INVESTIGATION OF PERFLUOROCHEMICAL (PFC) CONTAMINATION IN MINNESOTA PHASE ONE

Report to Senate Environment Committee

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EXECUTIVE SUMMARY

This paper describes a Phase I study in Minnesota on the environmental release and contamination issues related to a group of perfluorochemicals (PFCs) manufactured (past and present) by the Minnesota Mining and Manufacturing (3M) Company. This study investigated contamination by these PFCs in various environmental media and biota at selected sites including landfills, wastewater treatment facilities, the Mississippi River water and sediment, and Mississippi River fish. This is the first study to provide a complete evaluation of up to14 individual PFCs from release sources into the Minnesota environment.

This study evaluates PFCs that are related to, or break down into a chemical called perfluorooctane sulfonate (PFOS). PFOS is related to the production of PFCs that were manufactured primarily by 3M, and were used in a very broad range of industrial, commercial, and consumer products, sometimes known by the 3M brand name, Scotchgard. This study also evaluates contamination by a perfluorochemical (PFC) called perfluorooctanoic acid (PFOA), and carboxylic acid PFCs that are related to PFOA, or break down into PFOA. PFCs that were made in the 3M manufacturing processes for formulation into PFC products eventually break down into PFOS and PFOA in the environment. PFOS and PFOA do not breakdown further.

3M was the primary global producer of these PFOS-related PFCs, and PFOA, and manufactured these chemicals at its two U.S. plants in Decatur, Alabama and Cottage Grove, Minnesota, and in Europe at its plant in Antwerp, Belgium. 3M perfluorochemcial production began at the Cottage Grove, Minnesota plant around 1950.

In 2000 following discussion with the U.S. Environmental Protection Agency (EPA) and based on concerns about the widespread presence and long term risks associated with PFOS, 3M announced that it would end production of PFOS-related PFCs. 3M agreed that continued manufacturing and use of PFOS represented an unacceptable technology. Production of PFOS-related PFCs and PFOA was terminated by 3M at its plants by the end of 2002. At that time 3M PFC production and 3M fluorochemical “Scotchgard” products were changed to formulations based on a new four-carbon chain “cousin” to PFOS, called perfluorobutane sulfonate (PFBS). This study also includes evaluation of PFBS and related four-carbon PFCs, and several other PFCs including carbon-10 compounds.

PFOS has been found to be ubiquitous in the environment in tissues, blood and fetal cord blood of humans, wild birds, fish, and other animals, and in surface waters and sediments, sewage sludge, landfill leachates, and wastewater treatment effluents worldwide. Studies have confirmed widespread contamination of PFOS in blood of human populations worldwide. PFOS has been found to be persistent, bioaccumulative, and toxic to mammalian species. PFOS and PFOA are extremely persistent and do not biodegrade or break down in the environment, and are not metabolized in animals and humans. PFOS bioconcentrates and has been shown to bioaccumulate in fish and other aquatic organisms. PFOS has been shown to cause certain cancers in laboratory test animals. PFOA has also been shown to cause

certain toxic effects in laboratory animals, and was recently recommended as a "likely carcinogen" by a Science Advisory Board to the EPA.

The following summarizes the findings of this PFC contamination investigation at selected study sites and environmental media in Minnesota.

Washington County Closed Landfill

As a result of past disposal of 3M fluorochemical wastes at the landfill, soils and groundwater at the landfill site have been found to be contaminated with PFCs. The Washington County Landfill site is the source of contamination of PFOS and PFOA in a number of residential wells in the City of Lake Elmo "downgradient" from the landfill. The study determined the following:

- PFOS and PFOA significantly exceed the Minnesota Department of Health HBVs (health based values) or "drinking water standards" in groundwater at the site.
- The study determined that the groundwater below the site is contaminated with 8 PFCs. Some of these have not been analyzed in water from residential wells.
- One PFC, PFBA or perfluorobutane sulfonate, not tested for in the residential wells, was found in groundwater at a very high level of 1170 ppb (part per billion).
- PFCs have percolated through the site soils to a depth of at least 26 ft.
- Lower concentrations of PFOS, PFOA, and PFBA were found in "background" soils, suggesting the possibility that these PFCs, or precursor compounds that breakdown into these PFCs, may have been carried by aerosol drift from the landfill groundwater pumpout spray irrigation system.
- Spray irrigation of groundwater pumped out should be reviewed with respect to PFCs carried via aerosols. Activated carbon removal should be evaluated for treatment of pumpout water.
- Extensive long term monitoring of PFCs in the groundwater should be done. PFC monitoring in a phase 2 study should include particulate and vapor phases of the air, if spray irrigation is continued.
- Residential wells affected by the landfill should be tested for all PFCs, and the need for determination of HBVs for other PFCs should be assessed.
- The HBV for PFOS and PFOA should be determined for the sensitive population, including pregnant women and children.

3M Cottage Grove Wastewater Treatment Plant

3M operates a wastewater treatment plant at the Cottage Grove plant and discharges to the Mississippi River. The study evaluated perfluorochemical removal through the wastewater treatment system and determined the following:

- Eight PFCs were found in the 3M treated process wastewater discharge and cooling water discharge to the river. 3M routinely monitors for 5 PFCs.

- 3M installed a granular activated carbon (GAC) treatment system in 2004 as required by its NPDES permit. PFOS is being removed efficiently by the GAC system. The GAC system appears to be somewhat less effective in consistently removing PFOA.
- PFCs related to the past PFOS and PFOA-related production continue to be discharged, although production of these chemicals ceased at the end of 2002. The sources of continuing PFCs in the discharge are not completely understood but may be due, in part, to groundwater at the site contaminated with PFCs being pumped to the treatment systems and cooling water.
- Cooling water contains PFC contamination which is discharged untreated to the river. Perfluorohexane sulfonate (PFHxS) was found at a relatively high level in cooling water.
- The total PFC concentration discharged to the river from the plant, based on this study's results, is about 322 ppb (parts per billion), or about 3465 pounds per year.
- The 3M NPDES permit should be modifed to require monitoring for more PFCs. Note that PFBA, not currently monitored by 3M, was found at a high concentration.
- 3M should complete a thorough assessment of the efficiency for removal of all PFCs through the wastewater treatment plant and the GAC system.
- The impact of PFCs contained in contaminated groundwater pumpout on the discharge should be completely assessed, and the need for activated carbon treatment of this water and cooling water should be evaluated.
- Development of discharge standards for PFCs are needed.
- The contribution of PFCs from the incinerator wastewater GAC system, out of service during this study sampling, needs to be determined.

