on the resin were eluted with a total of 40-mL Optima-grade methanol three times into a 50-mL pre-cleaned polystyrene tube. The eluent was concentrated to 0.5 mL under a gentle stream of pre-purified nitrogen and filtered (0.22 μm) into a Wheaton vial. An aliquot of the filtrate was transferred into a 300 μL insert (Chrom Tech, Minneapolis, USA) in a second Wheaton vial, spiked with a pre-determined amount of each $^{18}\text{O}_2$ -PFOS and $^{13}\text{C}^8$ -PFOA (internal standard), crimp-sealed with a natural rubber septum (Chrom Tech, Minneapolis, USA), and stored at 4 °C for further instrumental analysis.

2.4 Method Detection Limits, QA and QC

Method detection limits (MDLs) were measured for replicate ($n = 7$) analyses of “samples” (the mixture of clay and sand) spiked with target compounds to a concentration of one to five times the estimated detection limit, and by multiplying the corresponding standard deviation for the peak areas calculated times a Student's t -value at a certain degree of freedom ($f = 6$) and alpha level of 0.01 (corresponding to 99% confidence level).

To avoid cross-contamination, the auger was thoroughly cleaned after each sample was processed by 1) cleaning with a tissue to remove the soil/particles attached on it, 2) rinsing with a mixture of methanol and R.O. water, 3) cleaning again with a new tissue, 4) a final rinse with R.O. water, and 5) wiping up with a new tissue. Three rinsate blanks were prepared by using R.O. water run over this decontaminated auger in order to assess the adequacy of cleaning processes in the field sampling procedure. The blanks were placed in sample containers for handling, shipment, and analysis identical to the field samples.

Three field blanks were prepared by bringing a mixture of PFC-free kaolinite clay and methanol-cleaned Ottawa sand (Fisher, 20–30 mesh) in three pre-cleaned polythene bags to the field. The bags were opened and the mixture was exposed to the sampling environment at the sampling site. The blanks were shipped back to the laboratory and treated as field samples.

Other QA/QC considerations also include using nitrile gloves, wearing old clothing (laundered several times), avoiding pre-wrapped food and snacks, and avoiding wearing water resistant clothing and insect repellent/sunscreen. Three procedure blanks were also prepared to assure that the target compounds detected were not originally from the laboratory.

Recoveries were determined from surrogate standards.

2.5 Instrumental Analysis and Calibration

The concentrations of PFOS and PFOA were determined using a Thermo–Finnigan triple stage quadrupole mass spectrometer coupled to an Agilent 1100 capillary high-pressure liquid chromatograph located at the Masonic Cancer Center of the University of Minnesota. The mobile phase consisted of eluent A (15 mM NH_4Ac in nanopure water) and eluent B (Optima grade

methanol). The A/B ratio changed linearly in the first 14 min from 40:60 to 16/84, and then changed back to the ratio of 40:60 at 14.5 min, which was held for until a total running time of 23 min. The analytical column was a Phenomenex Gemini C₁₈ column (150 × 2.0 mm, 5 micron). The injection volume was 50 µL, and the operating temperature was 25 °C.

The concentrations in some of the soil extracts were determined by a relative response factor method (*RRF*). The *RRF* was calculated by putting a known amount of internal standard into a standard with unlabeled PFOS and PFOA and then dividing the mass to area ratios of both labeled and unlabeled compounds. The peaks of all species were determined by the specific mass to charge ratio (*m/z*) shown in Table 1.2.

Figure 2.2: *m/z* ratios used for determining concentrations of PFOA and PFOS.

Species	<i>m/z</i>
PFOA	413.0→369.0 (369.8–369.2)
¹³ C ₄ -PFOA	417.0→372.0 (371.8– 372.2)
¹³ C ₈ -PFOA	421.0→376.0 (375.8–376.2)
PFOS	498.9→98.6 (98.4–98.8)
¹³ C ₄ -PFOS	502.9→98.6 (98.4 – 98.8)
¹⁸ C ₂ -PFOS	503.0→103.0 (102.8 – 103.2)

Chapter 3. Results and Discussion

3.1 Data Quality

High-quality data are always desirable in environmental modeling. With the standard method used herein, the average recoveries were $109.5 \pm 20.3\%$ (mean \pm standard error) and $106.1 \pm 19.7\%$ for PFOS and PFOA, respectively. The MDLs are 0.13 and 0.07 ng/g dw for PFOS and PFOA, respectively. PFOS and PFOA detected in all samples were at least two times higher than their corresponding MDL. Although PFOS was found in two of the field blanks with concentrations below the MDL, PFOS and PFOA were not found in rinsate and procedure blanks. Overall, the data quality is satisfactory. The mass spectra of the target species are given in Figure 3.1.

