



## **Perfluorinated Compounds in Michigan**

### **Current State of Knowledge and**

### **Recommendations for Future Actions**

Prepared by the Toxics Steering Group Perfluorinated Compounds Workgroup

Members:

Joy Taylor Morgan, Environmental Quality Specialist, Air Quality Division

Robert Delaney, Geologist, Remediation Division

Mark Henry, Environmental Engineer, Remediation Division

Eric Wildfang, Toxicologist, Remediation Division

Deb Mackenzie-Taylor, Toxicology Specialist, Resource Management Division

Amy Babcock, Toxicologist, Water Resources Division

Michigan Department of Environmental Quality

Christina Bush, Toxicologist

Michigan Department of Community Health

John Buchweitz, Toxicologist

Michigan Department of Agriculture & Rural Development

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## **ADDITIONAL CONTRIBUTORS**

The Perfluorinated Compounds Workgroup acknowledges the efforts of the following DEQ staff, whose work contributed significantly to the production of this report:

Mike Depa, Toxicologist, Air Quality Division

Jeff Fischer, Environmental Quality Analyst, Water Resources Division

Denise Page, Secretary, Water Resources Division

Seth Wright, Contractor, Great Lakes Environmental Center

## List of Acronyms

ATSDR	Agency for Toxic Substances and Disease Registry
BCF	Bioconcentration factor
CDC	Centers for Disease Control and Prevention
DEQ	Department of Environmental Quality
ECF	Electrochemical fluorination
EPCEU	European Parliament and the Council of the European Union
FTOH	Polyfluorinated fluorotelomer alcohol
LSGM	Least-square geometric mean
MDH	Minnesota Department of Health
MPCA	Minnesota Pollution Control Agency
N-EtFOSE	N-ethyl perfluorooctanesulfonamidoethanol
ng/g	Nanograms per gram
ng/kg	Nanograms per kilogram
ng/mL	Nanograms per milliliter
ng/L	Nanograms per liter
NHANES	National Health and Nutrition Examination Survey
N-MeFOSE	N-methyl perfluorooctanesulfonamidoethanol
NPDES	National Pollutant Discharge Elimination System
OECD	Organization for Economic Cooperation and Development
PFAA	Perfluoroalkyl acid
PFAS	Polyfluorinated alkyl sulfonate
PFBA	Perfluorobutanoic acid
PFBS	Perfluorobutane sulfonate
PFCA	Perfluorocarboxylic acid
PFC	Perfluorochemical; per- or poly-fluorinated compound
PFDA	Perfluorodecanoic acid
PFDoA	Perfluorododecanoic acid
PFDS	Perfluorodecane sulfonate
PFECHS	Perfluoroethylcyclohexane sulfonate
PFHpA	Perfluoroheptanoic acid
PFHxA	Perfluorohexanoic acid
PFHxS	Perfluorohexane sulfonate
PFNA	Perfluorononanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonate
PFOSA	Perfluorooctane sulfonamide
PFOSE	Perfluorooctane sulfoamidoethanol
PFOSF	Perfluorooctanesulfonyl fluoride
PFPeA	Perfluoropentanoic acid
PFSA	Perfluorosulfonic acid
PFUA	Perfluoroundecanoic acid
pg/m <sup>3</sup>	Picograms per cubic meter
ppb	Parts per billion
ppt	Parts per trillion
TDS	Total Dietary Study
TSCA	Toxic Substance Control Act
TSG	Toxics Steering Group
ug/kg	Micrograms per kilogram
USEPA	United States Environmental Protection Agency
WAFB	Wurtsmith Air Force Base
WWTP	Wastewater Treatment Plant

## EXECUTIVE SUMMARY

The presence of perfluorinated compounds (PFCs) in Michigan's environment was documented as early as 2001, when national headlines regarding PFCs prompted the Department of Environmental Quality (DEQ) to collect several statewide surface water samples. Today, the only known site of PFC contamination in Michigan is the former Wurtsmith Air Force Base (WAFB) in Oscoda, but it is expected that detectable concentrations of PFCs could be found virtually anywhere in the state.

PFCs are unique in their ability to resist both polar (e.g., water) and nonpolar (e.g., oil) substances. This has resulted in a wide variety of industrial uses for the chemicals, ranging from electroplating to circuit board and paper production. A partial list of PFC-containing products includes textiles, food packaging, fire-fighting foams, pesticides, and hydraulic fluid. While it is likely that PFC manufacturers and industrial users of the chemicals directly discharge some quantity of PFCs into the environment, the inclusion of PFCs in numerous commercial goods suggests that normal use and disposal of common household products also may be an important route of entry of the chemicals into the environment.

Despite the fact that there are several hundred individual PFCs, the majority of the data available on this class of chemicals pertains to perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA). These chemicals historically were used as intermediates in the production of Scotchguard™ and Teflon®, respectively. Much of this report focuses on PFOS and PFOA.

PFOS has a strong potential to bioaccumulate while PFOA is not considered bioaccumulative. Both compounds are highly persistent; they have been detected in locations as remote as the Arctic, and it is believed that several other PFCs degrade into PFOS or PFOA. Mammalian toxicity is of greater concern than aquatic toxicity. In laboratory animal studies, PFOS caused alterations in thyroid hormones and PFOA exerted toxic effects on the liver. Neither chemical has been determined to be carcinogenic to humans, although they did induce tumors in laboratory rodents. The most significant nonoccupational human exposure to PFCs is expected to occur via consumption of contaminated food and drinking water, thus protection of fish and drinking water sources is crucial to minimizing public health impacts from PFCs.

The Michigan-specific data set regarding environmental concentrations of PFOS and PFOA is sparse; however, the compounds have been detected in water, fish, and wildlife throughout the state. A limited sampling program to quantify the current levels of PFCs in Michigan's environment will allow the DEQ to determine whether the conditions at the WAFB represent the "worst-case" scenario for the state and if additional statewide action may be necessary.

There is clear evidence of widespread, global exposure of humans and wildlife to PFCs. Similar exposures are expected to be occurring in Michigan. Currently, however, there is not clear evidence to associate adverse human health outcomes with PFC exposures. Toxicity information from laboratory animals indicates a potential for adverse health effects associated with human and wildlife exposure to PFCs. There are limited PFC concentration data for surface water, fish, and wildlife, but they were not collected with consideration of likely point sources of PFCs. Additional information on the concentrations of PFCs in Michigan's environment would help inform the potential impact of these substances on public health and the environment.

## RECOMMENDATIONS

The Toxics Steering Group (TSG) PFC Workgroup recommends that the DEQ take the actions listed below. Recommendations are listed in order of importance, to be undertaken in a tiered approach as funding allows. Note that the samples mentioned should be analyzed for PFOS and PFOA at a minimum, with perfluorobutanoic acid (PFBA) and perfluorohexane sulfonate (PFHxS) analyses performed where possible.

### Department-Wide

- Support the development of in-house PFC analytical capabilities at the DEQ, Environmental Laboratory.
- Send at least one staff person to the annual PFC conference organized by the United States Environmental Protection Agency (USEPA).
- Establish external collaboration with the “research corridor” of Michigan State University, the University of Michigan, and Wayne State University.

### Water

Objective 1: Determine the scope and extent of PFC contamination in surface water and fish in the area of the WAFB. It is possible that the base is the state’s worst-case scenario, thus results from the site could inform other decisions regarding PFCs in the state.

#### Tasks:

- Obtain paired fish tissue and surface water samples from the Au Sable River and Van Etten Lake.
- Obtain groundwater samples from existing on-site monitoring wells.

Objective 2: Obtain data to test the hypothesis that the conditions at the WAFB represent the most severe PFC contamination in the state.

#### Tasks:

- Collect groundwater, surface water, fish, and mink/Bald Eagle/Herring Gull samples from:
  - An area likely to be minimally impacted by PFCs (e.g., Keweenaw, Luce, and Mackinac Counties).
  - An area likely to be significantly impacted by PFCs (e.g., Kent and Ottawa Counties and Southeast Michigan counties).
  - The Kalamazoo River watershed, as discussed by Kannan et al. (2005).

If the data collected to satisfy Objective 2 reveal “hot spots” of elevated ambient levels of PFCs, it may be necessary to identify specific sources of PFC entry into Michigan’s environment and develop a long-term monitoring plan. Potential sources are discussed in the text of this report.

### Air

- Conduct outdoor air sampling in identified urban centers to determine current ambient air levels.

- Identify industrial manufacturing emission sources and assess feasibility of stack testing as part of permitting program under the 1990 Clean Air Act Amendments.
- Assess overall impact to ambient outdoor air from elevated indoor air concentrations when data are available by encouraging the scientific community to quantitate PFC adsorption/desorption to dust and exchange rates of indoor PFC to outdoor PFC. Speciation and degradation information would also help to determine this as a source/reservoir for environmental concentrations.



## CHAPTER 1: BACKGROUND AND INTRODUCTION

This report has been prepared in response to a charge to the TSG from the DEQ executive management. The TSG was directed to provide recommendations for establishing an environmental monitoring plan for PFCs in the state of Michigan, in light of the PFC contamination detected at the former WAFB.

This report contains concentration data that have been reported in different units (Table 1.1) in most of the published literature for these chemicals. The concentration data have been converted to parts per trillion (ppt) in this report for ease of comparison.

Table 1.1. Concentration units converted to ppt.

Part		Water and Biota Fluids (e.g., blood)	Biota Tissue and Soil	Air*
per million	1x10 <sup>-6</sup>	ppm or mg/L	ppm or mg/kg	ppm or mg/m <sup>3</sup>
per billion	1x10 <sup>-9</sup>	ppb or ug/L	ppb or ug/kg	ppb or ug/m <sup>3</sup>
per trillion	1x10 <sup>-12</sup>	ppt or ng/L	ppt or ng/kg	ppt or ng/m <sup>3</sup>
per quadrillion	1x10 <sup>-15</sup>	ppq or pg/L	ppq or pg/kg	ppq or pg/m <sup>3</sup>

\* For air data there is a conversion equation of Xg/m<sup>3</sup> = (ppX x molecular weight)/24.45.

PFCs represent a class of man-made organic chemicals that is comprised of several hundred neutral and anionic surface active compounds. PFCs do not occur naturally in the environment; rather, they exist due to modern and historical manufacture, use, and disposal practices associated with PFC-containing industrial and commercial products. The majority of the available environmental and health effect data in the scientific literature are limited to PFOS and PFOA. Because of this limited data availability, some generalizations presented in this report have been extrapolated to PFCs as a chemical class based on data derived from PFOS, PFOA, or other specific PFC compounds. The more commonly investigated PFC groups and individual compounds are presented in Tables 1.2 and 1.3, respectively.

Table 1.2. Common Groupings of Perfluorinated Substances.

Acronym	Description
PFCs	Perfluorochemicals; per- or poly-fluorinated compounds
PFCAs	Perfluorocarboxylic acids
PFAAs	Perfluoroalkyl acids
PFASs	Polyfluorinated alkyl sulfonates
PFSAs	Perfluorosulfonic acids
FTOHs	Polyfluorinated fluorotelomer alcohols

Table 1.3. Common Individual PFCs.

Acronym	Chemical Name	CAS Number
PFBA	Perfluorobutanoic acid	375-22-4
PFBS	Perfluorobutane sulfonate	375-73-5
PFPeA	Perfluoropentanoic acid	2706-90-3
PFHxA	Perfluorohexanoic acid	307-24-4
PFHxS	Perfluorohexane sulfonate	355-46-4

Acronym	Chemical Name	CAS Number
PFHpA	Perfluoroheptanoic acid	375-85-9
PFOA	Perfluorooctanoic acid	335-67-1
PFOS	Perfluorooctane sulfonate	1763-23-1
PFOSA	Perfluorooctane sulfonamide	754-91-6
PFNA	Perfluorononanoic acid	375-95-1
PFDA	Perfluorodecanoic acid	335-76-2
PFDS	Perfluorodecane sulfonate	335-77-3/67906-42-7
PFUA	Perfluoroundecanoic acid	2058-94-8
PFDoA	Perfluorododecanoic acid	307-55-1
PFOSF	Perfluorooctanesulfonyl fluoride	307-35-7
N-EtFOSE	N-ethyl perfluorooctanesulfonamidoethanol	1691-99-2
N-MeFOSE	N-methyl perfluorooctanesulfonamidoethanol	24448-09-7

In general, PFCs are a class of partially (i.e., “poly-“) or completely (i.e., “per-“) fluorinated alkyl (i.e., straight or branched carbon chain) or cyclic organic compounds that may also have a charged hydrophilic (i.e., water-soluble) functional group. This functional group is typically carboxylic acid or sulfonate. A generic chemical structure of a perfluorinated alkyl PFC molecule is presented in Figure 1.1.