Pine Bend Landfill

The Pine Bend Landfill received sludges in the past from 3M which contained PFCs. The study determined the following:

- The landfill leachate contains 10 PFCs at relatively high levels.
- Groundwater at the site is contaminated with PFCs, although PFOS and PFOA are well below the applicable HBVs.
- This is the only study known to evaluate PFCs in gas condensate from gas generated and at the landfill. The gas condensate contains relatively high levels of PFCs. Gas emitted from the gas to energy saystem should be tested for PFCs.
- Leachate generated at the landfill is disposed of at the MCES Metro wastewater treatment plant. Based on limited data, the leachate represents about 10% of the total PFC mass load to the Metro plant.
- Groundwater should continue to be periodically monitored for PFCs.

MCES Metro Wastewater Treatment Plant

The Metro wastewater treatment plant (WWTP) receives leachate from the Pine Bend Landfill containing PFCs, contaminated groundwater containing PFCs from the Oakdale Dump, and domestic and industrial wastewaters which may contain PFCs from various waste products discharged. The study determined the following:

- PFOS and PFOA were found in the WWTP effluent at 81 and 78 ppt (part per trillion). These levels seem relatively low and are comparable to levels in WWTPs found in other studies.
- Influent concentrations of PFCs (PFOS and PFOA at 53 ppt and 46 ppt, respectively) were lower than effluent concentrations, probably due in part to PFC precursor degradation through the WWTP, also found in other studies to occur.
- Sludges tested contained 7 individual PFCs, with relatively high concentrations of PFCs in secondary sludge, with PFOS at 309 ppb (part per billion).
- Biosolids also contained PFCs, with PFOS at about 80 ppb.
- PFCs in sludges at the Metro WWTP are higher than those found in sludge from other studies, where WWTPs are not exposed to discrete PFC sources.
- Based on this study the Metro plant discharges about 123 pounds of PFCs per year.
- More extensive study of the fate, transport, and biodegradation pathways of PFCs in wastewater treatment plants would be useful.
- The potential repercussions of PFOS and PFOA in beneficially-used biosolids, and in sludges disposed, should be examined.
- The efficiency of destruction of PFCs though Metro WWTP sludge incineration should be evaluated.
- The impacts from landfill leachates and other discrete PFC sources directed to the Metro WWTP, and sludge PFC concentrations, should be further assessed to determine if pretreatment to remove PFCs from these discrete PFC sources should be done.
- The prevalance of domestic and industrial sources of PFCs in municipal wastewaters should be examined. It would be prudent to test other WWTP effluents to determine PFCs present.
- Discharge standards should be developed for PFC compounds.

Mississippi River Water and Sediment

Based on calculations done by MPCA staff Don Kreins, 3M may have discharged 50,000 pounds per year of PFCs from its wastewater treatment plant to the river over a period of several decades. As a result of this discharge, river sediments have been contaminated with PFCs, and provide a source of PFCs for subsequent bioconcentration and bioaccumulation in aquatic life. The study determined the following:

- The upstream river water sample contained only PFOS, at about 5 ppt (part per trillion), comparable to “background” PFOS found in other studies.
- PFOS and PFOA were found in river water downstream of the 3M discharge at 14 and 35 ppt, respectively. PFOA was higher, probably due to its greater solubility.
- PFC concentrations in the river cove water, immediately receiving the 3M discharge, were in the very high ppt ranges with PFOS at 18200 ppt and PFBS (perfluorobutane sulfonate) at 89800 ppt, and correlate with PFC concentrations found in the 3M wastewater treatment plant discharge.
- Although at high levels in the river cove water, PFBS was not found in the main river body, possibly due to volatility losses or other mechanisms.

- It is likely that higher concentrations of PFCs would be found at the top river water surface or "micro layer" due to their surface active properties. More river water samples should be taken, especially at the water surface or "micro layer" to determine PFC concentrations in river water.
- Sediments of the river cove water receiving the 3M discharge contain high concentrations of PFCs.
- Sediments downstream of the 3M discharge point in the river were contaminated with PFCs, comparable to PFC levels in sediments found in other studies with a PFC contamination source.
- The 10 cm depth sediment cores taken in this study are most likely indicative of the past few years of river sedimentation, correlating with discharge from 3M after PFOS-related PFCs and PFOA were phased out of production in 2002. These shallower sediment cores may contain less PFCs than deeper sediments, and deeper sediments may correlate with past 3M discharges containing high concentrations of PFCs.
- Deeper sediment cores, and a more extensive collection of river sediment cores, should be analyzed using sediment dating to characterize the mass loading of PFCs contained within river sediments.
- PFCs in river sediments further downstream should be analyzed, including Lake Pepin. Lake Pepin serves as a "sink" for sedimentation of upstream river suspended solids, and a "reservoir" for contaminants. PFCs may reside in Lake Pepin sediments due to this sedimentation effect.
- The bioavailability of PFC contaminated sediments needs to be evaluated. It is likely that sediments contaminated with PFCs pose a continuing source of exposure to aquatic life, resulting in biomagnification of PFCs in the food chain, similar to that found with other organic contaminants. A major route for PFC contamination in fish may be via sediments contaminated with PFCs.
- The extent of river cove sediment PFC contamination needs to be assessed. An evaluation should be done to determine whether the river cove sediments pose a continuing source of PFC contamination to the main river body and whether the cove sediments should be remediated (removed) to eliminate this source.
- Discharge standards should be developed for PFOS, PFOA, and possibly other PFCs.

Mississippi River Fish

A number of fish were collected in August 2004 in the river in the vicinity of the 3M Cottage Grove plant discharge, and in October 2005 in Mississippi River pool #2 just downstream of the 3M discharge. The study determined the following:

- Analysis of fish in the Mississippi River, collected in August 2004 and October 2005, demonstrate that these fish are heavily contaminated with PFC compounds, predominantly PFOS.
- The PFOS concentrations found in the August 2004 fish livers are at high levels and are indicative of exposure to a PFC contamination source, the 3M discharge.
- Past discharge concentrations of PFOS from the 3M Cottage Grove plant indicate that at times the discharge could have caused toxic effects on fish. This would have occurred prior to the PFOS-related and PFOA production phase-out. The limited data available

show that the PFOS concentration in the past, at times, could have exceeded the NOEC (no observable effect concentration) level for fathead minnows of 300 ppb at the point of discharge.