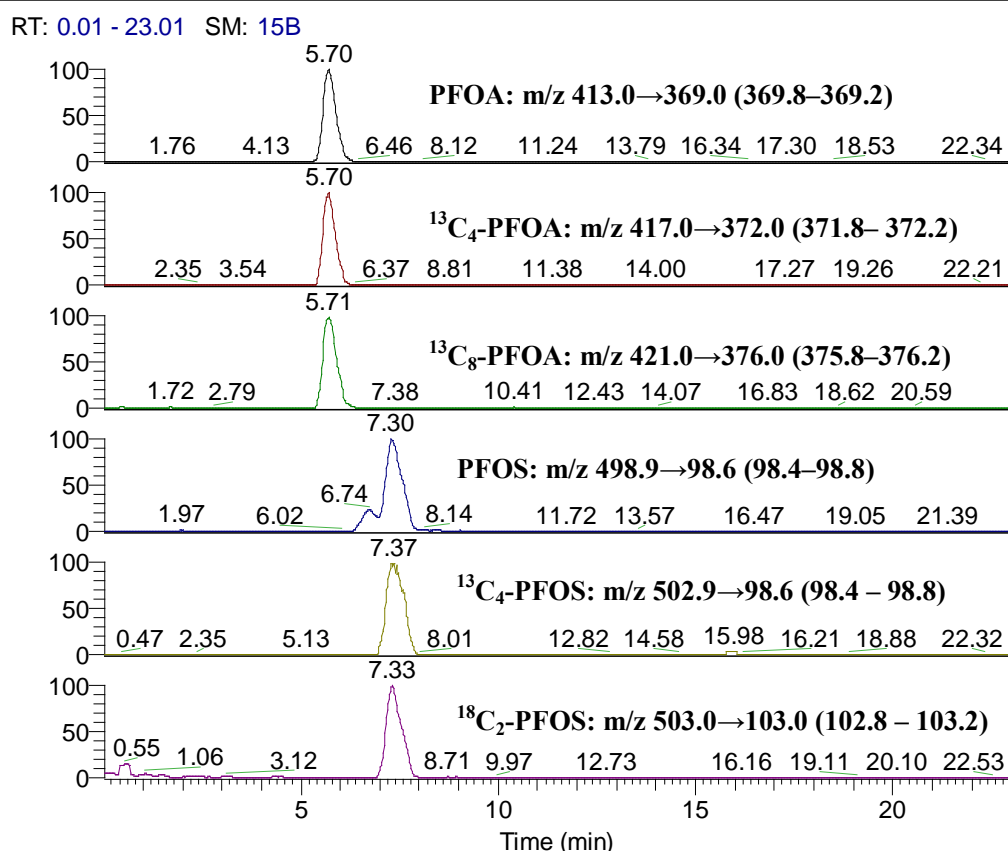


Figure 3.1: Mass spectra of target species.

3.2 PFOS and PFOA in Roadside Surface Soils

The U.S. Hwy 10 section studied is presented in a GIS map with detailed land use information presented (see Figure 2.1). The studied section of U.S. Hwy 10 starts from Cottage Grove, MN, runs across MSP, and extends to Big Lake, MN. The MSP is a typical mix of cropland, compact residential areas, commercial districts, and industrial areas (See Figure 2.1).

Concentrations of PFOS and PFOA (C_{PFOS} or C_{PFOA}) at each sampling site were tabulated in Table A1 (see Appendix). The surface soil in this study refers to topsoil in the upper layer of the earth (i.e., the top 2 in or 5 cm), and subsurface soil refers to soils collected > 2 in below the ground surface. The measured concentrations in surface soil samples ranged from 0.2–28.2 ng PFOA/g dw and 5.5–125.7 ng PFOS/g dw. The total concentration ($C_{PFOS} + C_{PFOA}$) ranged from 6.0 to 135.0 ng/g dw, with PFOS being the predominant pollutant. Both chemicals were found in all of the soil samples collected from urban and rural areas (see Table A1).

Global comparison of PFOS and PFOA concentrations in soils was made by gleaning information from the few soil studies available in the literature (see Table A1). Compared to other sites worldwide, the levels of PFOS and PFOA observed in this study were higher than those reported in Osaka and Hokkaido (Japan), Mexico City (Mexico), Tianjin and North Eastern region in China (Naile et al., 2010, Pan et al., 2011, Strynar et al., 2012, Wang et al., 2011), and some locations (North Carolina, Texas, Kentucky, and Indiana) in the U.S. (Strynar et al., 2012), but were comparable with the levels observed in soils following the long-term land application of municipal biosolids in Illinois (U.S.) (Sepulvado et al., 2011).

Table 3.1: Global comparison of PFOS and PFOA concentrations in soil. (ng/g dw)^a.

Location	Year	PFOS	PFOA	Reference
USA MSP, MN	2012	5.7–157.8	0.2–28.2	Present study
USA Illinois	2005–2008	2–483	–	(Sepulvado et al., 2011)
USA Research Triangle Park, North Carolina	–	<LOQ ^b –2.6	<LOQ ^b –32	(Strynar et al., 2012)
USA Houston, Texas	–	<LOQ ^b –2.2	<LOQ ^b –2.7	(Strynar et al., 2012)
USA Richmond, Kentucky	–	<LOQ ^b –1.6	<LOQ ^b –2.1	(Strynar et al., 2012)
USA W. Lafayette, Indiana	–	–	<LOQ ^b –2.2	(Strynar et al., 2012)
Japan Osaka and Hokkaido	–	<LOQ ^b –5.2	<LOQ ^b –1.8	(Strynar et al., 2012)
Mexico Mexico City	–	<LOQ ^b –10.1	<LOQ ^b –0.8	(Strynar et al., 2012)
China Tianjin	2008	0.15–0.27	0.22–0.41	(Pan et al., 2011)
China North-eastern region	2008	ND–0.7	ND–0.5	(Wang et al., 2011)
South Korea	2008	< 2	< 2	(Naile et al., 2010)

Note: ^a The global comparison was not intended to be representative of the region/nation of origin, but was to indicate the global variation of concentrations in soils at different parts of the world; ^b LOQ: Limit of quantification (~0.5 ng/g dw); ND: Not detected.

On the basis of comparing our data with other soil sampling data (see Table A1), significant sources of PFOS and PFOA appear to be present in current study region. To better identify hot spots/sources and the geographic trends of C_{PFOS} and C_{PFOA} , our data were modeled by a least-

squares geostatistical interpolation technique, kriging, with concentrations of PFOS and PFOA in surface soils (0.8–2.0 in or 2–5 cm) as the dependent variable (see the contour/geochemical maps presented in Figure 3.2). As shown in Figure 3.2, two hot spots (A and B) of elevated PFOS and PFOA concentrations were identified in the geochemical maps, and location A appears to be a major point source of surface soil contamination of PFOS and PFOA. Location A is around the former PFC manufacturing facility, and location B is near a major manufacturer’s former legal PFC disposal site (Oakdale dump site).