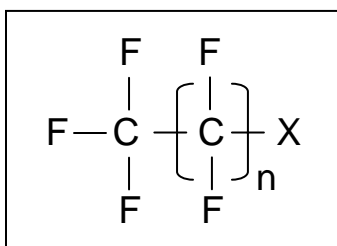


Figure 1.1. Generic structure of a perfluorinated alkyl PFC compound, where X represents a hydrophilic functional group.

PFCs are synthesized via two primary methods: (1) electrochemical fluorination (ECF) process; or (2) telomerization manufacturing process (Minnesota Pollution Control Agency [MPCA], 2008). ECF is the process that the 3M Company used to manufacture fluorinated surfactant compounds including PFOS, PFOA, and the volatile sulfonamidoethanol building blocks N-EtFOSE and N-MeFOSE. ECF is the only manufacturing process used to directly produce PFOS and PFOA. The ECF process begins with sulfonyl fluorides and results in the production of numerous branched and straight chain PFC isomers and by-products.

Telomerization is a step-wise building process used by the DuPont plant for synthesizing the carbon backbone of fluorinated alkyl compounds, especially FTOHs (MPCA, 2008). This manufacturing process results only in compounds consisting of linear alkyl chains with an even number of carbon atoms (Figure 1.2). FTOHs are not used directly in commercial applications; rather they are used as chemical intermediates in the manufacture of other PFC surfactants and polymers.

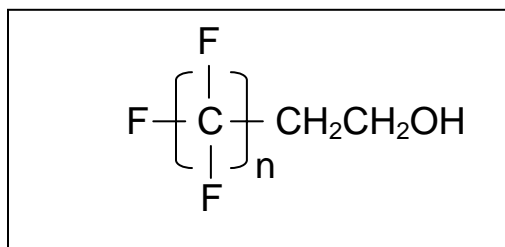


Figure 1.2. Generic chemical structure of an FTOH molecule, where n is an even number.

The fluorinated structures of PFCs make these substances both hydrophobic (i.e., water repelling) and oleophobic (i.e., oil repelling). Because of their unique chemical surfactant properties, these chemicals have been used extensively in various industrial and commercial surface coating and protectant applications including: protectants that enhance water and stain repellency for paper and cardboard packaging products, including those approved for food contact (e.g., plates, food containers, bags, and wraps); carpets; leather products, and textiles (Agency for Toxic Substances and Disease Registry [ATSDR], 2009; Organization for Economic Cooperation and Development [OECD], 2002). PFCs have also been used in fire-fighting foams as they are effective in extinguishing hydrocarbon fueled fires. Other reported uses of these compounds include processing aids in the manufacture of nonstick cookware coatings, apparel waterproofing agents, electrical wire coatings, fire- and chemical-resistant tubing, plumbing thread seal tape, and as emulsifiers in various industrial applications (ATSDR, 2009). Considering all of the forms of PFCs and the wide range of uses, it is not surprising that the literature is not clear on how PFCs are being replaced. Most indications are that PFCs are being replaced with other PFCs whose fate, transport, and toxicity are even less well known than for PFOS and PFOA.

PFCs are considered to be environmentally persistent compounds, as they are extremely stable and resistant to hydrolysis, biodegradation, photooxidation, and direct photolysis (OECD, 2002). The resistance is conferred to PFCs by their fluorinated molecular structure, in that the strength of the carbon-fluorine bonds protects the carbon group atoms from degradation. PFCs are essentially ubiquitous in the environment, as they have been detected in a variety of environmental media including air, water, sediments, and soils in nearly every country where they have been investigated, including the Arctic ice caps (Tardiff, et al., 2009). Details of the mechanisms of PFCs extensive transport in the environment remain unclear.

Similar to mercury, PFOA and PFOS do not partition to lipids but are instead protein-bound. The bioconcentration factors (BCFs) for PFOA and PFOS, however, are orders of magnitude lower than that for mercury. The BCF for PFOA is 4, meaning it has relatively limited potential to bioaccumulate. The BCF for PFOS, however, is 1124, which indicates a high potential to bioaccumulate up the food chain.

### **Toxicity and Toxicokinetics**

There is currently limited information related to human health effects associated with exposure to PFCs. This information has been primarily obtained from health evaluations of occupationally exposed populations, epidemiologic investigations of highly exposed communities (the largest of which is ongoing), and to a more limited extent, exposures of the general population (ATSDR, 2009). However, the sources and exposure routes of PFCs within the general population are not well understood. Contaminated drinking water, dust in homes, and food transfer from

packaging materials or cookware have been suggested as possible exposure routes (Lau et al., 2007). In general, most available human health effect data have been related to exposure to the two most widely studied and distributed PFAAs, PFOS, and PFOA.

Human and animal studies have demonstrated that PFCs are readily absorbed into the body following inhalation and oral exposure, whereupon they distribute to the circulatory system and remain bound to blood proteins. PFCs do not appear to undergo any significant metabolism once absorbed. Perhaps unique to humans, PFCs are poorly eliminated from the body, as demonstrated by their several year half-life estimates. With continuing exposure, these characteristics result in the bioaccumulation of PFCs in humans (OECD, 2002).

Consistent with the ubiquitous environmental distribution of PFCs, national biomonitoring studies have demonstrated that nearly 100 percent of human serum samples tested contained quantifiable levels of PFCs (Kato et al., 2011). Similarly, PFCs have been widely detected in umbilical cord blood and human breast milk (Fromme et al., 2010), indicating that exposure to PFCs can occur during critical developmental periods in the fetus and infant.

Numerous research projects have commenced in recent years with the goal of better understanding the toxicological effects of PFCs in humans. Most of this research has been focused on quantifying PFOS and PFOA exposure and establishing associations with any adverse health effects in exposed human populations. In general, this research has not demonstrated consistent associations between serum PFC levels and any adverse health outcomes in humans (Steenland, 2010; ATSDR, 2009). This is especially true of occupationally exposed populations, which characteristically have serum PFC levels an order of magnitude or higher than nonoccupationally exposed populations. However, due to the inherent limitations of these types of human health evaluations (e.g., small sample size, predominantly healthy male subject populations [i.e., the “healthy worker effect”], lack of temporal data, and reliance on mortality data for health outcomes), the data available to date are insufficient to establish firm conclusions between PFC exposure and potential adverse effects in humans.

In the absence of adequate human toxicological data, laboratory animal data become increasingly important to help establish a causal association between PFC exposure and adverse health outcomes. A substantial database of animal toxicity studies has demonstrated a wide array of adverse health outcomes that have not been adequately evaluated in humans. In PFC-exposed laboratory animals, including nonhuman primates, liver toxicity has generally been the most frequently observed adverse health effect. Adverse systemic, endocrine, immunological, reproductive, and developmental (including offspring lethality) health effects have also been well documented in a number of animal species (ATSDR, 2009). Gender-specific differences within a single species have also been reported for many of these adverse outcomes. Additionally, many of these animal studies have demonstrated a steep dose response to PFC exposure, which indicates that there is little margin of exposure between a PFC dose causing no adverse effect and that of a lethal dose.

PFOA has been demonstrated to induce cancer in several tissues in the rat through a mechanism generally considered unlikely to be relevant in humans. While there is no conclusive evidence that exposure to PFCs causes cancer in humans, the possibility cannot be ruled out. The USEPA (2005) stated that the available evidence of human carcinogenic potential of PFOA may be best described as “suggestive evidence of carcinogenicity, but not sufficient to assess human carcinogenic potential.” A USEPA science advisory board (USEPA, 2006) took a stronger stance on the subject by suggesting that PFOA cancer data are consistent with the USEPA cancer guidelines description “likely to be carcinogenic to humans.”

Extrapolation of adverse outcomes identified in laboratory rodent studies to PFC-exposed humans is difficult. The significantly longer half-lives of PFC compounds in humans subject to continuous exposure suggest the possibility for greater body burdens and duration of exposure to occur in humans as compared to animals. Also, the proposed internal mechanisms of action resulting in PFC-induced tumors in rodents may not be as active or even relevant in humans. Whether these mechanisms of action are involved in the reported noncarcinogenic adverse outcomes in animals is unclear at this time.

In summary, available research to date has not conclusively demonstrated adverse health outcomes resultant from PFC exposure in human populations. However, this statement should not be interpreted as lack of risk associated with PFC exposure in humans, as adequate data are not available to support such a conclusion. Given the uncertainties associated with the sources and routes of exposure of PFCs to the general population, the long half-lives of these compounds in humans, and the limited data currently available, continued exposure to PFCs may increase body burdens to levels that could result in adverse outcomes. Ongoing studies will help determine if adverse health outcomes in humans are associated with PFC exposure.

## CHAPTER 2: CONCENTRATIONS AT SITES OF ENVIRONMENTAL CONTAMINATION

The former WAFB, located in Iosco County, is one of the first sites in the state to be investigated for PFC contamination. The base was active from 1923 to 1993. As a part of the Strategic Air Command of the United States Air Force, the base maintained B-52s and their support craft. At its height of operation, approximately 10,000 people either worked or lived on the base.

It is believed that fire suppression and aircraft maintenance products are the major sources of PFC contamination at the site. Soil and surface water samples have yet to be obtained, with the exception of three soil samples from the former fire training area. The highest detected concentration of PFOS was 5,700,000 part per trillion (ppt) and the highest detected concentration of PFOA was 5,400,000 ppt. Results of a DEQ preliminary investigation of groundwater are presented in Figure 2.1. The concentrations are reported in ppt, equivalent to nanograms per liter (ng/L). All background samples were less than the reporting limit of 4.2 ng/L for PFOS and PFOA.



Figure 2.1. Detected concentrations of PFOS and PFOA at the former WAFB.

Moody et al. (2003) sampled multiple wells at the base for PFOS, PFOA, PFHxS, and PFHxA. According to the authors, samples were taken at least five years after the cessation of the source of the PFCs (i.e., fire-fighting training activities) from wells up to 500 meters downgradient from the point of use; this indicates both mobility and persistence of PFCs in groundwater. PFOS and PFHxS were detected in all samples; the results are summarized in Table 2.1, and sample locations are depicted in Appendix A-2.

Table 2.1. PFC concentrations in groundwater samples from WAFB.

	PFOS	PFOA	PFHxS	PFHxA
Concentration Range (ng/L)	4,000 - 110,000	<3,000 - 105,000	9,000 - 120,000	<3,000 - 20,000

It is known that historical jet fuel and solvent plumes have breached the property boundary of the base and vent to the Au Sable River, Van Etten Lake, and Van Etten Creek. PFCs have also been detected in these plumes, thus PFCs may likewise be venting to surface waters of the state.

Screening data indicate that groundwater that was historically used for drinking water may have been contaminated with PFCs while the base was being used by the United States Air Force. PFC contamination has been documented in the same volatile organic chlorinated chemical plumes that originally contaminated the drinking water well fields on the base. Additionally, preliminary PFC data have shown PFC contamination upgradient and downgradient of the historical drinking water well fields.

## CHAPTER 3: MONITORING DATA FROM MICHIGAN AND OTHER GREAT LAKES STATES

Limited data exist on PFC concentrations in the environment in Michigan. Some information is available regarding concentrations in groundwater, surface water, and fish. No Michigan-specific data were found regarding the occurrence of PFCs in finished drinking water, soil, sediments, indoor or outdoor air, and biosolids. Additionally, no source monitoring of potential air or water releases were found.

### Surface Water

Through a partnership with Michigan State University, the DEQ was able to analyze surface water samples collected in 2001 for PFOS and PFOA. The sampling sites (Appendix A-1) are active locations under the Water Chemistry Monitoring Program.

PFOS was detected in 44 of 49 samples, with statewide concentrations ranging from 0.87 ng/L in the Thunder Bay River to 29.26 ng/L in the upper Kalamazoo River. PFOA was detected in all samples. The lowest concentration (1.16 ng/L) was found in the Au Sable River, and the highest concentration (35.86 ng/L) was detected in the lower Kalamazoo River. The means and ranges of detected concentrations are summarized in Table 3.1. Nondetect results were treated as being equal to one-half of the detection limit in order to calculate mean concentrations. Note that concentrations are reported as ng/L, equivalent to ppt.