- PFOS levels in the Mississippi River fish liver are similar to levels studied in Belgium. The high PFOS levels in fish liver collected near a fluorochemical production plant in Belgium were associated with serum ALT (alanine aminotransferase) activity, a marker for hepatic damage, showing that PFOS may induce liver damage to fish at these levels.
- One smallmouth bass among fish collected in 2004 in this study contained a very high level of PFOS in liver, 6350 ppb, and is comparable to the highest PFOS levels found in fish liver to date worldwide, based on our knowledge and review of the literature.
- It is probable that sediments contaminated with PFCs are a source of PFC contamination in fish. Young smallmouth bass (2 year olds) livers in this study contained relatively high levels of PFOS at 1030 ppb, even though the levels of PFOS and other PFCs in the 3M discharge have been reduced during this 2 year period, since termination of PFOA and PFOS- related production by the end of 2002. The mechanism of bioavailability for exposure to fish needs to be understood, and whether sediments contaminated with past PFC discharges continue to be a source for contamination exposure to fish and aquatic life.
- The levels of PFOS found in blood of fish collected on October 3, 2005 from the Mississippi River pool #2, downstream and proximate to the 3M Cottage Grove plant discharge, are extraordinarily high and are the highest in blood of any animals tested worldwide, to our knowledge based on a review of the literature.
- The PFOS and related PFC contamination levels found in fish in this study likely pose a significant risk to humans and wildlife consuming these fish, and require immediate assessment.
- Fish collected in October 2005 in the Mississippi River pool #2 and the Mississippi River Lake Pepin should be immediately analyzed for PFCs in fillet and whole fish to determine the risk associated with human and wildlife consumption. These analyses and risk assessment should be done as soon as possible to assess the need for a fish consumption advisory. Analysis of more fish may be necessary to be able to adequately characterize PFC contamination levels in Mississippi River fish.
- Other aquatic species including fish from lower trophic levels should be analyzed and a model for bioaccumulation of PFCs should be developed.
- It would be prudent to test PFCs in higher trophic levels (wildlife biomonitoring), including mammals and birds consuming contaminated fish, considering the PFOS contamination levels found in fish blood and liver in this study.
- An analysis of fish contaminant trends and other media analyzed (water and sediment) should be completed.

INTRODUCTION

This paper describes Phase I of a study in Minnesota on the environmental release and contamination issues related to a group of perfluorochemical compounds manufactured (past and present) by the Minnesota Mining and Manufacturing (3M) Company.

The MPCA perfluorochemical investigation (Phase One) was proposed and conducted by Fardin Oliaei as the Principal Investigator (PI) in order to determine the presence and extent of contamination of perfluorochemicals in the Minnesota environment, and to initiate study of the behavior of these compounds in various environmental media. This information is essential to assess the human health and ecological impacts of perfluorochemicals in the Minnesota environment. This study was funded by the MPCA Closed Landfill Program (CLP). This investigation examined contamination by perfluorochemicals in Minnesota at selected sites including landfills, wastewater treatment facilities, the Mississippi River water and sediment, and Mississippi River fish.

This study evaluates perfluorochemicals that are related to, or break down into a compound called perfluorooctane sulfonate (PFOS). PFOS is related to the production of sulfonyl-based perfluorochemicals that were manufactured primarily by 3M, and were used in a very broad range of industrial, commercial, and consumer products, sometimes known by the 3M brand name, Scotchgard. 3M was the primary global producer of these PFOS-related perfluorochemicals. 3M produced millions of pounds of these perfluorochemicals annually at its plants in the United States and Europe. In 2000 3M produced 7.33 million pounds at its plants in the United States and Europe (Organisation for Economic Cooperation and Development report, 2002).

This study also evaluates contamination of the selected sites by a perfluorochemical called perfluorooctanoic acid (PFOA), or carboxylic acid perfluorochemicals that are related to PFOA, or break down into PFOA. PFOA is used to make fluoropolymers, substances with special properties that have numerous manufacturing applications and are used in making consumer products such as non-stick cookware (Teflon®) and similar products. 3M was a major manufacturer of PFOA. Other perfluorinated substances were made and presumably disposed by 3M. They were not addressed in this evaluation phase.

Production of PFOS-related perfluorochemicals and PFOA was terminated by 3M at its plants by the end of 2002, and 3M perfluorochemical production and 3M fluorochemical "Scotchgard" products were changed to formulations based on a new 4-carbon chain "cousin" to PFOS, called perfluorobutane sulfonate (PFBS). This study includes evaluation of PFBS and related 4-carbon perfluorochemicals, and several other perfluorochemicals including 10-carbon compounds.

The investigation consists of sampling and subsequent analysis of PFCs in various environmental media. The research and sampling for this investigation was completed with the assistance of the following MPCA staff: Dave Douglas, Joe Julik, Ingrid Verhagen, Katrina Kessler, Enrique Gentzsch, Harold Wiegner, and Don Kriens. Minnesota

Department of Natural Resources staff, Jack Enblom and Mark Briggs, collected all fish for PFC analyses in this study. Additionally, Don Kriens was extensively involved with the research and drafting of this report prior to my departure from the agency.

This is the first phase of a comprehensive perfluorochemicals investigation conducted in Minnesota, and is independent of the 3M Weston perfluorochemical study. A minimum of twelve individual perfluorochemical compounds are analyzed as a part of this investigation versus the 4 perfluorochemicals evaluated in the 3M Weston study. This is the first study to provide a complete evaluation of up to 14 individual perfluorochemicals from release sources into the Minnesota environment.