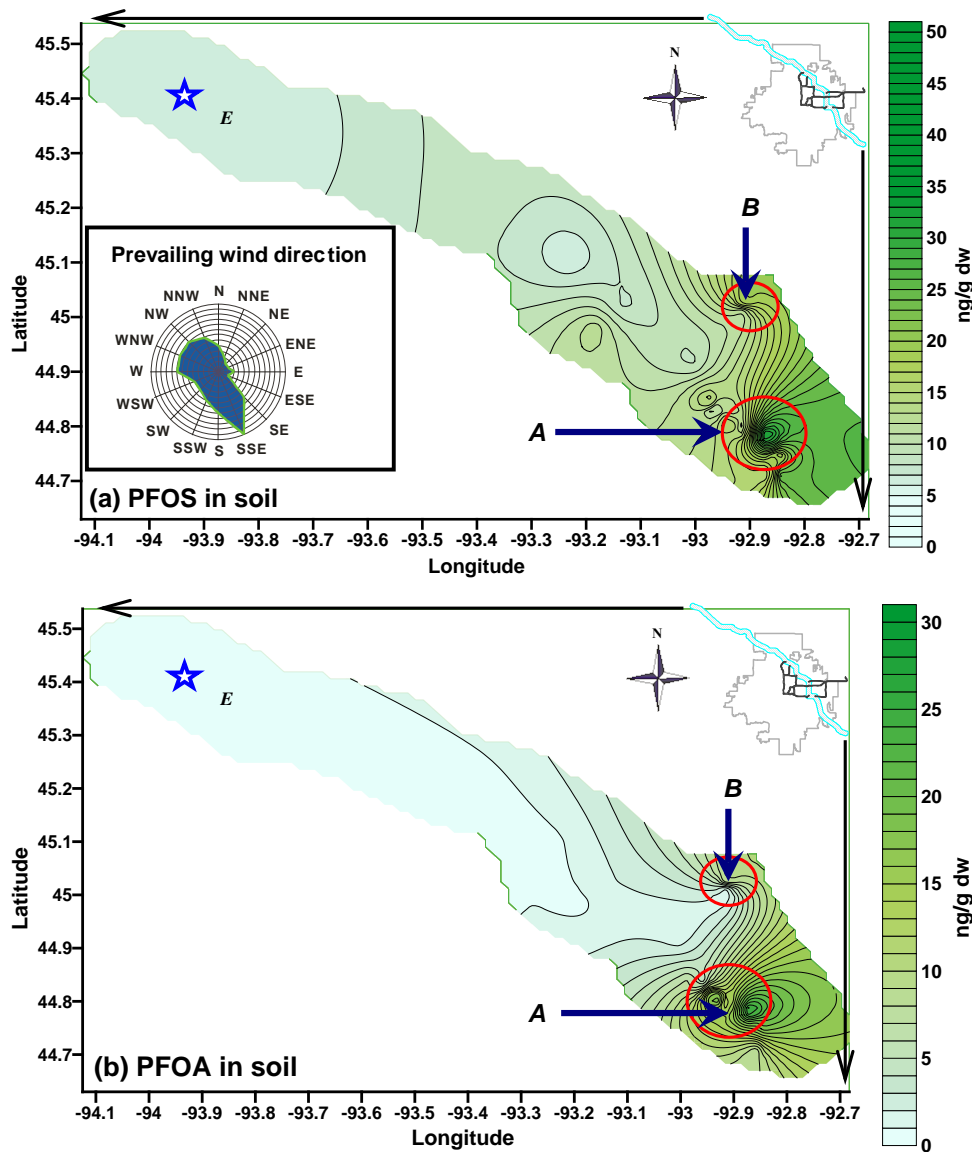


Figure 3.2: PFOA and PFOS in roadside Hwy 10 surface soils. Kriging was used as an interpolation technique to develop the lines of constant concentration.

An immediate question is how the chemicals were transported in space from their sources. Environmental transport mechanisms are a key to understand the regional and global distributions of persistent organic pollutants. These chemicals can be released to the environment through their uses in the field (e.g., fire-fighting foams and pesticides) and through emissions

from industrial facilities and wastewater treatment plants (WWTPs) (Xiao et al., 2012b; Xiao et al., 2011a). The suspected pathways for PFOS and PFOA migration include wind, vehicular transportation, precipitation, surface runoff, and groundwater movement. Previously efforts focus on the water and long-distance air transport mechanisms of PFOS and PFOA (Xiao et al., 2012). As a result the potential long half-lives in water, PFOS and PFOA can undergo regional or long-range transport with surface water and end up in remote areas. In addition, PFOS and PFOA can be atmospherically oxidized from their (semi-)volatile precursors that are subjected to long-range atmospheric transport (Ellis et al., 2003; Martin et al., 2006) and accumulate in other geographic regions with a substantial distance from their original sources (Giesy and Kannan, 2001; Smithwick et al., 2005; Wania and Mackay, 1996; Young et al., 2007). In our case, long-distance atmospheric transport and deposition can be ruled out as a significant source/transport pathway since both PFOS and PFOA were unevenly distributed in the geographic region (see Figure 3.2).

Based on our data and the geo-statistical modeling result, we believe that wind and vehicular transport serves as the principle pathway transporting PFOS- and/or PFOA-associated particles from the hot spots/contaminated soils to other areas.

First, from the geochemical maps (see Figure 3.2), both chemicals can migrate **in all directions** from the source (location A), signifying a wind-transport mechanism. Further, as illustrated by the high zones (dark patches), PFOS and PFOA tend to be preferentially carried in the southeast direction from the source (location A), which is in the dominant direction of wind flow (southeast) (see Figure 3.2).

The concentration profile of PFOS and PFOA on a hill (site C) was examined in detail to further investigate the transport mechanism. The hill is located approximately 4.0 mi (6.5 km) away from location A. The highest concentrations were found half way up to the hill on the side facing toward location A and U.S. Hwy 10. At the other side of the hill, concentrations of PFOA dropped to approximately zero (see Figure 3.3). The results indicate that particles containing PFOS/PFOA were retained by the soil when wind hits the hill, suggestive of a spatial retardation effect. This retardation effect can partially explain the elevated PFOS and PFOA concentrations detected in offsite soils 10 years later after phasing-out production of PFOS- and PFOA-related substances by a major manufacturer. The results also indicate that the transport pathway by wind is strongly influenced by the configuration of the earth's surface and urban buildings, and thus it is believed to be a more important pollutant-transport mechanism in the plains regions. Stronger winds may carry PFOS- or PFOA- contaminated soil/particles a longer distance within a short period of time.