Table 3.1. PFC concentrations in Michigan surface waters.

Location (Number of Samples)	Mean [PFOS] ng/L (range)	Mean [PFOA] ng/L (range)
Detroit Region (n=10)	3.50 (<0.5 – 6.13)	9.16 (3.96 – 16.14)
Flint Region (n=4)	4.90 (1.50 – 12.31)	14.13 (5.75 – 23.01)
Lansing Region (n=3)	2.68 (1.04 – 4.96)	9.87 (7.91 – 13.37)
Northeast Michigan (n=2)	3.61 (0.87 – 6.34)	2.37 (1.16 – 3.58)
Northwest Michigan (n=2)	2.37 (<0.5 – 4.48)	12.51 (11.96 – 13.06)
Saginaw Bay Region (n=5)	7.52 (3.10 – 12.69)	14.12 (7.13 – 24.08)
Southwest Michigan (n=5)	16.09 (7.22 – 29.26)	21.64 (8.74 – 35.86)
Upper Peninsula (n=12)	2.34 (<0.5 – 3.52)	6.15 (1.44 – 13.77)
West Michigan (n=6)	1.87 (<0.5 – 5.32)	8.34 (4.01 – 15.17)

In other work, Boulanger et al. (2004) reported mean concentrations of numerous PFCs in Lake Erie and Lake Ontario. PFOS and PFOA were present in Lake Erie water samples at average concentrations of 31.2 and 35.6 ng/L, respectively, and in Lake Ontario were 54.3 and 42.5 ng/L, respectively.

Additionally, Kannan et al. (2005) found PFOS and PFOA in the River Raisin and the St. Clair River. PFOS concentrations were 3.5 and 2.6 ng/L, respectively, while PFOA was detected at 14.7 and 4.4 ng/L, respectively.

### Air

To our knowledge, no air samples have been collected to date in Michigan and no temporal or spatial trend data exist for PFCs in Michigan air. PFC air data have been collected in other parts of the country and world. Some air samples have been collected within the Great Lakes basin, including samples in Minnesota, Ohio, New York, and Ontario, Canada (MPCA, 2008; Stock et al., 2004; Kim and Kannan, 2007; Genualdi et al., 2010; Scott et al., 2006).



Air samples were collected in Minnesota at an urban and a rural site for PFOS, PFOA, and PFBA. Concentrations were approximately 50 percent higher in the urban location as compared to the rural site. The concentrations measured in Minnesota were similar to samples collected in different areas by others. Stock et al. (2004) found much higher levels of FTOHs associated with higher population centers. For example, Long Point, Ontario with a population of 500 had a mean concentration of FTOHs of 26 picograms per cubic meter ( $\text{pg}/\text{m}^3$ ) as compared to the city of Toronto with a population of approximately 2.5 million people at  $165 \text{ pg}/\text{m}^3$ . This study also found the highest concentration of PFASs in Griffen, Georgia, at approximately  $1500 \text{ pg}/\text{m}^3$  near a carpet manufacturing facility.

### **Aquatic and Wildlife Monitoring**

Canadian researchers analyzed individual whole-body homogenates of four-year old lake trout from each of the Great Lakes in 2001. Lake Erie lake trout had the highest average concentration of total PFCs and PFOS ( $152 \pm 14$  nanograms per gram ( $\text{ng}/\text{g}$ ) and  $121 \pm 14 \text{ ng}/\text{g}$ , respectively), whereas Lake Superior had the lowest concentration of total PFCs and PFOS ( $13 \pm 1 \text{ ng}/\text{g}$  and  $5 \pm 1 \text{ ng}/\text{g}$ , respectively). The average PFOS concentrations observed in fish from each Great Lake showed a statistically significant exponential relationship with the fish weight, with fish size in Lake Erie being approximately three times that in Lake Superior. PFOA concentrations were roughly three times higher in Lake Michigan fish samples than in the other Great Lakes' fish, even though all Great Lakes had similar PFOA concentrations in water samples.

The USEPA Great Lakes Fish Monitoring and Surveillance Program sampled lake trout from each of the Great Lakes, as well as walleye in Lake Erie, in 2008 and analyzed them for 11 PFCs (Table 3.2) (E. Murphy [USEPA] presentation, 2011). PFOS was the predominant PFC present. Lake Erie trout had the highest PFOS concentration ( $180.1 \text{ ng}/\text{g}$ , wet weight), whereas Lake Superior trout had the lowest PFOS concentration ( $7.1 \text{ ng}/\text{g}$ , wet weight). Walleye from Lake Erie had the third highest PFOS concentration ( $46.9 \text{ ng}/\text{g}$ , wet weight).

Table 3.2. PFCs measured in fish for the USEPA Great Lakes Fish Monitoring and Surveillance Program.

Perfluorobutane sulfonate (PFBS)	Perfluorooctanoic acid (PFOA)
Perfluorodecanoic acid (PFDA)	Perfluorooctane sulfonate (PFOS)
Perfluorododecanoic acid (PFDoA)	Perfluorooctane sulfonamide (PFOSA)
Perfluoroheptanoic acid (PFHpA)	Perfluoroundecanoic acid (PFUA)
Perfluorohexane sulfonate (PFHxS)	Perfluorodecane sulfonate (PFDS)
Perfluorononanoic acid (PFNA)	

The USEPA is conducting a Great Lakes human health fish tissue study, which involves collecting samples of fish commonly consumed by humans at a statistically representative group of about 150 nearshore Great Lakes sampling locations (Figure 3.1). The study will measure the PFCs listed in Table 3.2 with the exception of PFDS and the addition of PFBA, PFPeA, and PFHxA. Fish sample collection was completed in 2010, with data expected to be reported in 2012 and 2013 (L. Stahl [USEPA] presentation, 2011).

The Minnesota Department of Health (MDH) lists waters (in Minnesota) where fish have been tested for PFOS (MDH, 2011). Of the 140 lakes where fish were sampled, 29 have a fish advisory for PFOS. These consumption advisories recommend eating no more than one meal of fish per week when PFOS levels in fish exceed  $40 \text{ ng}/\text{g}$ , and eating no more than one meal per month when PFOS levels exceed  $200 \text{ ng}/\text{g}$  (Delinsky et al., 2010).

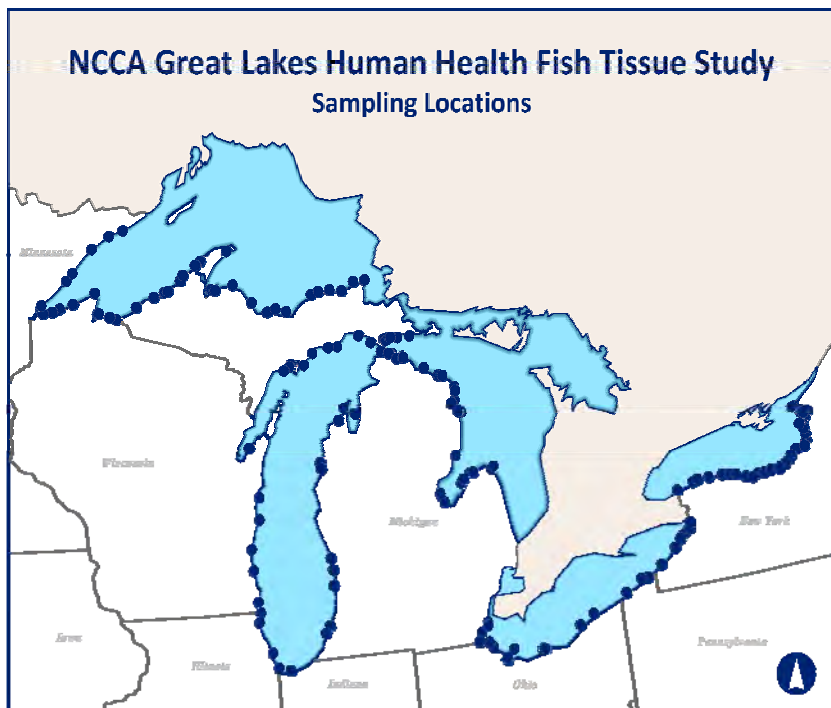


Figure 3.1. Locations of Great Lakes fish collection.

The Wisconsin Department of Natural Resources collected a variety of fish species in 2006 and 2009 from the Fox and Mississippi Rivers and Lakes Michigan and Superior, respectively. Average PFOS concentrations ranged from 4.6 ng/g (cisco/lake herring from Lake Superior) to 163 ng/g (white bass from the Mississippi River; K. Groetsch, MDCH, personal communication, 2011).

Giesy and Kannan (2001) measured PFOS concentrations in numerous species of wildlife worldwide. Birds (double-crested cormorants, herring gulls, and ring-billed gulls) from Lake Huron, fish

(lake whitefish, brown trout, Chinook salmon, and carp) from “Michigan waters,” green frogs from southwest Michigan, and snapping turtles from Lake St. Clair were included in their analyses. The highest concentration of PFOS in the plasma of birds and snapping turtles was 270 nanograms per milliliter (ng/ml) and 170 ng/ml, respectively. The highest concentration of PFOS found in the liver of fish, muscle of fish, and liver of green frogs was 170 ng/g, 300 ng/g, and 290 ng/g, respectively.

Kannan et al. (2005) measured the concentration of PFCs in water, benthic algae, amphipods, zebra mussels, crayfish, round gobies, and smallmouth bass from the River Raisin, the St. Clair River, and Chicago’s Calumet River in an effort to quantify the BCFs and biomagnification factors associated with PFOS, PFOA, PFOSA, and PFHxS. Sample locations are noted in Appendix A-2. Table 3.3 shows that neither PFOA nor PFHxS were detected in any of the organisms studied. PFOS was detected in all of the biota examined from the Raisin River. The concentration of PFOS increased through each trophic level, with concentrations in smallmouth bass up to 17 times higher than those found in the algae.

A similar trend appeared to occur in the St. Clair River, except the concentration detected in smallmouth bass was low compared to the Raisin River (this may have been due to the small number of smallmouth bass collected). In the St. Clair River and the River Raisin, PFOSA was found in several organisms sampled, but the compound did not biomagnify up the food chain. Kannan et al. (2005) also examined the concentration of PFOS in the following fish samples: (1) eggs from Lake Huron lake whitefish and Lake Superior brown trout; (2) livers from Grand River Chinook salmon and Lake Huron lake whitefish; and (3) muscle from Saginaw Bay carp. Concentrations of PFOS in samples collected from Chinook salmon and lake whitefish ranged from 32 ng/g to 381 ng/g. In addition, the concentration of PFOS ranged from 49 ng/g to 75 ng/g in the brown trout and 59 ng/g to 297 ng/g in the carp (Table 3.3).

Table 3.3. The highest detected concentration (ng/g) of various PFCs (adapted from Kannan et al., 2005).

Location	Species/Specimen	PFOS	PFOSA	PFOA	PFHxS
Raisin River	Water (ng/L)	3.5	<10	14.7	<1
	Benthic algae	2.4	<1	<0.2	<2
	Amphipods	2.9	<2	<5	<1
	Zebra mussels	3.1	3.8	<5	<1
	Crayfish	4.3	1.6	<0.2	<2
	Round gobies	11.2	2.1	<0.2	<1
	Smallmouth bass	41.3	4.1	<2	<1
St. Clair River	Water (ng/L)	3.9	<10	4.4	<1
	Benthic algae	2.6	<1	<0.2	<2
	Amphipods	<2	<2	<5	<1
	Zebra mussels	<2	<2	<5	<1
	Crayfish	2.4	1.4	<0.2	<2
	Round gobies	21.5	5.2	<0.2	<1
	Smallmouth bass	2.7	6.3	<2	<1
Calumet River	Benthic algae	3.1	<1	<0.2	<2
	Amphipods	<2	<2	<5	<1
	Zebra mussels	<2	<2	<5	<1
	Crayfish	3.7	<1	<0.2	<2
	Round gobies	4.1	<1	<0.2	<1
	Smallmouth bass	7.6	<1	<2	<1
Grand River	Chinook salmon (liver)	173	<19	<72	<17
Lake Huron	Lake whitefish (liver)	81	<19	<72	<17
	Lake whitefish (eggs)	381	<19	<36	<34
Lake Superior	Brown trout (eggs)	75	<19	<18	<34
Saginaw Bay	Carp (muscle)	297	<19	<36	<34
Kalamazoo River	Mink (liver)	59,500	181	12.2	40
	Green frogs (liver)	285	<19	<72	<6
Lake St. Clair	Snapping turtles (ng/ml) (plasma)	169	15.5	<2.5	<1

It is noteworthy that the authors reported a PFOS concentration of 59,500 ng/g (equivalent to parts per billion [ppb]), wet weight, in the liver of an adult male mink from the Kalamazoo River watershed. At the time of the study, this was the highest concentration of PFOS ever reported in any organism. The authors also noted that PFOS concentrations in mink from the Kalamazoo River watershed were generally 10 to 20 times higher than those in mink from Illinois and Massachusetts. Finally, various tissues of bald eagles collected from the Upper Peninsula were found to have detectable levels of PFOS, with the highest concentration of 1,740 ng/g being found in a liver sample.