I. PERFLUROCHEMICAL CONTAMINATION PROBLEM

A. Discovery of the Worldwide PFOS and Perfluorochemical Contamination Problem

In 1997, a 3M lab comparing 3M workers' blood to randomly chosen Red Cross samples found that PFOS and PFOA were present not only in the blood samples from the 3M workers, but also in the blood bank samples. The blood bank samples were from the normal population not occupationally exposed to these chemicals. The results of this comparative study indicate that by 1997 3M perfluorochemical contamination had become widespread in humans. As a result of this startling finding 3M commissioned a number of studies to determine the extent of contamination of these perfluorochemicals in the environment. The initial study was done in 1999 by Michigan State University and included the analysis of archived animal samples, collected in 1989, 1992, and 1993 during other unrelated studies (Giesy et al, 2001). The specimens were analyzed for PFOS. Additional studies on human blood confirmed the widespread contamination of PFOS in human blood.

The Michigan State University study found PFOS in the blood and liver of numerous animals worldwide including bald eagles in the Great Lakes region, river otters in the Northwest, birds and turtles in the Southeast, and in animals at very remote locations, such as polar bears in Alaska and albatrosses in the Pacific Ocean. Subsequent studies by Michigan State University and others have confirmed that numerous wildlife and fish around the world have been contaminated with PFOS. At the same time studies of human blood determined that populations worldwide have PFOS in their blood. In individual blood serum samples obtained from adults and children in various regions of the U.S., mean PFOS levels were approximately 43 ppb (parts per billion).

3M manufactured these perfluorochemicals at plants in the U.S in Decatur, Alabama and Cottage Grove, Minnesota and in Europe in Antwerp, Belgium, as discussed further below. In 2000 following a series of discussion with the U.S. Environmental Protection Agency (EPA) and based on concerns about the widespread presence and long term risks associated with PFOS, 3M announced that it would end production of the PFOS-related perfluorochemicals. 3M agreed that continued manufacturing and use of PFOS represented an unacceptable technology that should be eliminated to protect human health and the environment from potentially severe long term consequences. In 2000 3M began a phase out of PFOS-related perfluorochemical production. Production of these chemicals at the 3M Minnesota, Alabama, and Belgium facilities was terminated by the end of 2002.

B. Concerns about PFOS and Related Perfluorochemicals

PFOS has been found to be ubiquitous in the environment in tissues of wild birds, fish, and other animals, surface waters and sediments, sewage sludge, landfill leachates, and wastewater treatment effluents worldwide. PFOS is extremely persistent and does not

biodegrade or break down in the environment, and it is not metabolized in animals and humans. PFOS is bioaccumulative and has been shown to bioconcentrate in fish and other aquatic organisms. Perfluorochemicals based on the sulfonyl perfluorochemical chemistry that were made in the 3M manufacturing processes for formulation into perfluorochemical products eventually break down into PFOS in the environment. The fluorochemicals that eventually break down to PFOS are sometimes referred to as PFOS precursors. Similarly, other precursors, such as fluorochemical telomer alcohols, may break down into PFOA.

PFOS has been found to be persistent, bioaccumulative, and toxic to mammalian species. Animal studies show that PFOS is readily absorbed orally and distributed mainly to the liver and blood. No further metabolism has been observed. Elimination from the body is slow and occurs mainly in the urine and feces. There are significant differences in the elimination half-life of PFOS in different animals. The mean half-life in humans is estimated to be 8.67 years (Burris et al 2002).

1. PFOS Toxicity and Carcinogenicity

PFOS has been shown to cause moderate toxicity in rats. Numerous studies done on the exposure of rats and primates to PFOS have shown that it is toxic to the liver. Adverse signs in 90 day rat studies include increase in liver enzymes, hepatic vacuolization and hepatocellular hypertrophy, gastrointestinal effects, hematological abnormalities, weight loss, and convulsions. Adverse effects in Rhesus Monkey studies include anorexia, emesis, diarrhea, hypoactivity, convulsions, atrophy of the salivary glands, thymus and the pancreas, marked decreases in serum cholesterol, and lipid depletion in the adrenals.

The potential carcinogenicity of PFOS was examined in a dietary 2 year bioassay in rats, where a significant increase in the incidence of hepatocellular (liver) adenomas in both males and females at the highest PFOS dose occurred. This study also found that female rats had a significant increase in combined hepatocellular adenomas and carcinomas. The study also found that there was a significant increase in follicular cell adenomas and combined thyroid follicular cell adenomas and carcinomas in the male rats at high PFOS doses (Organisation for Economic Cooperation and Development report, 2002).

In a mortality study of 3M workers at the 3M Decatur, Alabama plant, which spanned a 30 year period, there was a stastically significant association between PFOS levels in workers blood and bladder cancer. Statistical analysis of the mortality data indicated that workers who were employed in high exposure jobs were 13 times more likely to die of bladder cancer than the general population of Alabama. The study concluded that bladder cancer is a potentially significant yet uncertain endpoint in the analysis of risks from PFOS-related substances (Alexander et al, University of Minnesota, 2001).

To evaluate morbidity outcomes an “episode of care” analysis was completed for 3M employees who had worked at the 3M Decatur, Alabama plant during 1993 and 1998. Increased incidences of cancer and non-malignant growths were not found to be of significance and no mortality risks were reported for most of the cancer types. However, the analysis found an increased risk of episodes of neoplasms of the male reproductive system,

as well as an increase in the the overall category of cancers and benign growths, and neoplasms of the gastrointestinal tract. Risk ratios were highest in employees with the highest and longest exposures to fluorochemicals (Olsen et al., 2001).

Postnatal deaths and other developmental effects were reported in offspring in a 2-generation reproductive toxicity study of rats exposed to low doses of PFOS. Prenatal developmental effects were also reported in toxicity studies done with rats and rabbits at slightly higher dose levels. During the high dose studies significant decreases in fetal body weight and significant increases in external and visceral anomalies, delayed ossification, and skeletal variations were observed (Organisation for Economic Cooperation and Development report, 2002).