Second, concentrations of both PFOS and PFOA decrease with distance from hot spots; however, the data set of PFOS is more variable than that of PFOA. Along the road, the continuous low zones (light green patches) are, on the average, smaller for C_{PFOA} than for C_{PFOS} . The ratio of PFOA/PFOS decreases substantially from 1.2 at location A to less than 0.3 at sites D and E (see Figure 3.4). Sites D and E are both outside MSP, in the **upwind** direction from the major source (location A) and in lowly urbanized areas with surrounding land use of cropland. From D to E (Big Lake), PFOS dominates in soil samples, including those collected from MSP. Therefore, the source of PFOS at these two sites is likely to be transportation activities which transport PFOS from hot spots.

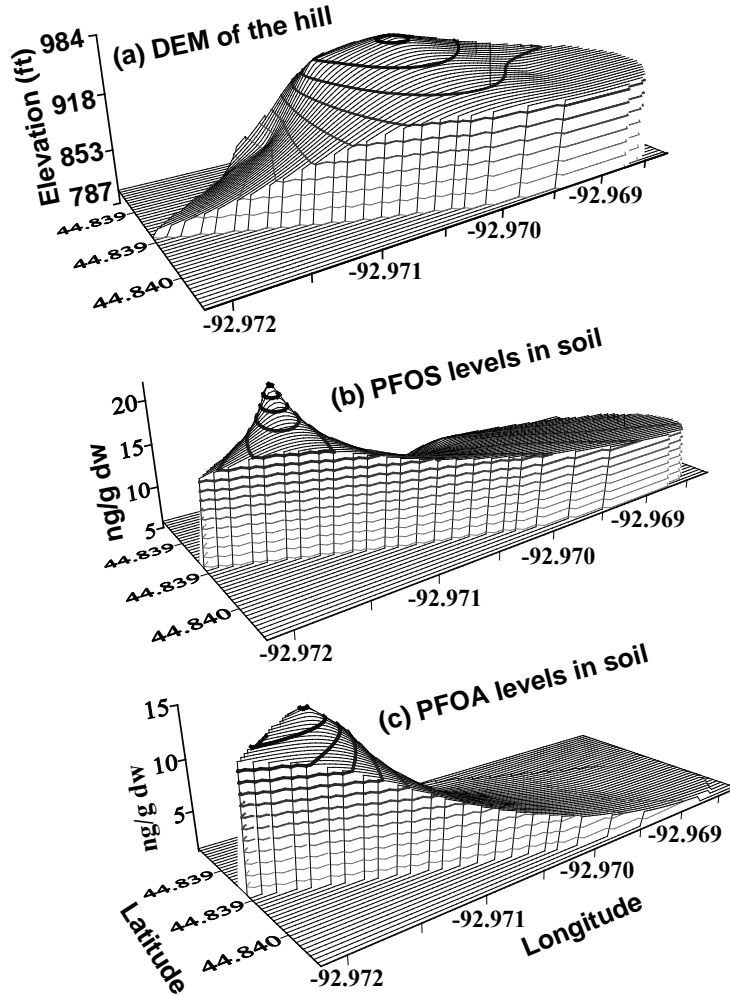


Figure 3.3: PFOA and PFOS concentration profiles in a hill with a distance (D) of ~4.0 mi (6.5 km) from location A. DEM is the digital elevation model.

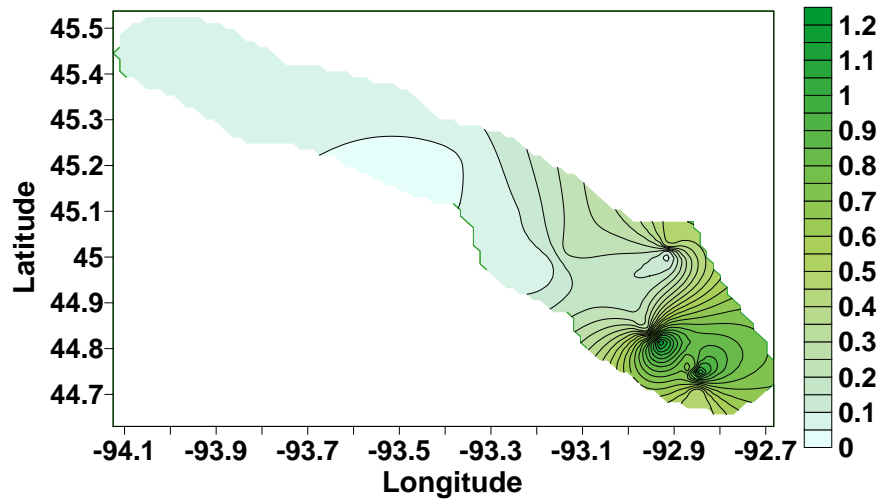


Figure 3.4: The ratio of C_{PFOA} to C_{PFOS} in roadside surface soils.

We also investigated the possibility of runoff as a transport carrier. If runoff is a major carrier, elevations of sampling sites and organic matter contents of soils could be two important predictors of C_{PFOS} or C_{PFOA} because 1) a low-elevation location tends to receive a relatively high percentage of surface runoff (Davis and Masten, 2004), and 2) PFOS and PFOA can interact with soil organic matter and thus being retained on soils (Higgins and Luthy, 2006). In addition, the transport and movement of hydrophilic species as PFOS and PFOA in soils with water can be strongly affected by the cation exchange capacity (CEC) of soils (Xiao et al., 2011). However, as shown in Figure 3.5, no discernable trends were seen in the levels of PFOS and PFOA in soil samples as a function of either the elevations of sampling plots, the organic matter percentage (OM), or the CEC of soils. Therefore, it is less likely that PFOS and PFOA detected in off-site soils were carried by runoff from sources or by wet deposition. The receiving medium corresponding to runoff will be municipal wastewater and surface water, but not soils. Results of CEC and OM can be found in Table A2 of the Appendix.