The news media recently covered an article published by Canadian researchers regarding a PFC not previously mentioned in this report (De Silva et al., 2011). Perfluoroethylcyclohexane sulfonate (PFECBS), used in aircraft hydraulic fluids, was detected in water samples from all five Great Lakes, in lake trout from Lakes Erie and Ontario, and in walleye from Lake Erie. Samples were also analyzed for several other PFCs, including PFOS and PFOA. The results are presented in Tables 3.4 and 3.5.

Table 3.4. Mean PFC Concentration (ng/L) in Great Lakes (De Silva et al., 2011).

Lake	PFECBS	PFOS	PFOA	PFBS	PFPeA	PFHxS	PFHxA	PFHpA	PFNA	PFDA
Superior	0.16	0.26	0.65	0.14	0.90	0.013	0.88	0.19	0.086	0.067
Huron	2.13	2.25	3.22	0.87	1.86	0.44	2.39	0.75	0.33	0.39
Michigan	5.65	2.00	4.10	0.49	1.29	0.53	2.99	0.77	0.16	0.043
Erie	2.63	2.84	5.46	0.84	1.63	0.81	2.22	0.75	0.29	0.11
Ontario	4.35	5.51	4.31	0.76	1.03	0.94	1.83	0.94	0.49	0.12

Table 3.5. Mean PFC Concentration in Whole Fish (ng/g, wet weight) (De Silva et al., 2011).

Lake	Species	PFECBS	PFOS	PFOA	PFHxS	PFNA	PFDA	PFUA	PFDoA
Superior	Lake trout	<0.10	2.3	<0.42	<0.10	0.70	0.39	1.1	0.38
Huron	Lake trout	<0.10	17	<0.42	<0.10	1.4	1.3	1.8	0.74
Erie (eastern)	Lake trout	1.1	96	<0.42	1.4	2.6	6.1	5.7	2.0
Erie (western)	Walleye	2.5	54	0.50	<0.10	1.2	3.6	3.1	1.1
Ontario	Lake trout	25	52	0.88	0.70	0.90	1.4	2.1	0.32

### **Wildlife Exposure to PFCs and Potential Impacts**

Biomonitoring data indicate that a significant cross-section of wildlife throughout the world have been exposed to PFCs. The sources and routes of PFC exposure in wildlife are generally unclear. PFCs have been detected in biological specimens collected from polar bears, seals, dolphins, bald eagles, herring gulls, mink, otters, salmon, trout, turtles, and frogs. Specific impacts to these organisms, however, are generally unknown at this time, as population-level research associating environmental PFC exposure to adverse effects are sparsely reported in the scientific literature.

As noted in Chapter 1, a substantial laboratory animal toxicity database exists that demonstrates a broad spectrum of adverse outcomes following PFC exposure. Within this well controlled laboratory animal population there have been significant differences in PFC-induced outcomes reported for genetically similar species (e.g., rats and mice) as well as between genders within a single species. Therefore, as with human comparisons, extrapolation of laboratory animal data to their wildlife counterparts may not be straightforward. While those wildlife species most genetically similar to the laboratory animal species would be expected to demonstrate similar responses to PFC exposure, the PFC doses necessary to produce such effects are unknown. For example, wood mice collected from a nature reserve located adjacent to a fluorochemical plant in Belgium demonstrated a significant positive association between liver PFOS concentration and adverse liver effects that were not observed in the same species collected 3 kilometers away from the plant (Hoff et al., 2004). It is generally unclear how PFC exposure and bioaccumulation may adversely affect wildlife species lacking a laboratory animal surrogate. However, some laboratory-controlled studies using wildlife species are available. Newsted et al. (2006) reported that the liver concentrations of PFOS in juvenile mallard and bobwhite quail that were associated with mortality in these species were at least 50-fold greater than the single maximum PFOS concentration that had been measured to date in the livers of avian wildlife.

In addition, the presence of PFCs in wildlife suggests that human consumption of these species could represent an additional, and perhaps significant, route of exposure that would need to be considered in evaluating human exposure to these compounds. Currently available Michigan wildlife data are inadequate to determine if consumption advisories would be necessary to protect humans from PFC levels present in wildlife.

## CHAPTER 4: NATIONAL AND INTERNATIONAL MONITORING DATA

### Water

Numerous surface water samples have been collected from an 80-mile stretch of the Tennessee River near Decatur, Alabama, which is home to a 3M Company (Hansen et al., 2002). PFOS and PFOA concentrations ranged from 16.8 to 144 ng/L and <25 to 598 ng/L, respectively. As expected, concentrations were higher downstream of the fluorochemical facility's discharge.

Rumsby et al. (2009) reviewed several papers documenting the occurrence of PFOS and PFOA in drinking water and "environmental waters." Tables 4.1 and 4.2 were adapted from their work and show the range of detections in ng/L.

Table 4.1. Levels (ng/L) of PFOS and PFOA in environmental waters (Rumsby et al., 2009).

<b>Country</b>	<b>PFOS</b>	<b>PFOA</b>	<b>Reference</b>
<i>USA</i>			
California	20-190	10-190	Larabee & Reinhard (2008)
North Carolina	132	287	Nakayama et al. (2007)
Kentucky	7.0-149	22-334	Loganathan et al. (2007)
Georgia	1.8-22	1-227	Loganathan et al. (2007)
<i>Japan</i>			
Osaka	0.26-22	5.2-92	Takagi et al. (2008)
Yodo River	0.4-123	4.2-2600	Lein et al. (2008)
Tsurumi River	180	13-16	Zushi et al. (2008)
Kyoto	<5.2-10	7.9-110	Senthilkumar et al. (2007)
Other	0.24-37.3	0.10-456	Saito et al. (2004)
<i>Italy</i>			
Lake Maggiore	9	3	Loos et al. (2007)
River Po	10	60-1300	Loos et al. (2007)
<i>South Korea</i>	2.4-651	0.9-62	Rostkowski et al. (2006)
<i>Germany</i>	1-195	0.7-250	Skutlarek et al. (2006)
<i>United Kingdom</i>			
EA GW <sup>a</sup>	<100-6300	<100-600	EA (2007)
EA SWAD <sup>b</sup>	<100-14500	<100-340	EA (2007)
EA TRBM <sup>c</sup>	<100-33900	<100-2000	EA (2007)
WRc	<11-208	<24-370	Atkinson et al. (2008)
<i>China</i>			
Pearl River	0.99-99	0.85-13	So et al. (2007)
Yangtze River	<0.01-14	2-260	So et al. (2007)

<sup>a</sup>Environment Agency groundwater monitoring.

<sup>b</sup>Environment Agency Surface Water Abstraction Directive, monitoring sites near abstraction points for drinking water abstraction.

<sup>c</sup>Environment Agency Targeted Risk-Based Monitoring, mainly sites that monitor effluent from sewage treatment works or rivers receiving such effluent.

Table 4.2. Levels (ng/L) of PFOS and PFOA in drinking water (Rumsby et al., 2009).

Country	PFOS	PFOA	Reference
USA - West Virginia	n/a	3550	Paustenbach et al. (2007)
Japan	0.16-51	0.7-84	Takagi et al. (2008), Fujii et al. (2007)
Germany - Rhine-Ruhr	0-22	22-519	Skutlarek et al. (2006)
Canada	n/a	0.2	Fujii et al. (2007)
China	1.5-13.2	1.1-109	Fujii et al. (2007)
Malaysia	0.1	0.1	Fujii et al. (2007)
Sweden	0.3-0.8	1.3	Fujii et al. (2007)
Thailand	0.1-1.9	0.2-4.6	Fujii et al. (2007)
United Kingdom	<11-45	<24-240	Atkinson et al. (2008)

A study from Singapore (Nguyen et al., 2011) analyzed surface water, storm water runoff, and rain water samples for several PFCs including PFOS, PFOA, PFHpA, PFNA, PFUA, PFDoA, and PFHxS. The ranges of total PFCs are presented in Table 4.3.

Table 4.3. Mean total PFC concentrations (ng/L) in water samples from Singapore (adapted from Nguyen et al., 2011).

	Mean [Total PFC] (range)
Surface Water	60.1 (17.6-235.7)
Storm Water	60.5 (30.8-301.5)
Rain Water	6.4 (5.2-11.5)

### **Outdoor Air**

A study by Piekarz et al. (2007) found that air masses measured in the western United States were substantially higher than air masses measured in Japan and were positively correlated with gas phase polyaromatic hydrocarbons and polychlorinated biphenyls. Substantial evidence has demonstrated the volatility of PFCs and the widespread global distribution of these pollutants via atmospheric transport and deposition (Ahrens et al., 2010; Dreyer et al., 2009; Armitage et al., 2009; and Young et al., 2007).

The compounds considered to be semi-volatile include PFOSAs, perfluorooctane sulfoamidoethanols (PFOSEs), and FTOH. PFOSAs and PFOSEs are “hoppers,” meaning that there is a continuous cycle of transportation and deposition through the environment. FTOH, on the other hand, is considered a “flier” due to its great capacity for global atmospheric transport. All three are common in air masses around urban areas (Goosey, 2010). The compounds most likely to undergo atmospheric transport and deposition include the shorter chained PFCs.

PFCs also have been detected in rain samples across North America, with the highest concentrations found in urban areas ranging from 0.1 to 2400 ng/L (Scott et al., 2006).

A Japanese study found that precipitation loadings via storm water runoff associated with train stations and/or transportation-related land use are a significant source to a water body. Train stations associated with use of cars, paint, paper, and cloth that contain PFCs had higher concentrations contributing to inputs into the Hayabuchi River in Yokohama, Japan (Yasuyuki and Shigeki, 2008). A study by Ahrens et al. (2010) in the French Alps determined that PFOS was more homogeneously distributed while PFCAs seemed to be more influenced by a local atmospheric source.

Table 4.4. Summary of Selected Atmospheric PFC Measurements (Outdoor Air).

Location	Sample Duration and Dates	PFC	Concentration (Range or Mean)	Reference
Ontario, Canada – Wastewater Treatment Plant (WWTP)	63 days	Total PFCs FTOH PFOS PFBA	2280-24040 pg/m <sup>3</sup> 895-12290 pg/m <sup>3</sup> 43-171 pg/m <sup>3</sup> 55-116 pg/m <sup>3</sup>	Ahrens et al., 2011
Ontario, Canada - Landfill	63 days	Total PFCs FTOH PFBA	2780-26430 pg/m <sup>3</sup> 1290-17380 pg/m <sup>3</sup> 101-102 pg/m <sup>3</sup>	Ahrens et al., 2011
Red Rock River, MN	3-4 days	PFOS	3.3-19.4 pg/m <sup>3</sup>	MPCA, 2008
Cleves, OH	15 days	FTOH	132 pg/m <sup>3</sup>	Stock et al., 2004
Albany, NY	62 days	Total PFASs	11.3 pg/m <sup>3</sup>	Kim and Kannan, 2007
Long Point, Ontario	12 days	FTOH	26 pg/m <sup>3</sup>	Stock et al., 2004
Toronto, Ontario	12 days	FTOH	165 pg/m <sup>3</sup>	Stock et al., 2004
Lake Ontario		PFOS (particulate)	6.4 +/- 3.3 pg/m <sup>3</sup>	Boulanger et al., 2005
Griffin, GA	20 days	FTOH	148 pg/m <sup>3</sup>	Stock et al., 2004
Bermuda	7/12/07-8/5/07	FTOH	34 pg/m <sup>3</sup>	Schoeib et al., 2010
Sable Island, Nova Scotia	7/12/07-8/5/07	FTOH	16 pg/m <sup>3</sup>	Schoeib et al., 2010
USA - Northeast Coast	7/12/07-8/5/07	FTOH	156 pg/m <sup>3</sup>	Schoeib et al., 2010
Arctic		PFASs and PFCAs	<0.1-5.9 pg/m <sup>3</sup>	Stock et al., 2007

It should be noted that an intercomparison study on sampling techniques for PFC samples revealed that published concentrations on airborne PFCs have to be compared and evaluated with caution (Dreyer et al., 2010). The authors of this study also pointed out that the sampling method of choice for atmospheric PFCs depends on the intention of the monitoring. If the purpose is to assess short-term temporal trends, then high-volume sampling should be conducted. Passive samplers are effective at capturing the average air concentration because they are time integrated; however, they lose the temporal resolution. Additionally, the analytical technique should also be reviewed when comparing data; analysis with gas chromatography mass spectrometry excludes the majority of PFCs due to their low volatility (Boulanger et al., 2005).