PFOS appears to have low to moderate toxicity in aquatic organisms. The lowest LC50 reported for fish is 96-hour at 4.7 mg/l for the fathead minnow *Pimephales promelas* for the lithium salt. (The LC50 is the concentration of a chemical that kills 50% of the test animals.) For aquatic invertebrates, the lowest EC50 for freshwater species is a 48-hour EC50 of 27 mg/l for *Daphnia magna.* (The EC50 is the effective concentration of a substance that has a specified non-lethal effect on half of the test organisms within a specified period of time.) For saltwater species, the lowest EC50 is a 96-hour LC50 at 3.6 mg/l for the Mysid shrimp *Mysidopsis-bahia*. Long-term toxicity data is available for fish and aquatic invertebrates. The lowest NOEC for fish is a 42 day NOEC (survival) at 0.3 mg/l in an early life stage test with *Pimephales promelas* using potassium salt. (The NOEC or no observable effect level is the highest concentration of a toxicant to which organisms are exposed in a full life-cycle or partial life-cycle (short term) test that causes no observable effect on survival ($NOEC_{survival}$); and no observable effect on growth and reproduction ($NOEC_{growth}$) of the test population. The lowest NOEC for aquatic invertebrates is a 35-day NOEC reproduction at 0.25 mg/l for *Mysidopsis bahia* using the potassium salt (3M Fluorochemical EPA Submissions, 2000, 2001, 2002)

PFOS is resistant to biodegradation by microorganisms and it does not appear to be degraded or removed through biological wastewater treatment. However, PFOS does not appear to be toxic to sewage sludge microorganisms (Wildlife International, 2000). No data were found regarding the effects of PFOS on soil-dwelling or sediment-dwelling species.

PFOS has been tested on two species of bird, the Mallard duck, *Anas platyrhynchos*, and the Northern Bobwhite quail, *Colinus virginianus.* A lowest acute dietary LC50 value of 220 mg/kg of food was determined in the test with the quail, while a lowest NOEC of 37 mg/kg of food for effects on body weight was obtained in the test with the duck (Wildlife International, 2000).

There are data available from acute oral and contact toxicity tests on the Honey bee (*Apis mellifera*) using PFOS potassium salt. These studies indicate moderate to high toxicity of PFOS to bees when administered via these routes (3M Fluorochemical EPA Submissions, 2000, 2001, 2002).

2. PFOA Toxicity and Carcinogenicity

The EPA Office of Pollution Prevention and Toxics has been investigating the toxicity of PFOA. PFOA is used extensively in coated (Teflon) cookware and other similar products. Most of the toxicity studies have been conducted with the ammonium salt of PFOA. Epidemiological studies on the effects of PFOA in humans have been conducted on workers. A retrospective mortality study demonstrated a statistically significant association between prostate cancer mortality and employment duration in a PFOA manufacturing plant. However, an update to this study did not find a significant association. A study which examined hormone levels in workers reported an increase in estradiol levels in workers with the highest PFOA serum levels. Cholesterol and triglyceride levels were positively associated with PFOA exposures. A statistically significant positive association was reported for PFOA and T3 (thyroid hormone) levels in workers but not for any other thyroid hormones (EPA, OPPT Draft Risk Assessment of PFOA, 2005).

Studies have shown that PFOA readily crosses the placenta and is present in the breast milk of rats. Distribution studies have shown that PFOA is distributed primarily to the serum, liver, and kidney (EPA, OPPT Draft Risk Assessment of PFOA, 2005).

Repeat dose studies in rats and mice demonstrate that the liver is the primary target organ. Chronic dietary exposures to PFOA (ammonium salt) for 90 days resulted in significant increases in liver weight and hepatocellular hypertrophy in female rats at 1000 ppm and in male rats at doses as low as 100 ppm. Chronic dietary exposure of rats to 300 ppm of PFOA (ammonium salt) for 2 years resulted in increased liver weight, hepatocellular hypertrophy, hematological effects, and testicular masses in males; and reductions in body weight and hematological effects in females (EPA, OPPT Draft Risk Assessment of PFOA, 2005).

The carcinogenic potential of PFOA has been investigated in two dietary carcinogenic studies in rats. Under conditions of these studies there is some evidence that PFOA is carcinogenic, inducing liver tumors, Leydig cell tumors (LCT), and pancreatic acinar cell tumors (PACT) in male rats. There is sufficient evidence to indicate that PFOA is a PPARα agonist and that the liver carcinogenicity (and toxicity) of PFOA is mediated by binding to the PPARα in the liver. A mode of action analysis has demonstrated that the hepatic effects are due to PPARα agonism, and that this mode of action is unlikely to occur in humans. The LCT and PACT induced in the rat by PFOA probably do not represent a significant cancer hazard for humans because of quantitative differences in the expressions of receptors and of other toxic dynamic differences between the rat and human. Based on no adequate human studies and uncertain relevance of the tumors from the rat studies, the EPA in its January 2005 summary stated that PFOA may be best described as "suggestive evidence of carcinogenicity, but not sufficient to assess human carcinogenic potential". (EPA, OPPT Draft Risk Assessment of PFOA, 2005).

In February 2006, however, the EPA Science Advisory Board recommended to EPA that PFOA is a "likely carcinogen" based on its assessment of available studies.

C. 3M Perfluorochemical Production

PFOS, perfluorooctane sulfonate, was the eventual byproduct of breakdown and degradation from other perfluorochemicals that were produced and used in 3M perfluorochemical products. PFOS is also a residual produced in the manufacturing process. PFOS is an 8-carbon straight chain compound that is saturated with fluorine molecules. The parent compound for PFOS-related chemicals is perfluorooctanesulfonyl fluoride (POSF). POSF is manufactured through a process known as Simons Electro-Chemical Fluorination (ECF), discovered and patented by 3M. The ECF process replaces the carbon-hydrogen bonds on molecules of the organic feedstock with carbon-fluorine bonds. Perfluorination occurs when all of the carbon-hydrogen bonds are replaced with carbon-fluorine bonds. The ECF process yields between 30-45 percent straight chain (normal) POSF, along with a variable mixture of byproducts and impurities. The output of the ECF process is not a pure chemical, but instead a mixture of isomers and homologues including higher and lower straight-chain homologues; branched-chain perfluoroalkyl fluorides of various chain lengths; straight chain, branched, and cyclic perfluoroalkanes and ethers; and other byproducts (3M Company, 2000b). The PFOS-related perfluorochemicals produced eventually breakdown to PFOS in the environment. PFOS does not breakdown further in the environment nor is it metabolized further in animals.

Perfluorochemicals related to PFOS were produced by 3M using the electro-chemical fluorination process. Certain perfluorochemicals are also produced by a telomerization process, which is used by Dupont to produce related products. In addition Dupont uses PFOA to form emulsions in the manufacture of Teflon®. PFOA was formerly produced by 3M at the Minnesota Cottage Grove plant, but production was terminated by the end of 2002.