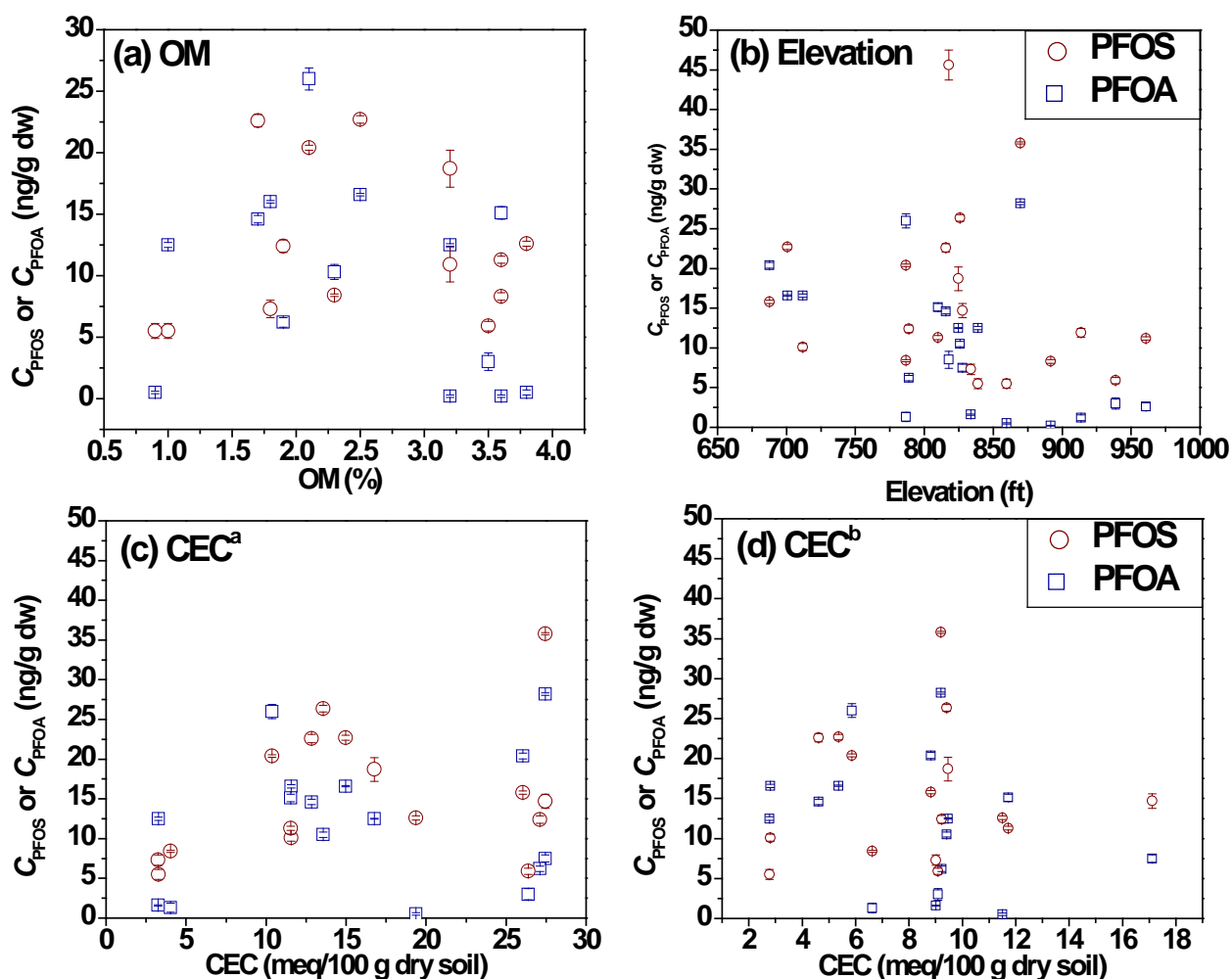


Figure 3.5: Soil concentrations of PFOS and PFOA as a function of (a) organic matter content (OM, %); (b) elevation of the sampling site; (c) CEC of soils determined by a summation method; (d) CEC determined by a direction method.

3.3 PFOS and PFOA in Roadside Subsurface Soils

Precipitation and runoff, however, can be a major carrier of PFOS and PFOA to the deeper layer of soils. As a result of their moderate K_{oc} , PFOS and PFOA can be transferred from surface soils to water and move downward into subsurface soils and eventually to the groundwater table. We studied subsurface soil concentrations of PFOS and PFOA, and found that the concentrations of both chemicals generally increased with the depth at which soil samples were collected. The exception of this trend is the PFOS concentration profile in Tong soils collected at location B (see Figure 3.6). The level of PFOS at this location reached a maximum of 160 ng/g dw at a depth of 27.6 in (70 cm), and then decreased sharply to 35 ng/g dw at a depth of 31.5 in (80 cm). The concentration profiles shown in Figure 3.6 are different from those observed by Higgins and coworkers (Sepulvado et al., 2011), who found that levels of PFOS and PFOA decreased with depth at sites receiving approximately 30-year biosolids application. Another finding from Figure 3.6 is that the ratio of the PFC concentration at the depth of 27.6 in (70 cm) to the PFC concentration in the surface soil increases with increasing chain length; in other words, PFOS seems to move more effectively than PFOA underground. This is the opposite of Higgins and coworkers' results (Sepulvado et al., 2011). The intuitive sense is that a shorter-chained PFC (i.e., PFOA) with a lower sorption potential should move more effectively than longer-chained PFC (i.e., PFOS) as claimed by others (Sepulvado et al., 2011). However, the transport of polar chemicals underground is a complicated process (Schwarzenbach et al., 2003, Yong and Thomas, 2004), which is not solely controlled by sorption or desorption. A survey of PFC concentrations at different depths of subsurface soils can shed some light on the issue, but may not be sufficient to distinguish which one, PFOS or PFOA, transports more easily in soils. It is possible that most of the PFOA molecules previously adsorbed by soils have been washed to a deeper layer or even groundwater because of a relatively fast transport rate. This is circumstanced by the nonexistence of a peak in the concentration profile of PFOA (see Figure 3.6), whereas a peak in the PFOS concentration profile was observed (see Figure 3.6c). In addition, the different PFOS concentration-depth files in Tong soils and Jane soils may be attributed to the different soil structure, such as the porosity, and groundwater levels.