### **Indoor Air**

A study conducted by Langer et al. (2010) determined that the concentrations of fluorinated compounds in indoor air are much higher than outdoor air by several orders of magnitude. The authors determined that certain nonresidential indoor air concentrations were the most elevated, including samples taken in stores that sold outdoor equipment, a furniture store, and a carpet store. Indoor air environments can therefore be a source to outdoor air through building ventilation and other air exchanges.



Studies by Shoeib et al. (2004 and 2005) found that indoor air concentrations of fluorinated chemicals used to make fabric and carpet coatings were roughly 10 to 100 times greater than outdoor concentrations of the same chemicals. Martin et al. (2002) states that these compounds may, in turn, break down into PFOS, which could expose people to PFOS through ingestion and inhalation inside of homes that contain fabric-coating products.

Table 4.5. Summary of Selected Atmospheric PFC Measurements (Indoor Air).

Location	Sample Duration And Dates	PFC	Concentration	Reference
Hamburg, Germany	April-May 2008 and March 2010	Total PFCs	82000-458000 pg/m <sup>3</sup>	Langer et al., 2010
Ottawa, Canada	Winter 2002-2003	N-MeFOSE N-EtFOSE	1490 pg/m <sup>3</sup> 740 pg/m <sup>3</sup>	Shoeib et al., 2005
Residential Homes In North America	2003	N-MeFOSE N-EtFOSE	2590 pg/m <sup>3</sup> 772 pg/m <sup>3</sup>	Shoeib et al., 2004

PFCs have also been measured in indoor dust in a few studies as summarized in Table 4.6.

Table 4.6. Summary of Selected Indoor Dust PFC Measurements.

Location	Sample Type and Year	PFC	Concentration Mean/Median (Range) Units	Reference
US, Ohio and North Carolina	102 Homes + 10 Daycare Centers – Vacuum Cleaner Bags 2000-2001	Total PFCs PFOS PFOA	2,264,000/917,000 (na-52,900,000) pg/g 761,000/201,000 (<8,930-12,100,000) pg/g 296,000/142,000 (<10,200-1,960,000) pg/g	Strynar and Lindstrom, 2008
Ottawa, Canada	66 Homes – Vacuum Cleaner Bag Winter 2002-2003	N-MeFOSE N-EtFOSE	412,000/NA (3,300-8,886,000) pg/g 2,200,000/NA (1,400-75,440,000) pg/g	Shoeib et al, 2005
Sweden	10 Houses – filter, industrial vacuum 2006/2007	PFOS PFOA	NA/39,000 (15,000-120,000) pg/g NA/54,000 (15,000-98,000)	Björkland et al, 2009
Japan	16 Homes – Vacuum Cleaner Bag ≤2003	PFOS PFOA	200,000/24,500 (11,000-2,500,000) pg/g 380,000/165,000 (70,000-3,700,000) pg/g	Moriwaki et al, 2003

A Japanese study found concentrations of PFOS and PFOA in vacuum cleaner dust in all of the samples collected (Moriwaki et al., 2003). Since that time, additional studies have found PFOS, PFOA, and other PFCs in indoor dust from homes in other countries, with the highest concentrations found to date in the United States (Shoeib et al., 2005; Strynar and Lindstrom, 2008; and Björkland et al., 2009). Shoeib et al. (2005) estimated that indoor air was likely a greater contributor to PFC exposure in adults than indoor dust, but that dust was likely a greater contributor to exposure in children; however, their estimates did not compare other exposures. Strynar and Lindstrom (2008) and Björkland et al. (2009) estimated that indoor dust PFC

exposure would not exceed dietary exposures in most cases, but may be an important pathway in some circumstances, especially for children.

### **Human Exposure to PFCs**

There are no Michigan-specific or region-specific data pertaining to human exposure to PFCs. The National Health and Nutrition Examination Survey (NHANES) sampling plan is a complex, stratified, multistage, probability-cluster design, which selects a representative sample of the civilian, noninstitutionalized population in the United States based on age, gender, and race/ethnicity. Because of this design, straightforward analysis of exposure levels by geographic region, seasons of the year, proximity to sources of exposure, or use of particular products is not permitted (Centers for Disease Control and Prevention [CDC], 2009). Researchers looking for region- or state-specific data must submit their request and research proposal to the National Center for Health Statistics (W. Wattigney, ATSDR Division of Health Studies, personal communication, 2011).

The CDC analyzed PFC serum levels reported in NHANES for the years 1999-2000 and 2003-2008 (4 survey cycles; Kato et al., 2011). Serum results were reported for all participants as a group, by age group (teens versus adults), gender, and ethnicity (Mexican Americans, Non-Hispanic blacks, and Non-Hispanic whites). About 1,500 participants comprised the sample size in 1999-2000, whereas about 2,100 participants were sampled in each of the subsequent survey cycles. Each cycle measured for 12 PFCs; however, 4 were found in nearly all participants (Table 4.7).

Table 4.7. PFCs tested for in the NHANES. Those in bold print were most commonly detected.

Perfluorobutane sulfonate (PFBS)	<b>Perfluorooctanoic acid (PFOA)</b>
Perfluorodecanoic acid (PFDA)	<b>Perfluorooctane sulfonate (PFOS)</b>
Perfluorododecanoic acid (PFDoA)	Perfluorooctane sulfonamide (PFOSA)
Perfluoroheptanoic acid (PFHpA)	2-(N-Ethyl-perfluorooctane sulfonamide) acetic acid (Et-PFOSA-AcOH)
<b>Perfluorohexane sulfonate (PFHxS)</b>	2-(N-Methyl-perfluorooctane sulfonamide) acetic acid (Me-PFOSA-AcOH)
<b>Perfluorononanoic acid (PFNA)</b>	Perfluoroundecanoic acid (PFUA)

Figure 4.1 shows the time trends, by gender, for the geometric means for the 4 most commonly detected PFCs in the NHANES results for all participants. The CDC determined that males had higher least-square geometric mean (LSGM) concentrations of PFOS, PFOA, and PFHxS than females regardless of age. Also, males had higher LSGM concentrations of PFOA, PFHxS, and PFNA than females regardless of race/ethnicity. The researchers suggested the disparity may be due to the possibility of sex-related differences in exposure (Kato et al., 2011).

There have been changes in the manufacturing practices for PFCs, which is reflected in a downward trend in the concentrations of several PFCs. However, the concentrations for PFNA have shown an upward trend. PFNA was a reaction by-product in ECF-based materials, which are no longer produced in the United States. The increase in PFNAs may be related to the degradation of volatile FTOHs (Kato et al., 2011).

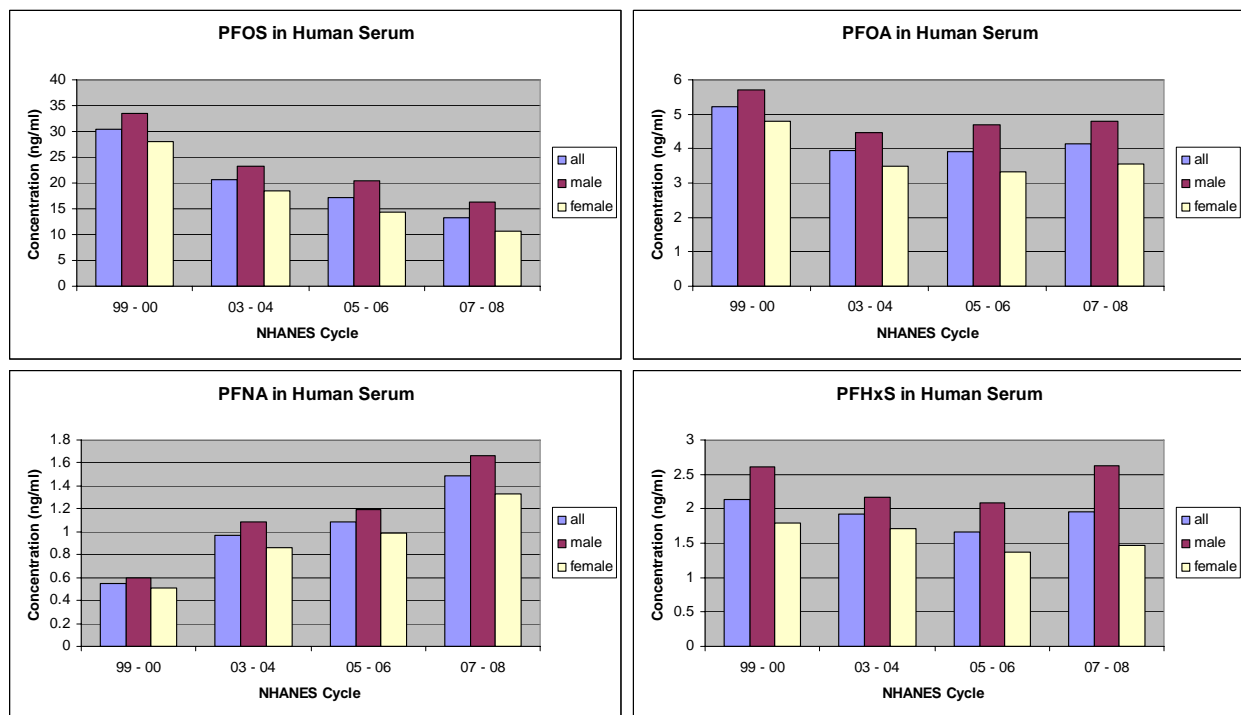


Figure 4.1. Time trend, by gender, for PFOS, PFOA, PFNA, and PFHxS in human serum.

In addition to being exposed to PFCs through the consumption of fish and other commercial foods, people may be exposed through public drinking water supplies. In the United States, Olsen et al. (2009) have reviewed epidemiologic studies done on communities in Washington County, Ohio, living near the DuPont plant (located across the Ohio River in West Virginia) and drinking PFOA-contaminated water. In Germany, Hölzer et al. (2008, 2009, and 2011) and Wilhelm et al. (2009) have conducted follow-up studies on communities exposed to PFOA-contaminated drinking water obtained from the Möhne River.

PFCs have been detected in human cord blood (Midasch et al., 2007; Hanssen et al., 2010; Needham et al., 2011) and in human breast milk (Kärrman et al., 2007, 2010; Tao et al, 2008 a,b; Völkel et al, 2008; vonEhrenstein et al., 2009; Fromme et al, 2010; Liu et al., 2010; Needham et al., 2011; Sundstrom et al., 2011).

### **Dietary Data**

Dietary intake is a main route of exposure to environmental pollutants such as metals and classical persistent organic pollutants such as dioxins, furans, and polychlorinated biphenyls (Ericson et al., 2008). Although not as well established, dietary intake has also been a documented route of human exposure to PFCs. Certainly, there are various routes by which PFCs can enter food including: (1) exposure of food-producing animals to environmental PFCs through inhalation, adsorption, or consumption of contaminated food or water; and (2) the transfer, or migration, into food from items involved in food preparation and storage, particularly food packaging (Tittlemier et al., 2006). The most complete dietary studies, to date, were conducted in the United Kingdom (U.K. Food Standards Agency, 2006), Canada (Tittlemeir et al., 2006; Tittlemeir et al., 2007; Ostertag et al., 2009), and Spain (Ericson et al., 2008).

The United Kingdom 2004 Total Dietary Study (TDS) revealed that PFOS was present at concentrations above the limit of detection in potatoes, canned vegetables, eggs, and sugars

and preserves food groups. PFOA was only detected in the potatoes food group. The estimated average adult dietary intakes were 100 ng per kg body weight per day for PFOS and 70 ng/kg body weight/day for PFOA (U.K. Food Standards Agency, 2006).