1. PFOS-related Products Produced by 3M Used Worldwide

3M started production of these fluorochemicals, which are components of several important product lines due to their unique properties, around 1950. According to 3M, the chemical physical properties of the chemicals include the ability to: repel both water and oil, reduce surface tension much lower than other surfactants, act as catalysts for oligomerization and polymerization, and function where other compounds would rapidly degrade.

According to 3M typically a fluorochemical product contains a small amount of fluorochemical residue of unreacted or partially reacted starting materials or intermediates. Residues which are common include PFOS, n-methyl and n-ethyl FOSA (perfluorooctanesulfonamide) and n-methyl and n-ethyl FOSE alcohols (perfluorooctanesulfonamidoethanol) and PFOA. With the exception of PFOA, these fluororchemical residuals, along with others related to fluorinated sulfonyl production, eventually degrade to PFOS.

3M produced a very large number of products using PFOS-related perfluorochemicals that were distributed worldwide. In some cases 3M made the final commercial product. In other cases 3M sold a fluorochemical to another company which then incorporated it into the final

product (e.g. carpet manufacturers). The 3M product lines that included PFOS-related fluorochemicals are described in detail in information taken from 3M Fluorochemical Use, Distribution, and Release Overview report, 1999, briefly summarized, in part, as follows:

Surface Treatments - PFOS-related chemicals were used very widely in a large number of consumer products including carpet, fabric and upholstery, apparel and leather clothing, and protective products for aftermarket and consumer applications (such as Scotchgard sprays).

3M surface treatment products have extensive aftermarket applications and are distributed through retail and commercial channels for direct treatment of upholstery, carpet, auto interiors, apparel and leather by individual consumers or professional applicators. Retail products in this category are aerosol can spray cleaners and protectors for residential use.

Paper and Packaging Protectors - PFOS-related chemicals were used widely in food packaging and paper products. 3M markets fluorochemical sizing agents to the packaging and paper industries. These products impart grease, oil and water resistance to paper and paperboard substrates. They were used for food contact applications (plates, food containers, bags and wraps), and nonfood applications (folding cartons, containers and carbon-less forms and masking papers.

Fluorochemical sizing agents are applied to paper and paperboard substrates predominantly by paper mills which treat paper fibers and, to a much lesser extent, by converters who transform paper and/or paperboard into wraps, bags or cartons for desired end-uses.

3M sold grease, oil and water repellent products for non-FDA applications which are similar in composition to its food contact products.

Performance Chemicals - Performance chemicals manufactured are sold by 3M, or incorporated by 3M customers into formulated products, for use as surfactants in a range of industrial or consumer applications. Other performance chemicals are used as intermediates from which 3M or its customers make other finished products.

Fire fighting foams are products that are sold to firefighters who mix the concentrate with water to form a foam and apply it to the fire or flammable liquid either manually or through an automated system. User categories for the foams include chemical and petroleum plants, fire departments, vessels, off-shore drilling platforms, the military, and environmental remediation companies.

3M sells surfactants to copper and gold mines to increase wetting of the sulfuric acid or cyanide that leaches the ore, enhancing the amount of metal recovery. Oil well service firms and oil companies also use these surfactants in a “well stimulation” formulation that is injected into wells to enhance oil or gas recovery.

Surfactants were sold to a variety of formulators to improve the wetting of water-based products marketed as alkaline cleaners, floor polishes, photographic film, denture cleansers and shampoos. Several of these products were marketed to consumers; some products are

also sold to janitorial and commercial cleaning services. Some of the alkaline cleaners are spray-applied and could result in inhalation or ingestion exposure.

3M supplied a non-polymeric fluorochemical to formulators of carpet spot cleaners in which the fluorochemical provides stain and soil resistance. These products are marketed to consumers in pump and aerosol cans for spray application to carpets.

3M made products used in insecticides and processed by 3M customers into active ingredients in bait stations for leaf cutter ants, pharoah ants, cornfield ants and a variety of household ants. These products are used mainly in commercial and industrial applications.

2. 3M PFC Production Facilities

3M was the dominant global producer of PFOS-related fluorochemicals. As noted above 3M has 2 plants in the U.S. (Decatur, Alabama and Cottage Grove, Minnesota) and one plant in Antwerp, Belgium where all of these 3M fluorochemicals were produced. The 3M Decatur, Alabama plant produced most of the PFOS-related fluorochemicals in the U.S. The other 3M fluorochemical manufacturing plant in the U.S. at Cottage Grove, Minnesota produced PFOA (perfluorooctanoic acid). The 3M Cottage Grove plant also made PFOS-related fluorochemicals during the 1950s and 1960s and continued to produce PFOS-related fluorochemicals after that in pilot scale projects. Fluorochemical production at the Cottage Grove plant started around 1950. As discussed above, 3M produced millions of pounds of these fluorochemicals per year; in 2000 3M produced 7.33 million pounds at its plants in the United States and Europe (Organisation for Economic Cooperation and Development report, 2002).

Following 3M's decision to terminate production of PFOS-related fluorochemicals, and PFOA, 3M changed its fluorination chemistry and reformulated its products such that they are now based on a 4-carbon fluorinated compound called perfluorobutane sulfonate (PFBS). PFBS is a four-carbon cousin of the chemical used in the old Scotchgard, and is the building block for Scotchgard's new generation fluorochemicals. 3M received EPA approval for, and is manufacturing, 18 new fluorochemicals based on this 4-carbon (C-4) PFBS compound, which serve as substitutes for the 8-carbon chain perfluorinated chemicals associated with PFOS, PFOA, etc. 3M conducted some 40 toxicity and other tests to demonstrate the relative non-toxicity of these new PFBS-based fluorochemicals. However, based on fluorocarbon compounds currently in the environment, we have some reservations with regard to the behavior and environmental impacts of PFBS-based fluorocarbons. Although PFBS is not expected to bioaccumulate, it is relatively non-biodegradable, by design, and therefore is expected to persist in the environment. Accordingly, further evaluation of PFBS environmental impacts and evaluation of long term chronic toxicity is warranted.