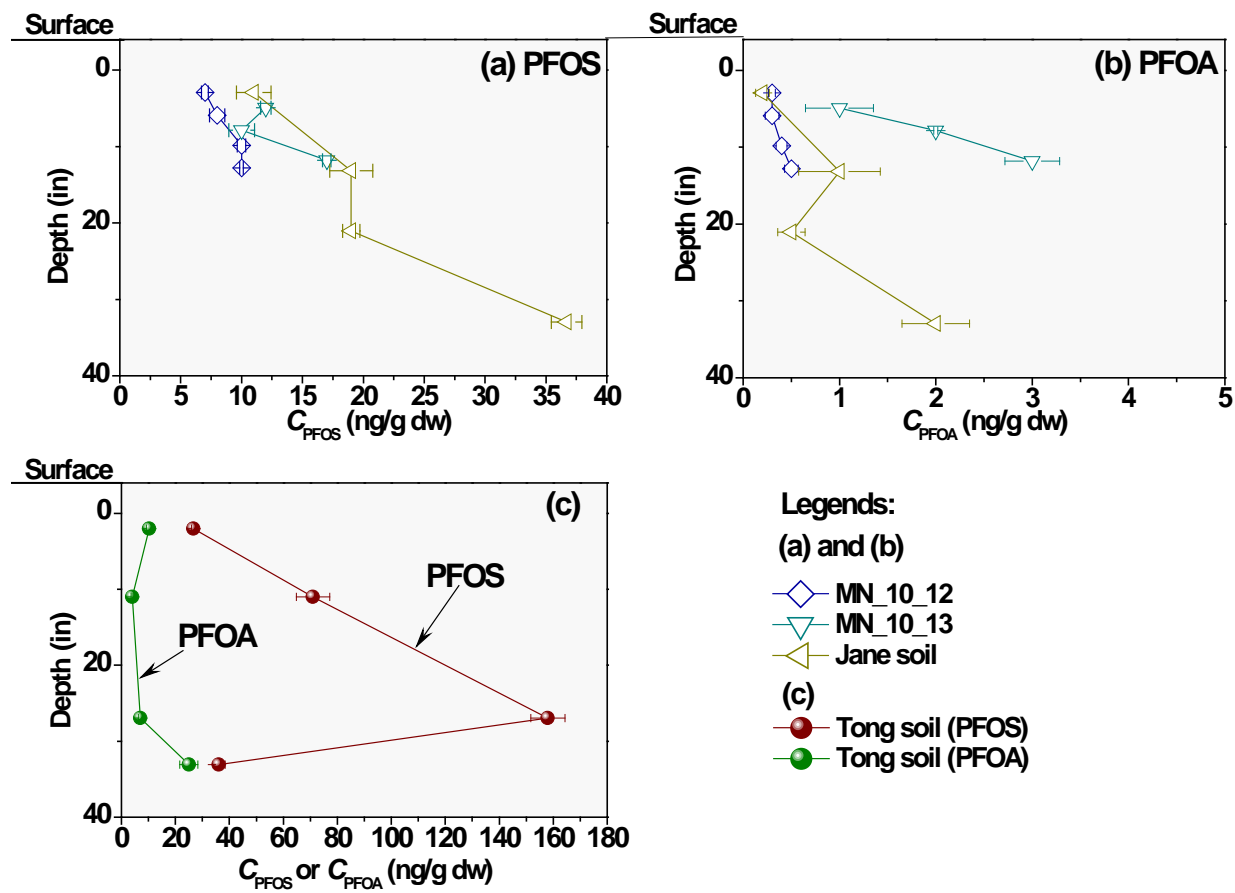


Figure 3.6: Concentrations of PFOS or PFOA in subsurface soils.

3.4 Environmental Significance

The relatively high concentrations of PFOS and PFOA detected in surface and subsurface soils poses a health threat to humans and animals. Table 3.2 presents a source-to-receptor model based on the results of the project. The conceptual site model will help to understand what is currently understood about the contamination condition and where there are still research gaps. As shown in Table 3.2, the potential receptors include humans, rodents, birds of prey, farm animals, natural vegetation, and agricultural crops. Possible routes for exposure include breathing air containing contaminated dust particles and ingesting groundwater, contaminated soil because of the hand-to-mouth contact, and products from contaminated farm animals and agricultural crops grown on the site. Future work is therefore suggested to monitor PFOS and PFOA levels in groundwater and farming products including crops, cow milk, and meats.

Table 3.2: A source-to-receptor model of PFOS and PFOA contamination of soils.

Primary Source of Contamination	Secondary Source of Contamination	Migration pathways	Exposure Routes	Receptors
Contaminated soils	Contaminated groundwater	Wind, vehicular transportation, infiltrate, groundwater	Direct exposure, inhalation, ingestion	Humans, soil-born microbes, rodents, birds of prey, farm animals, natural vegetation, agricultural crops

Chapter 4. Conclusions

High levels of PFOS and PFOA were observed in soils, the second largest so far reported in the scholarly literature. The low level of partitioning from the dissolved state to particles indicates that the high concentrations result from small particles that contain PFOS and PFOA in their matrix, i.e., were produced containing the compounds. The occurrence of these chemicals in sites away from hot spots is less likely to be caused by the transfer from precipitation/runoff to soils or by long-range atmospheric deposition. Our results point to an important but overlooked pathway of PFOS and PFOA dispersion to other regions, low elevation winds which will carry these particles. This identified transport mechanism can account for the soil contamination of PFCs in fields where they have never been produced or used. We are aware of no study linking the widespread contamination of the environment by PFCs to lower atmosphere wind as an important transport carrier of PFC-contaminated particles. The closest were studies about the release of PFOA from air emission stacks, transported by wind and deposited to soils (Barton et al., 2010; Davis et al., 2007). Shin and co-workers also included this air emission stack–soil transport mechanism into their modeling work (Shin et al., 2012; Shin et al., 2011). However, the stack release and deposition mechanism may not be as important in our case because the production of PFOS- and PFOA-related products was phased-out 10 years ago in Minnesota.