The Canadian TDS included food samples collected from 1992 to 2004. The composite included foods that were ready for consumption, prepared and processed, or raw. The study included food products such as baked goods and candy, dairy, eggs, fast food, fish and seafood, meat, and foods prepared in their packaging. The median dietary intake of PFOSA for teenagers and adults was estimated to be 90 and 55 ng/day, respectively. The most significant dietary source of PFOSA from this study was from foods that were packaged in paper products treated with PFCs for oil resistance (Tittlemeier et al., 2006). PFOS and PFOA were additionally analyzed within selected TDS composites for 1998 and 2004 (Tittlemeier et al., 2007). Dietary exposure to PFOS was estimated to range from 0.1-0.2 ng/kg body weight/day in 1998 to 0.8-2.0 ng/kg body weight/day in 2004. Furthermore, PFOA exposure ranged from 0.2-0.4 ng/kg body weight/day in 1998 and from 0.1-0.4 ng/kg body weight/day in 2004 (Ostertag et al., 2009). The Canadian TDS also highlighted inconsistencies in the reporting of PFOS in meat and fish samples suggesting that more studies need to be conducted to better elucidate the sources of contamination of meat products, and analytical methods need to be standardized to enable comparison between studies.

Within the Spain TDS of 2008, PFOS and PFOA concentrations were monitored in food samples from vegetables, cereals, a variety of fish, livestock, eggs, dairy products, fruit, margarines, and oils. The TDS additionally examined PFOS dietary exposure across gender and age. It was specifically noted that PFOS intake concentrations were highest among males between ages 20 and 65. This intakes in this age-range were further stratified as follows: 65.2 ng/day (51-65 years), 62.9 ng/day (35-50 years), and 59.3 ng/day (20-34 years). However, when daily intakes were estimated according to respective age body weight, children aged 4-9 years showed the highest values (1.9 and 1.8 ng/kg body weight/day for boys and girls, respectively).

In summary, there have been several different approaches to gathering exposure data to PFOS and PFOA for the TDS of each country represented to date. More data need to be generated regarding the source(s) of PFC contamination of food, and the standardization of collection and analytical techniques will help drive consistency in data generation and comparison.

### **Current Research in the Great Lakes Region**

The Great Lakes Atmospheric Deposition Program, administered by the Great Lakes Commission, has funded a project by Trent University ([www.glc.org/glad](http://www.glc.org/glad)) to study atmospheric PFCs. The title of the project is, "Measurement and Modeling of the Contribution of Atmospheric Particulate Deposition to the Fluorinated Surfactants Burdens in Great Lakes Sediments." The objective of this research is to establish the contribution of the atmospheric particulate matter to the contribution of PFCAs within the lake sediments. The research will be conducted through environmental field monitoring, atmospheric modeling, and laboratory experimentation. No results are available yet, but this study is scheduled to be completed by the end of 2012.

In Minnesota, the MPCA conducts ongoing PFC monitoring. The 2008 and 2009 reports are available at the MPCA's Web site:

<http://www.pca.state.mn.us/index.php/waste/waste-and-cleanup/cleanup-programs-and-topics/topics/perfluorochemicals-pfc/perfluorochemicals-pfcs.html?menuid=&redirect=1>.

The state of Illinois was awarded \$44,000 as part of a 2010 Section 106 monitoring grant and will monitor for PFCs primarily in fish tissues, with some sampling of macroinvertebrates, sediment, and groundwater in the summer and fall of 2011. The state of Ohio has preliminary plans for a monitoring program, but no details are available at this time.

## CHAPTER 5: POTENTIAL ROUTES OF ENTRY INTO MICHIGAN'S ENVIRONMENT

### Uses

PFCs are used in a large number of commercial and industrial products. Because of their unique chemical characteristics, they are added to products to impart water repellency and stain, oil, and grease resistance. PFCs also allow products to withstand temperature extremes, provide lubrication, and reduce surface tension. The variety of products that contain PFCs ranges from dental floss to fluids utilized in the aerospace industry. A partial listing of industries that use PFCs includes:

- Auto manufacturing.
- Automotive parts manufacturing.
- Chemical manufacturing.
- Metal plating operations.
- Furniture making.
- Paper production.
- Cardboard production.
- Construction materials manufacturing (flooring, building materials, coatings).
- Consumer product manufacturing (shampoos, cleaning supplies, paints, home pesticides, etc.).
- Aerospace manufacturing and maintenance.
- Airports (fire extinguishing agents, maintenance).
- Transportation (maintenance, transportation corridors).
- Mining from the 1960s on.
- Oil extraction (pits, supply yards, leakage from impacted oil formations).
- Farming (pesticide applications and land applied sludge).
- Fabric manufacturing.
- Car washes.
- Electronics manufacturing.
- Lithographic and printing facilities.
- Metal etching facilities.
- Any facility handling flammable liquids that had fire suppression systems.
- Any site where hydrocarbon or metal fires were extinguished.
- Fire stations.
- Oil refineries.
- Forest fire break lines.
- WWTPs (municipal and industrial).
- Landfills (municipal and industrial).
- Waste incinerators.
- Carpet manufacturers.
- Clothing manufacturers.
- Shoe and leather goods manufacturers.
- Military bases.
- Fire fighting training facilities.
- Boat and other marine equipment manufacturers.

### PFCs in Products

Use and disposal patterns of PFCs result in a variety of release mechanisms to the environment and also result in varied human exposures to PFCs. Table 5.1 lists uses of PFCs as found in the literature.

Table 5.1 Uses of PFCs by industrial sector.

Food Industry	Personal Care	General Consumer Products	Farming	Transportation	Other
Paper food wrappers	Shampoos	Cleaners and detergents	Pesticides	Gaskets, hoses, tires	Aqueous Fire Fighting Foam
Non-stick coatings	Cosmetics	Waxes	Biosolids	Additives to lubricants	Foam water (forest fire fighting foam)
Paper and cardboard containers	Dental Floss	Flooring treatments		Additives to fuels	Oil field surfactants
Dish soap	Soaps	Fabric Treatments		Aerospace hydraulic fluids	Mining surfactants and foaming agents
	Pharmaceuticals	Paints		Windshield washer fluids	Treatments of construction materials
		Home pesticides		Soaps and waxes for vehicles	
		Printer Ink		Fabric treatments	
		Carbonless paper		On board electronics	
		Waterproof and breathable fabrics		Coatings and paints	
		Treated leather products			
		Furniture			
		Electronics including computers			

### Water

According to work conducted in the state of Minnesota (home to a 3M Company, a former major manufacturer of PFCs and their precursors), the discharges most likely to contain elevated levels of PFCs are those from chromium electroplaters and WWTPs. The locations of National Pollutant Discharge Elimination System (NPDES)-permitted discharges from metal platers, major industrial users, and WWTPs (greater than one million gallons per day) to surface water are depicted in Appendices B1-B4.

Groundwater discharges that are of high volume and generally have the most significant potential to impact the environment are typically permitted under Rule 2218 of the Part 22 rules, Groundwater Quality, promulgated under Part 31, Water Resources Protection, of the Natural Resources and Environmental Protection Act, 1994 PA 451, as amended (NREPA). The locations of these discharges are shown in Appendix C-1.

### Air

No atmospheric deposition PFC data for either wet or dry deposition are available in Michigan.

Information does exist in the published literature on atmospheric deposition of PFCs. PFC compounds can be removed by wet and dry deposition, although removal is negligible for FTOH (Goosey, 2010).

A study by Barton et al. (2007) found that rain events are not likely significant sources of vapor phase PFOA to North America. Because PFOA exists primarily in the particulate phase, it is efficiently scavenged near direct sources by rain droplets making wet deposition an important removal mechanism and important pathway for depositing PFOA to soils and aquatic environments (Kim and Kannan, 2007). The perfluorooctanoate anion and PFOA are the likely species that could be found during a rain event (Barton et al., 2007).

PFCs can be released into the air through industrial and consumer uses as well as manufacturing processes. PFCs can also be formed in the atmosphere from the breakdown of PFASs and FTOHs (FTOHs are also called “neutral” PFCs). FTOHs are produced by the DuPont plant using a telomerization process and are more apt to undergo long-range atmospheric transport and deposition (Figure 5.1) (Goosey, 2010; MPCA, 2008; Shoeib et al., 2010; Dreyer et al., 2009; Stock et al., 2007; Kim and Kannan, 2007; and Piekarz et al., 2007). There are over 10 million pounds of FTOH produced each year; this amount is sufficient to maintain the currently observed concentrations of PFOA in the environment (MPCA, 2008; Ellis et al., 2004). FTOH emissions worldwide during 2000-2002 were 5,000 tons per year and increased to 11,000-14,000 tons per year in 2010 (Langer et al., 2010). The USEPA, however, reports that environmental emissions in the United States of the compounds manufactured using the telomerization process have been reduced within the last ten years (USEPA, 2009a).

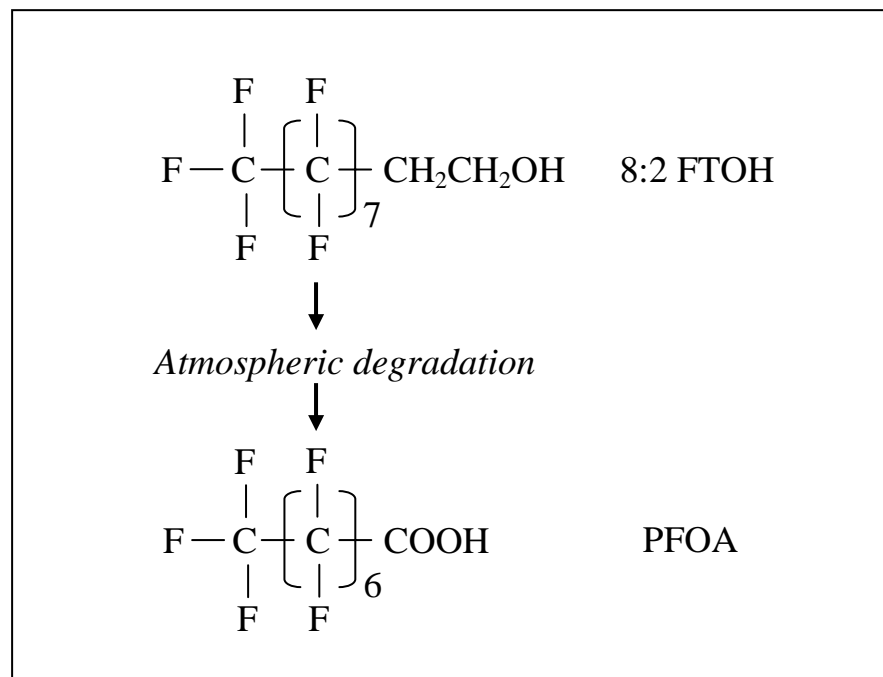


Figure 5.1 Atmospheric degradation of FTOH into PFOA.

The 3M Company uses an ECF process, which is the only process that directly produces PFOA and PFOS, and in 2000 produced over 6 million pounds. In 2002, the 3M Company phased out the production of PFOA and PFOS (MPCA, 2008). Several other PFCs are also known to be transferred by the atmosphere, some of which include PFASs and PFOSEs (Goosey, 2010; Langer et al., 2010; Dreyer et al., 2010).

Overall releases to the environment appear to be primarily from direct discharges to the water, although in certain areas atmospheric inputs seem to be the primary mechanism for PFCs to



enter aquatic ecosystems. Additionally, atmospheric emissions, transport, and subsequent deposition contribute to the global impact from these pollutants.

Some source sectors outside of Michigan have been identified that are known or likely sources of atmospheric emissions of PFCs. Testing and monitoring is needed to confirm sources in Michigan and efforts are also needed to understand the environmental fate and transport of these pollutants in Michigan's environment.

## **Sectors**

While no specific atmospheric sources have been confirmed through testing in Michigan, the published literature suggest that there are likely atmospheric sources of PFCs that should not be overlooked (Ahrens et al., 2010). Ahrens et al. (2011) did confirm emissions of PFCs from landfills and WWTPs.

Sources of PFCs have been confirmed in water discharged from a variety of source sectors and with the confirmation of air releases from two sectors, there is a potential for the sectors identified that discharge PFCs directly to also release PFCs to the atmosphere. Other published literature has found several sources of PFCs discharged to water including WWTPs with airport wastewater input, landfills, and chromium electroplaters (Ahrens et al., 2011; Stock et al., 2007; Yasuyuki and Shigeki, 2008; Schultz et al., 2006; MPCA, 2008). The USEPA's Web site indicates they have requested certain industries to conduct stack testing for PFCs, and because of the widespread use of products that contain PFCs it is reasonable to consider sewage sludge and municipal waste incinerators as potential sources of PFCs (USEPA, 2009a).