As noted above, 3M also terminated manufacture of PFOA (perfluorooctanoic acid), made at its Cottage Grove plant. The PFOA compound was used widely as processing aids in the production of fluoropolymers and fluoroelastomers and other surfactant uses, including manufacture of Teflon by Dupont. Following termination of production of PFOA by 3M, DuPont began making PFOA at a plant in Fayetteville, North Carolina at the end of 2002.

Most all of the current PFBS-based fluorochemicals and products produced by 3M are now manufactured at the 3M Decatur, Alabama plant. The 3M Cottage Grove plant currently produces one PFBS fluorochemical, a flame retardant. The Cottage Grove plant also continues to do some pilot scale production of PFBS fluorochemicals and other perfluorochemicals.

D. PFC Contamination in Minnesota from 3M Cottage Grove Plant

The 3M Cottage Grove plant in Minnesota is one of the 2 plants in the U.S. where the PFOS-related fluorochemicals were produced and the 3M plant that produced PFOA. As noted above, the Cottage Grove plant now produces only one perfluorochemical product based on the new PFBS based chemistry, with some pilot plant production of other PFBS based products. Although the current fluorochemical production at Cottage Grove is limited, past production of PFOS-related fluorochemicals and PFOA at the plant resulted in PFOS and PFOA fluorochemical contamination of certain sites and groundwater in Minnesota due to disposal of fluorochemical wastes. Potential areas of contamination include Mississippi River sediment and fish due to 3M wastewater discharges to the Mississippi River, leachate generated at landfills where fluorochemical wastes and 3M wastewater treatment plant sludges were deposited, and wastewater and related sludge in wastewater treatment plants receiving landfill leachates. Following are some of the sites related to 3M fluorochemical contamination in Minnesota.

1. PFC Contamination from Washington County Closed Landfill

3M disposed of fluorochemical wastes generated during production at the Cottage Grove plant at the Washington County Landfill near Lake Elmo and at the Oakdale Dump in Oakdale. The Washington County Landfill is a closed landfill which received municipal and industrial wastes from 1969 through 1975. During that period 3M deposited a variety of industrial wastes at the landfill including solvents and fluorochemical wastes. Volatile organic hydrocarbon and metals contamination of groundwater below and downgradient of the site was discovered in 1981. A pump and treat system and groundwater gradient control system was installed in 1983. The treatment consists of a spray irrigation system which strips VOCs into the atmosphere. Downgradient residential wells were also found to be contaminated at that time, and residents with wells impacted or potentially impacted from the VOCs were connected to alternate water supplies.

Groundwater PFC Contamination - Perfluorochemical compounds were detected in the groundwater monitoring system at the Washington County landfill site during 2004. This Phase I study also evaluated the groundwater contamination by perfluorochemicals at the site. PFOA was found to exceed the HBV (Health Based Value), *for adults,* established by the Minnesota Department of Health (MDH) for drinking water in several monitoring wells at the site. Residential wells downgradient of the landfill were sampled during 2004 by the MDH. Thirty two residences were sampled downgradient of the landfill in the Lake Elmo area and two residences were sampled upgradient as control wells. Sampling of the

downgradient residences were completed in June and July 2004. The results of downgradient sampling indicated that PFOA was present in 7 residential wells.

Lake Elmo Residential Well PFC Contamination - An expanded residential well monitoring program for perfluorochemical contamination "downgradient" of the landfill in the Lake Elmo area was conducted in March and April 2005 by the MDH which discovered that a number of additional residential wells were contaminated with PFOS and PFOA. PFOS was found to exceed the HBV drinking water standard of 1.0 ug/l (ppb) for PFOS at a number of wells. Expanded monitoring of residential wells has continued with a number of additional residential wells found contaminated with PFOS and PFOA. Bottled water has been provided to these residences since, and a number of activated carbon treatment systems have been installed at affected residences. Monitoring of this site is continuing. To date over 238 residential wells have been tested in the Lake Elmo area downgradient of the landfill, and 77 wells sampled show PFOS and/or PFOA contamination. 11 wells have levels of PFOS above the MDH Health-Based Value (HBV) of 1.0 ppb and 7 wells have PFOS and PFOA that, when their potential health effects are looked at in combination (Hazard Index), are above health-based exposure limits. 57 wells have either PFOS or PFOA (or both) at levels below the HBVs, and 160 wells did not show delectable PFCs. It should be noted that HBVs were developed to protect only the adult and are not necessarily protective of sensitive populations (i.e. children and pregnant women). PFCs in blood from some residents exposed to PFOS and PFOA contaminated water has been monitored by others.

2. PFC Contamination from 3M Oakdale Dump

3M disposed of fluorochemical wastes at the Oakdale Dump in the 1950s. The Oakdale Dump is a former Superfund site which has been under remediation (pump out of contaminated groundwater) for many years as a result of contamination with VOCs and other wastes deposited there by 3M and others.

PFC Contamination of Oakdale City Well Water - In December 2004 the Oakdale city well water was sampled and analyzed by the MDH which found contamination with PFOS and PFOA. The results indicated that on average less than one part per billion (ppb) of PFOS and PFOA were present in five city wells. The average levels of PFOS and PFOA in the wells were below HBVs recommended by MDH (1 ppb and 7 ppb, respectively). PFCs in blood from some residents exposed to PFOS and PFOA contaminated water has been monitored by others.

Continuing monitoring of the Oakdale city wells confirmed this contamination. The PFOS levels have increased slightly and at one well, well # 5, the PFOS level has at times exceeded the MDH Health Based Value of 1.0 ppb. Well # 5 has been taken out of service. 3M has agreed to install an activated carbon treatment system for treatment of the Oakdale city water for removal of the PFOS and PFOA contamination. The fluorochemical contamination at the Oakdale Dump is now under investigation by the MPCA. Groundwater contaminated with PFOS and other perfluorochemicals is pumped out from the remediation system at the Oakdale Dump site, and is discharged to the sewer system to the MCES Metro wastewater

treatment plant. The MPCA will evaluate the impacts of this discharge and determine if any additional pretreatment is required.