After the major sources and transport mechanisms have been identified, further studies are needed to understand the soil pollution of PFOS and PFOA in locations leeward of the sources. In addition, our subsurface soil data strongly suggest the leaching of PFOS and PFOA from the surface soil to deeper layers, which indicates that the compounds are associated with small particles. Therefore, a surficial groundwater monitoring activity to determine the levels of PFOS and PFOA down-wind of hot spots is recommended.

The transport mechanism for these PFOS and PFOA hot spots is therefore hypothesized to be the following:

1. Particles containing PFOS and PFOA are picked up from a hot spot by wind and transported to a location where they are deposited on vegetation, soil or other solid.
2. These particles are later picked up by infiltrating rain water and transported into the soil and towards the surficial groundwater.
3. The particles containing PFOS and PFOA are also filtered by the soil as the water moves through small pore spaces.

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Appendix A: Data Collected Along US Highway 61

Table A1: Concentrations of PFOA and PFOS (C_{PFOA} or C_{PFOS}) in highway roadside soils (\pm standard error, ng/g dry weight) at different depths (in or ft).

C_{PFOA}	C_{PFOS}	$C_{\text{PFOA}} / C_{\text{PFOS}}$	n	Sampling sites
24.1 \pm 0.9	27.9 \pm 2.3	1.16	3	U.S. 10 Site 1 (0–0.8 in or 0–2 cm)
10.5 \pm 0.3	26.3 \pm 0.4	2.5	2	U.S. 10 Site 1 (0.8–2.0 in or 2–5 cm)
11.8 \pm 0.1	28.7 \pm 0.7	2.4	2	U.S. 10 Site 1 (2.0–3.9 in or 5–10 cm)
8.5 \pm 1.1	45.6 \pm 1.9	5.4	3	U.S. 10 Site 2 (0.8–2.0 in or 2–5 cm)
7.5 \pm 0.5	14.7 \pm 0.9	2.0	2	U.S. 10 Site 3 (0.8–2.0 in or 2–5 cm)
20.4 \pm 0.4	15.8 \pm 0.2	0.8	2	U.S. 10 Site 4 (0.8–2.0 in or 2–5 cm)
16.6 \pm 0.2	10.1 \pm 0.5	0.2	2	U.S. 10 Site 5 (0.8–2.0 in or 2–5 cm)
16.6 \pm 0.1	22.7 \pm 0.3	1.4	2	U.S. 10 Site 6 (0.8–2.0 in or 2–5 cm)
28.2 \pm 0.2	35.8 \pm 0.1	1.3	2	U.S. 10 Site 7 (0.8–2.0 in or 2–5 cm)
9.3 \pm 0.8	125.7 \pm 4.6	13.5	3	U.S. 10 Site 8 (0.8–2.0 in or 2–5 cm) ^a
15.1 \pm 0.5	11.3 \pm 0.3	0.8	2	U.S. 10 Site 9 (0.8–2.0 in or 2–5 cm)
26.0 \pm 0.9	20.4 \pm 0.2	0.8	2	U.S. 10 Site 10 (0.8–2.0 in or 2–5 cm)
6.2 \pm 0.4	12.4 \pm 0.5	2.0	2	U.S. 10 Site 11 (0.8–2.0 in or 2–5 cm)
0.5 \pm 0.2	9.5 \pm 0.1	19	2	U.S. 10 Site 12 (11.8–13.8 in or 30–35 cm)
0.4 \pm 0.3	10.2 \pm 0.4	25.5	2	U.S. 10 Site 12 (7.9–11.8 in or 20–30 cm)
0.3 \pm 0.2	7.8 \pm 0.6	26.0	2	U.S. 10 Site 12 (3.9–7.9 in or 10–20 cm)
0.3 \pm 0.0	7.0 \pm 0.3	23.3	2	U.S. 10 Site 12 (2.0–3.9 in or 5–10 cm)
3.2 \pm 0.3	17.3 \pm 0.4	5.4	2	U.S. 10 Site 13 (9.8–13.8 in or 25–35 cm)
1.9 \pm 0.0	9.8 \pm 1.1	5.2	2	U.S. 10 Site 13 (5.9–9.8 in or 15–25 cm)
1.0 \pm 0.4	11.7 \pm 0.4	11.7	2	U.S. 10 Site 13 (3.9–5.9 in or 10–15 cm)
14.6 \pm 0.3	22.6 \pm 0.5	1.5	2	U.S. 10 Site 14 (0.8–2.0 in or 2–5 cm)
12.5 \pm 0.2	5.5 \pm 0.6	0.4	2	U.S. 10 Site 15 (0.8–2.0 in or 2–5 cm)
3.0 \pm 0.7	5.9 \pm 0.4	2.0	2	U.S. 10 Site 16 (0.8–2.0 in or 2–5 cm)
2.6 \pm 0.5	11.2 \pm 0.2	4.3	2	U.S. 10 Site 17 (0.8–2.0 in or 2–5 cm)
1.2 \pm 0.4	11.9 \pm 0.5	9.9	2	U.S. 10 Site 18 (0.8–2.0 in or 2–5 cm)
11.4 \pm 0.5	10.7 \pm 0.7	0.9	2	U.S. 10 Site 19 (0–0.8 in or 0–2 cm)
12.5 \pm 0.1	18.7 \pm 1.5	1.5	2	U.S. 10 Site 19 (0.8–2.0 in or 2–5 cm)
13.6 \pm 0.1	13.7 \pm 0.8	1.0	2	U.S. 10 Site 19 (2.0–3.9 in or 5–10 cm)
1.6 \pm 0.1	7.3 \pm 0.7	0.5	2	U.S. 10 Site 20 (0.8–2.0 in or 2–5 cm)
1.3 \pm 0.6	8.4 \pm 0.1	0.8	2	U.S. 10 Site 21 (0.8–2.0 in or 2–5 cm)
0.5 \pm 0.2	12.6 \pm 0.2	25.2	2	U.S. 10 Site 22 (0.8–2.0 in or 2–5 cm)
0.7 \pm 0.2	9.8 \pm 0.5	14	2	U.S. 10 Site 23 (Target filed) (0.8–2.0