A Lake Superior loading study by Scott et al. (2010) found that, overall, tributaries and precipitation were estimated to be the major sources of PFCAs and PFSAs to Lake Superior. Tributaries were estimated to be the largest source contributing 59 percent of PFOA and 57 percent of PFOS inputs to the lake. A 2003 Lake Ontario mass balance study with limited air data demonstrated that the most important input to the lake was from direct WWTP discharge (Boulanger et al., 2005).

A study conducted in Ontario, Canada, estimated that annual emissions of PFCs were 2,560 grams/year from a WWTP and 99 grams/year from a landfill. Compared to aqueous releases, FTOH emissions from WWTPs and landfills were found to be important contributors to atmospheric PFC burdens. For the other PFCs, aqueous releases appear to be most prevalent (Ahrens et al, 2011). An earlier study (Ahrens et al., 2010) found a correlation between total mercury and PFCAs that were emitted from a similar source and atmospherically deposited into the French Alp lakes that were studied.

Based on the potential atmospheric and water sources of PFCs in the literature (Ahrens et al., 2010 and 2011), a map (Appendix D-1) of some of the possible sources of PFCs to Michigan's environment has been developed utilizing air quality data for Michigan for 2008 that includes airports (with greater than 25,000 passengers a year), municipal and sewage sludge incinerators, military airport bases, and chromium electroplaters. Metal electroplaters have used a PFOS-containing mist suppressant (i.e., Fumetrol 140®) in order to comply with the chromium (VI) maximum achievable control technology standard (USEPA, 2009c). The state of Minnesota and USEPA found PFOS in most of the wastewater samples from chromium electroplaters studied (MPCA, 2008; USEPA, 2009c).

## CHAPTER 6: REGULATIONS AND/OR POLICIES THAT ADDRESS RELEASES TO THE ENVIRONMENT, DISPOSAL, AND REMEDIATION OF CONTAMINATED SITES

### MICHIGAN

#### Water

Rule 57 (R 323.1057) of the Part 4 rules, Water Quality Standards, of the NREPA, human health and aquatic life water quality criteria are available for PFOA and are currently being developed for PFOS. The human health criteria for both compounds are more restrictive than those for aquatic life. The human noncancer values for PFOA for drinking water and nondrinking water sources are 420 ng/L and 12,000 ng/L, respectively. Because of the high bioaccumulation factor associated with PFOS, it is expected that the human noncancer values for PFOS could be up to an order of magnitude more restrictive than those for PFOA.

PFCs are not currently regulated under the Clean Water Act. The DEQ has not issued any NPDES permits that contain discharge limits or monitoring requirements for PFCs.

To date, the DEQ has not issued any permits under the Part 22 rules, Groundwater Quality, of the NREPA, that contain discharge limits or monitoring requirements for PFCs. The Part 22 standard for PFOA that could apply to groundwater discharge permits is 110 ng/L.

No federal maximum contaminant levels and no state drinking water standards currently exist for PFCs. Six PFCs (PFOS, PFOA, PFNA, PFHxS, PFHpA, and PFBS) have been placed on the draft Unregulated Contaminant Monitoring Regulation. Comments on the Unregulated Contaminant Monitoring Regulation were due to the USEPA on May 2, 2011.

#### Air

The DEQ, Air Quality Division, could regulate sources that emit PFCs into the atmosphere under the Air Toxics Rules for new or modified sources. The source would need to apply the best available control technology for toxics (T-BACT) for PFCs. After the application of T-BACT, the emissions of PFCs cannot result in a maximum ambient concentration that exceeds the applicable health-based screening level (R 336.1225 of Part 55, Air Pollution Control, of the NREPA). For certain sources such as hazardous waste incinerators or municipal waste combustors, a multi-pathway risk assessment may also be required. To date, no sources undergoing New Source Review air permitting had characterized PFC emission in the permit application or review.

#### Sediments

There are currently no regulations or departmental policies that specifically address PFCs in sediment.

#### Soil

PFCs are not currently hazardous substances identified under Part 201, Environmental Remediation, or Part 213, Leaking Underground Storage Tanks, of the NREPA. However, the DEQ has the authority to determine if PFCs shall be considered hazardous substances subject to environmental regulation under Section 324.20101(1)(t)(i) of Part 201. No data were located regarding detection of PFCs in Michigan soils associated with the environmental regulatory roles of either of these programs.

## **Waste**

Currently, there are no standards or data for PFCs related to Part 115, Solid Waste Management, of the NREPA. If PFCs are found to be associated with a release from a Part 115-regulated facility at levels of concern, the DEQ is able to pursue cleanup using the authority of Part 115. PFCs are not hazardous waste constituents subject to regulation under the Resource Conservation and Recovery Act or Part 111, Hazardous Waste Management, of the NREPA. If PFCs are found at a Part 111-regulated facility at levels of concern, the DEQ is able to pursue cleanup using the authority of Part 201, Environmental Remediation, of the NREPA.

## **FEDERAL AND OTHER STATES**

PFCs, as a chemical class, do not appear to be regulated under any federal environmental regulatory program. However, individual PFCs and some PFC subsets have received federal attention. Federal and state regulatory standards that were located for PFCs in drinking water and soils are presented in Tables 6.1 and 6.2, respectively. Note that the drinking water standards have been modified from their original format to maintain consistency with the use of the ng/L unit in this report.

In 2002, the USEPA published two significant new use rules under the Toxic Substances Control Act (TSCA) to limit any future manufacture or importation of 88 PFAS chemicals specifically included in a 2000-2002 voluntary phase-out agreement between the 3M Company and USEPA. Subsequently, the USEPA has published a third significant new use rule containing an additional 183 PFAS chemicals.

In 2006, to help minimize the impact of PFOA on the environment, the USEPA and eight major fluoropolymer and telomere manufacturers voluntarily joined in a global stewardship program (USEPA, 2009b). A goal of this program included reduction of facility emissions and product content of PFOA and related chemicals on a global basis by 95 percent no later than 2010. In addition, the group committed to working towards the elimination of these chemicals from emissions and products by 2015.

In 2009, the USEPA released its *Long-Chain Perfluorinated Chemicals (PFCs) Action Plan* (USEPA, 2009a) in which the agency indicated its intention to propose actions in 2012 under the TSCA to address the potential risks from long-chain PFCs.

Table 6.1. Federal and State Agency PFC Drinking Water Regulations.

<b>Agency</b>		<b>Drinking Water Regulation</b>	<b>Year</b>	<b>PFC</b>
<b>FEDERAL</b>				
USEPA	Office of Water	Provisional Health Advisory	2009	PFOA: 400 ng/L PFOS: 200 ng/L
<b>STATE</b>				
Minnesota	Department of Health	Chronic Noncancer Health Risk Limit	2009 2009 2011 2011	PFOA: 300 ng/L PFOS: 300 ng/L PFBS: 7000 ng/L PFBA: 7000 ng/L
New Jersey	Department of Environmental Protection	Preliminary Health-Based Guidance	2007	PFOA: 40 ng/L
North Carolina	Department of Environment and Natural Resources	Maximum Allowable Concentration (draft)	2010	PFOA: 900-1600 ng/L

Table 6.2. Federal and State Agency PFC Soil Regulations.

<b>Agency</b>		<b>Soil Regulation</b>	<b>Year</b>	<b>PFC</b>
<b>FEDERAL</b>				
USEPA	Region 4 Superfund Division	Soil Screening Level	2009	PFOA: 16 mg/kg PFOS: 6 mg/kg

## **INTERNATIONAL**

### **Canada**

In June 2006, Environment Canada and Health Canada published an *Action Plan for the Assessment and Management of Perfluorinated Carboxylic Acids and their Precursors* (Environment Canada, 2006). Based on the Action Plan, a proposed agreement has been developed between the Canadian government and its industry partners with PFOA product phase-out goals similar to those presented in the aforementioned USEPA stewardship program.

### **European Union**

In 2006, the European Parliament and the Council of the European Union (EPCEU) amended a Council directive on the marketing and use of certain dangerous substances and preparations to include PFOS (EPCEU, 2006).

In May 2009, PFOS, its salts, and PFOSF (a precursor of PFOS synthesis) were among 9 new chemicals added to the previous group of 12 persistent organic pollutants recognized under the Stockholm Convention (2009). Under Annex B, the Convention has recommended that the manufacture, import, and use of PFOS-related substances shall be “eliminated by all Parties except for identified restricted uses” and except for the production of PFOS as an intermediate to produce other chemical substances having identified restricted uses.

The Stockholm Convention has identified certain essential uses of PFOS, its salts, and PFOSF. The Convention has also identified essential uses as defined by Brazil, Canada, the Czech Republic, the European Union,\* Japan, Norway, and Switzerland. The list of acceptable uses by country can be found in Annex B of the Convention report (Stockholm Convention, 2010); it includes:

- Photo imaging.
- Photo-resistant and anti-reflective coatings for semiconductors.
- Etching agent for compound semiconductors and ceramic filters.
- Aviation hydraulic fluids.
- Metal plating (hard metal plating) only in closed-loop systems.
- Certain medical devices (such as ethylene tetrafluoroethylene copolymer [ETFE] layers and radio-opaque ETFE production, *in vitro* diagnostic medical devices, and CCD color filters).
- Fire fighting foam.\*\*
- Insect baits for control of leaf-cutting ants from *Atta spp.* and *Acromyrmex spp.*

\* The EU restriction is not limited to PFOS, its salts, and PFOSF, but covers all PFOS derivatives defined as  $C_8F_{17}SO_2X$ , where “X” equals a hydroxyl group (OH), metal salt, halide, amide, and other derivatives including polymers.

\*\* Only existing stocks of fire-fighting foam may be used in case of emergencies until 2014 for mobile applications and until 2018 for stationary installations.

## CHAPTER 7: CONTROL TECHNOLOGY AND REMEDIATION TECHNIQUES

Very little work has been done to identify remedial technologies to address PFC contamination. Because of the very strong carbon-fluorine bonds in PFCs, the chemicals are not readily degraded by biologic or abiotic (such as photodegradation or low temperature incineration) processes typically employed in treatment technologies or seen in nature. Granular activated carbon has been shown to effectively remove PFCs from drinking water (Qiu, 2007). Reverse osmosis has also been shown to effectively remove PFCs from water (Thompson, 2011). No *in situ* technologies have been shown to remove or breakdown PFCs in soils and sediments. At this time, the only known removal option is physical removal with either burial or high temperature incineration. There is some expectation that certain strains of bacteria may be able to degrade these compounds, but this has not been proven.

Possibly the most significant issue with regard to remediating PFCs is that the most commonly used remedial technologies employed to treat water, both drinking water and contaminated water, do not remove or degrade PFCs. PFCs pass through filtration; oxidation; air stripping; primary, secondary, and tertiary sewage treatment; low temperature incineration; biotreatment; ionization; and chlorination (de Voogt, 2004). As noted above, the only effective remedial treatments of PFC-contaminated water that have been demonstrated, are the use of activated carbon or reverse osmosis. Where PFCs are entering into existing treatment systems, the PFC contamination is either being transferred to different media or is simply passing through the system to be distributed to the environment.

It is important to understand the potential impact and relevance of these facts. For example, PFCs that are entering into drinking water distribution systems through either surface water or groundwater supplies will, with most systems, pass through treatment and be distributed to the end users of that water.

Where municipal or industrial wastewater is impacted with PFCs, the PFCs passing through the WWTP will be concentrated in the sludge and/or simply pass through the system and be either discharged into surface water or groundwater. If the sludge is land applied, PFCs will become incorporated in the soils where they will be taken up into vegetation/crops, ingested by livestock and wildlife, and/or contaminate groundwater and surface water. If the sludges are incinerated, the PFCs will either transfer to the smoke or to the ash. Unless the sludges are properly landfilled, the PFCs will simply be transferred to another environmental media and available to human or ecological receptors.

Remedial systems designed to treat groundwater at sites of environmental contamination currently impacted with PFCs, will simply transfer the PFC contamination to the systems' discharge point, usually contaminating a different location and/or environmental matrix.

With the evident widespread contamination of sewage, surface water, and groundwater being found around the globe, it is possible that Michigan has numerous sites where treatment is failing to remove PFCs from water distribution systems and wastewater effluents.