				in)
0.5 ± 0.1	5.5 ± 0.6	11	2	U.S. 10 Site 24 (Fridley) (0.8–2.0 in)
0.2 ± 0.1	8.3 ± 0.3	41.5	2	U.S. 10 Site 25 (Anoka) (0.8–2.0 in)
0.3 ± 0.1	5.7 ± 0.0	19	2	U.S. 10 Site 26 (Big Lake) (0.8–2.0 in)
24.9 ± 3.3	35.6 ± 2.4	1.4	2	U.S. 10 Site 27 (Tong soil) (2.5–3 ft or 76–91 cm, or)
6.4 ± 0.7	157.8 ± 6.4	24.7	2	U.S. 10 Site 27 (Tong soil) (2–2.5ft or 61–76 cm)
3.9 ± 0.4	71.5 ± 6.1	18.3	2	U.S. 10 Site 27 (Tong soil) (9–13 in or 23–33 cm)
10.3 ± 1.4	26.7 ± 0.9	2.6	2	U.S. 10 Site 27 (Tong soil) (0–4 in or 0–10 cm)
C_{PFOA}	C_{PFOS}	$C_{\text{PFOA}} / C_{\text{PFOS}}$	n	Sampling sites
2.0 ± 0.4	36.7 ± 1.3	18.4	2	U.S. 10 Site 28 (Jane soil) (30–35 in or 76–89 cm)
0.5 ± 0.2	18.9 ± 0.7	37.8	2	U.S. 10 Site 28 (Jane soil) (18–24 in or 46–61 cm)
1.0 ± 0.4	18.8 ± 1.8	18.8	2	U.S. 10 Site 28 (Jane soil) (12–18 in or 31–46 cm)
0.2 ± 0.1	10.9 ± 1.4	54.5	2	U.S. 10 Site 28 (Jane soil) (0–6 in or 0–15 cm)
<p>Note: C_{PFOA} and C_{PFOS} stand for the concentrations of PFOA and PFOS in soils, respectively, and $C_{\text{PFOA}} / C_{\text{PFOS}}$ standards for the ratio of C_{PFOA} to C_{PFOS}. Tong soils were collected from one of the waste dumping sites of a former PFOS & PFOA manufacturer, and other soil samples were collected along highways. The high concentration of PFOS detected at Site 8 was considered as an outlier, and was not included in the geo-statistical modeling (kriging).</p>				

Table A2: Elevations of sampling sites and the cation exchange capacities (CEC) and organic matter contents (OM) of soil samples.

Sampling sites	Elevation (ft)	CEC ^a (meq/100 g dry soil)	CEC ^b (meq/100 g dry soil)	OM (%)
U.S. 10 Site 1 (0.8–2.0 in or 2–5 cm)	826	13.6	9.4	–
U.S. 10 Site 2 (0.8–2.0 in or 2–5 cm)	818			–
U.S. 10 Site 3 (0.8–2.0 in or 2–5 cm)	828	27.5	17.1	–
U.S. 10 Site 4 (0.8–2.0 in or 2–5 cm)	688	26.0	8.8	–
U.S. 10 Site 5 (0.8–2.0 in or 2–5 cm)	712	11.6	2.8	–
U.S. 10 Site 6 (0.8–2.0 in or 2–5 cm)	701	15.0	5.4	2.5
U.S. 10 Site 7 (0.8–2.0 in or 2–5 cm)	870	27.5	9.2	–
U.S. 10 Site 8 (0.8–2.0 in or 2–5 cm)	864	15.1	8.8	–
U.S. 10 Site 9 (0.8–2.0 in or 2–5 cm)	810	11.6	11.7	3.6
U.S. 10 Site 10 (0.8–2.0 in or 2–5 cm)	787	10.4	5.9	2.1
U.S. 10 Site 11 (0.8–2.0 in or 2–5 cm)	789	27.1	9.2	1.9
U.S. 10 Site 14 (0.8–2.0 in or 2–5 cm)	816	12.8	4.6	1.7
U.S. 10 Site 15 (0.8–2.0 in or 2–5 cm)	839	3.3	2.8	1.0
U.S. 10 Site 16 (0.8–2.0 in or 2–5 cm)	939	26.4	9.1	3.5
U.S. 10 Site 17 (0.8–2.0 in or 2–5 cm)	961			–
U.S. 10 Site 18 (0.8–2.0 in or 2–5 cm)	914			–
U.S. 10 Site 19 (0.8–2.0 in or 2–5 cm)	825	16.8	9.5	–
U.S. 10 Site 19 (0.8–2.0 in or 2–5 cm)				3.2
U.S. 10 Site 20 (0.8–2.0 in or 2–5 cm)	834	3.2	9.0	1.8
U.S. 10 Site 21 (0.8–2.0 in or 2–5 cm)	787	4.0	6.6	2.3

U.S. 10 Site 22 (0.8–2.0 in or 2–5 cm)		19.4	11.5	3.8
U.S. 10 Site 24 (Fridley) (0.8–2.0 in)	860			0.9
U.S. 10 Site 25 (Anoka) (0.8–2.0 in)	892			3.6
U.S. 10 Site 28 (Jane soil) (0 – 6 in)				3.2
Note: ^a CEC was determined by a direction method; ^b CEC was determined by a summation method (see Chapter 2).				