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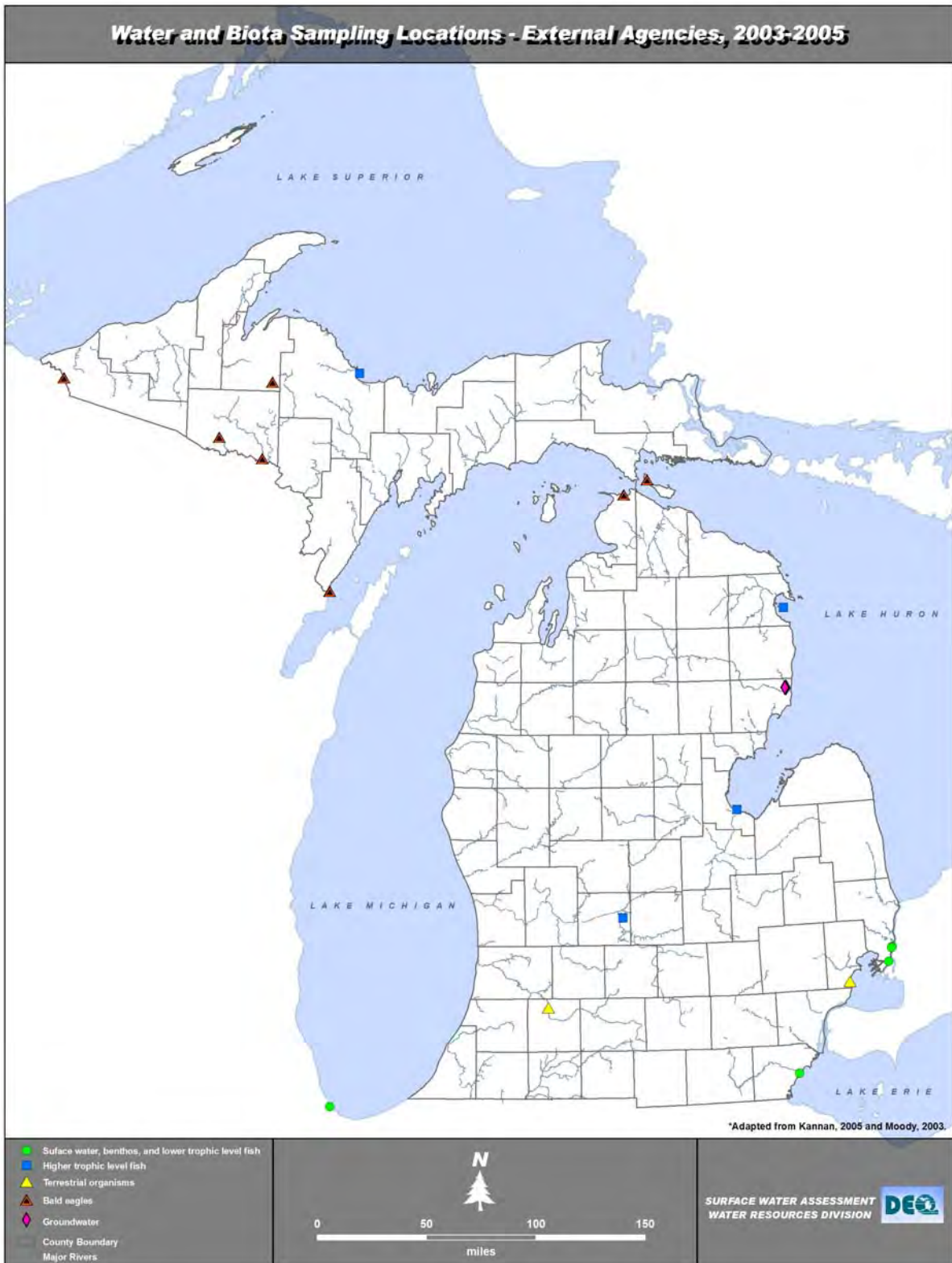
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## APPENDIX A – LOCATIONS OF PREVIOUS SAMPLING EVENTS

A-1. DEQ Water Chemistry Monitoring Program sampling locations.



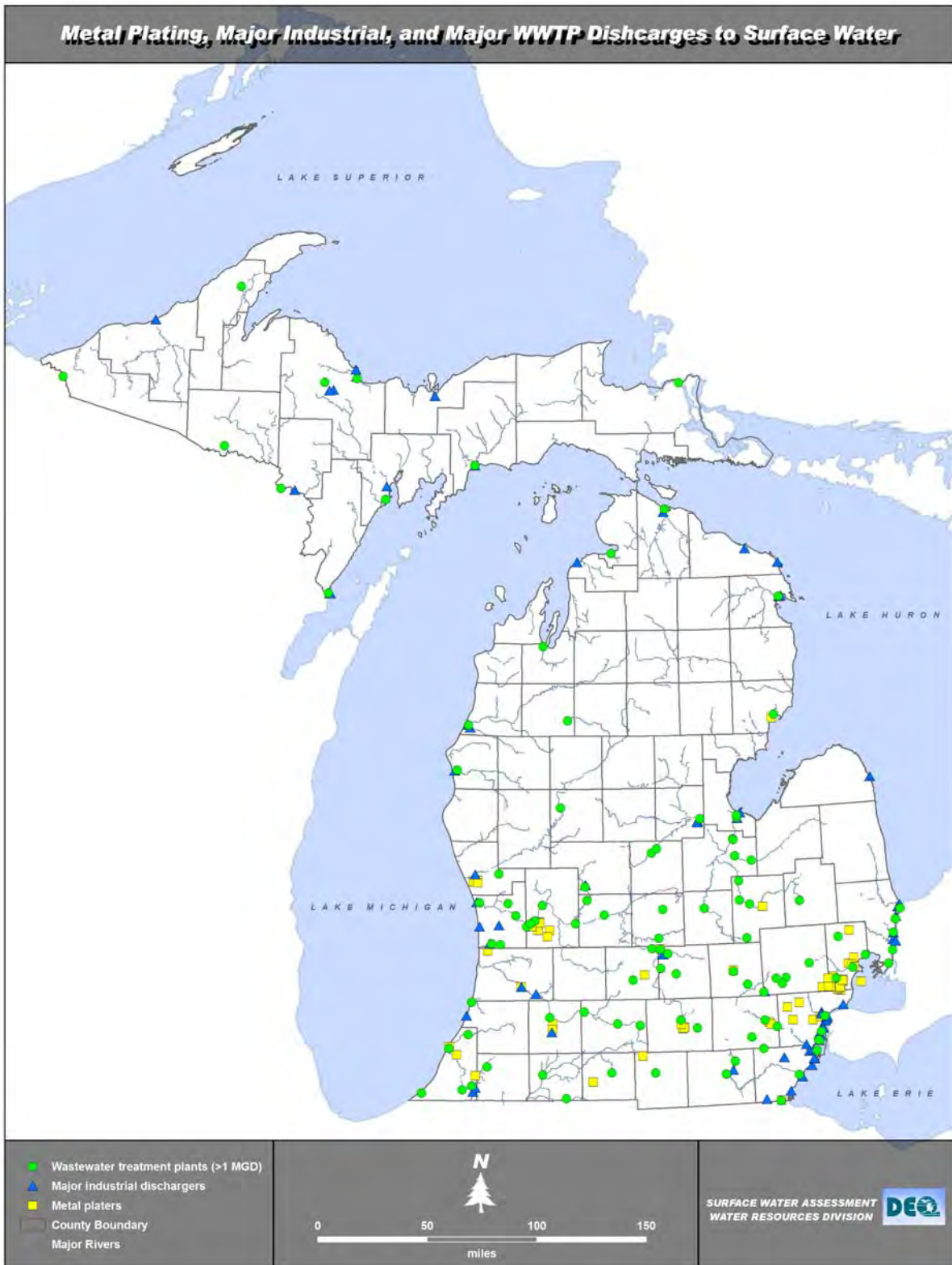
A-2. Michigan-specific data collected from agencies other than the DEQ. Adapted from Moody et al., 2003 and Kannan et al., 2005.





## APPENDIX B – POTENTIAL DISCHARGES TO SURFACE WATER

B-1. Combined electroplating, industrial, and WWTP discharges.





B-2. NPDES-permitted electroplating discharges to surface water.



B-3. NPDES-permitted major industrial discharges to surface water.



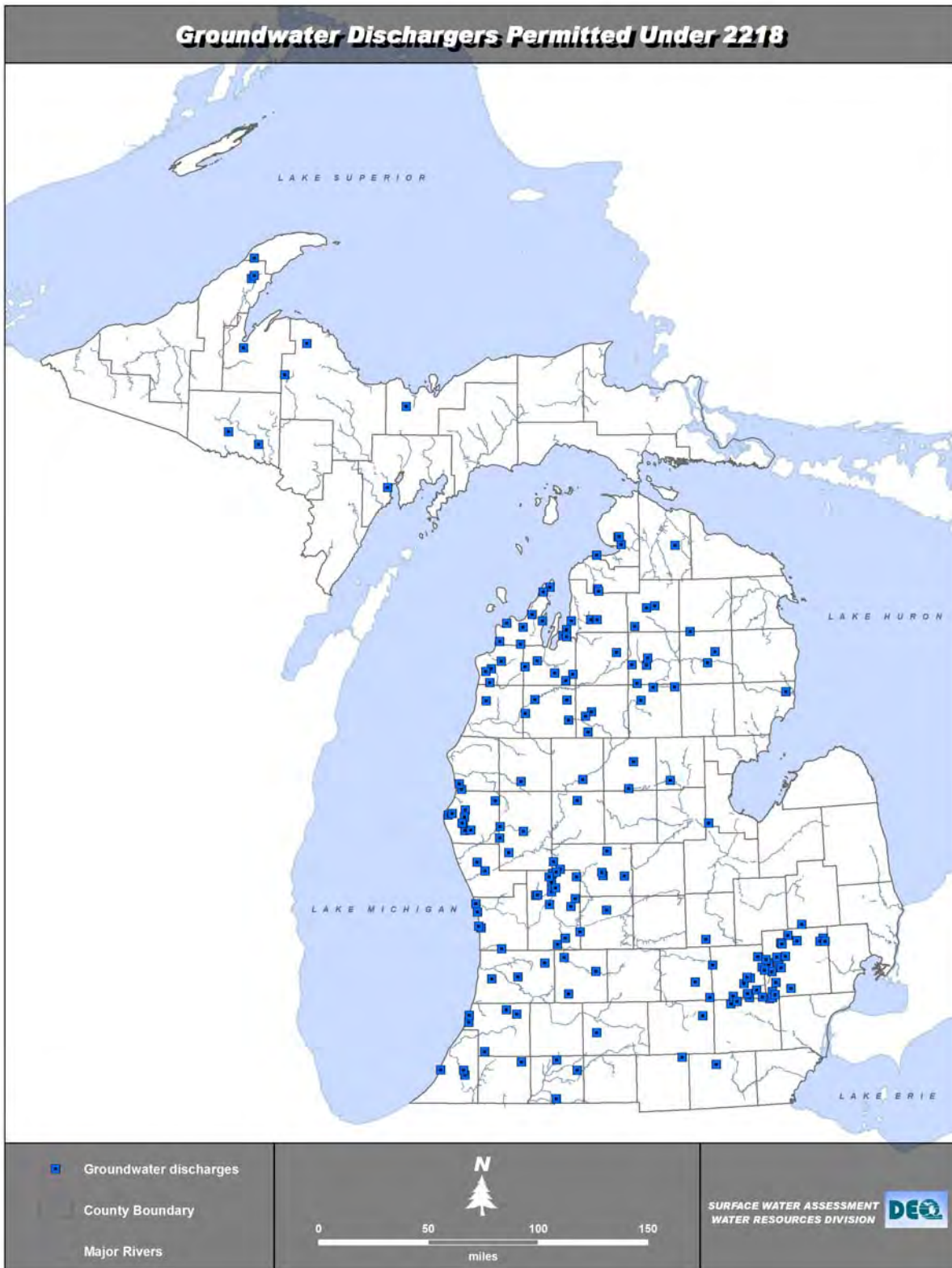
B-4. NPDES-permitted major WWTP discharges to surface water.





## APPENDIX C – POTENTIAL DISCHARGES TO GROUNDWATER

C-1. Locations of groundwater discharges permitted pursuant to Rule 2218 of Part 22.



# APPENDIX D – POTENTIAL DISCHARGES TO AIR

## D-1. Potential sources of PFCs.