3. PFC Contamination from 3M Woodbury Disposal Site

Groundwater at a former disposal site associated with 3M activities in Woodbury, Minnesota has been found to contain levels of PFOS and related fluorochemicals. The Woodbury site consists of four disposal locations used for solid waste burial, industrial solvents and acids from 3M's Cottage Grove and Saint Paul manufacturing facilities during the 1960s. In 1996 isopropyl alcohol was discovered in a shallow well on a nearby property. A variety of hazardous substances, particularly volatile organic compounds (VOCs), were found at the site in both the soil and groundwater. A remediation system was installed at the Woodbury site consisting of four groundwater pump-out wells to limit the spread of contaminants in the groundwater. The 3M Woodbury groundwater is pumped to the 3M Cottage Grove plant for use in production processes and cooling water. Since 1992, the site has been in the Voluntary Investigation and Cleanup (VIC) Program at the Minnesota Pollution Control Agency (MPCA). In the Spring 2005, low levels of PFCs were detected in the pump-out system at the 3M Woodbury site, prompting a PFC investigation of residential wells by MDH and MPCA. Seventeen private wells located near the 3M Woodbury site were sampled in June 2005 to determine if PFCs were migrating from the disposal site in groundwater. No PFCs were detected at any of the private wells.

4. PFC Contamination from 3M Cottage Grove Plant

3M disposed of fluorochemical wastes and wastewater sludges at the 3M Cottage Grove plant which resulted in contaminated soil at several locations at the plant site. As a consequence of these practices groundwater beneath the 3M Cottage Grove site is contaminated with PFOS, PFOA, and related fluorocarbons.

Groundwater Contamination - Groundwater contamination under the 3M Cottage Grove site exceeds the recently developed MDH standard for PFOS. Groundwater under the 3M Cottage Grove site is no longer used as a drinking water source for 3M Cottage Grove employees. The MPCA Superfund Program has been overseeing site investigation and cleanup activities. Due to other contamination issues the site was added to the Permanent List of Priorities, the state Superfund List, in 1985. 3M has been conducting various investigations and response actions under a consent order with the MPCA for the Cottage Grove site since that time.

Mississippi River Contamination - Very limited past monitoring data is available for fluorochemicals present in the 3M wastewater discharge to the Mississippi River. However, it is likely that 3M discharged significant amounts of PFOA, PFOS, PFOS precursors, and related fluorochemicals from the 3M Cottage Grove wastewater system to the Mississippi River since the 1950s. Based on a January through March 2000 sample of the 3M discharge analyzed by 3M, MPCA staff calculated that up to 50,000 pounds per year of fluorochemicals may have been discharged to the river. These calculations show that at certain times in years past, during low river flow periods, the 3M discharge may have

resulted in a mixed river downstream concentration (at lock and dam # 2) of PFOS exceeding the HBV drinking water standard of 1.0 ppb. As this report discusses, the 3M discharge of PFOS and related fluorochemicals to the river has resulted in contamination of sediments and fish in the river. The limited fish numbers and species analyzed thus far indicate relatively high levels of PFOS contamination in fish livers, with one fish liver sampled in 2004 containing PFOS at a level comparable to the highest levels we are aware as described in the literature for any fish sampled worldwide. In addition, analysis of samples thus far from fish collected in October 2005 from the area downstream of the 3M discharge determined very high levels of PFOS in fish blood. The October 2005 fish blood PFOS levels found are the highest PFOS in blood of animals tested worldwide to our knowledge based on a review of the available literature.

PFC Contamination in Pine Bend Landfill (3M Disposal Site) - The 3M Disposal Site also disposed of wastewater treatment plant sludges containing PFOS, PFOA, and related fluorochemicals at certain landfills in Minnesota. At these locations the MPCA is analyzing groundwater wells and landfill-generated leachate for PFOS and related fluorochemicals. The Pine Bend Landfill received 3M sludges beginning in 1975. This study evaluated leachate, landfill gas condensate, and groundwater at the Pine Bend Landfill for 12 perfluorochemicals including PFOS and PFOA. PFOS and PFOA were found in the leachate, gas condensate, and downgradient groundwater monitoring wells at the Pine Bend Landfill site. The Pine Bend Landfill generates approximately 6.3 million gallons per year of leachate which is discharged to the MCES wastewater treatment system. The impact of the leachate containing PFOS, PFOA, and related perfluorochemicals on effluent concentrations and sludges for wastewater treatment systems receiving this leachate needs to be examined.

II. INVESTIGATION OF PERFLUOROCHEMICAL CONTAMINATION IN MINNESOTA – PHASE ONE

A. Scope of Perfluorochemical Investigation in Minnesota

This section of the report describes a phase one perfluorochemical compounds investigation in Minnesota on the environmental release and contamination issues related to a group of perfluorochemicals primarily manufactured by the Minnesota Mining and Manufacturing (3M) Company.

This MPCA perfluorochemical investigation (Phase One) was proposed and conducted in order to determine the presence and extent of contamination of perfluorochemicals in the Minnesota environment, and to initiate study of the behavior of these compounds in various environmental media. This information is essential to assess the human health and ecological impacts of perfluorochemicals in the Minnesota environment. This investigation examined contamination by PFOS, PFOA, as well as other related perfluorochemical contamination in Minnesota at selected sites including landfills, wastewater treatment facilities, the Mississippi River water and sediment, and Mississippi River fish. The study includes some of those areas and sites briefly discussed above.

B. List of Perfluorochemicals Analyzed

This phase I study included analysis for 12-14 individual perfluorochemicals which include PFOS and PFOA. This is the first comprehensive study in Minnesota to provide a complete evaluation of these individual perfluorochemicals from release sources into the Minnesota environment. Other perfluorinated substances were made and presumably disposed by 3M. They were not addressed in this evaluation phase.

Hereinafter, this report refers to perfluorochemical as PFC, and these 12-14 individual PFCs and all perfluorochemicals collectively as PFCs (perfluorochemicals). The PFCs analyzed in this study include:

1. PFBA perfluorobutanoic acid
2. PFPeA perfluoropentanoic acid
3. PFHxA perfluorohexanoic acid
4. PFHpA perfluoroheptanoic acid
5. PFOA perfluorooctanoic acid
6. PFNA perfluoronanoic acid
7. PFDA perfluorodecanoic acid
8. PFUnA perfluoroundecanoic acid
9. PFDoA perfluorododecanoic acid
10. PFTA perfluorotridecanoic acid
11. PFBS perfluorobutane sulfonate
12. PFHxS perfluorohexane sulfonate

13. PFOS perfluorooctane sulfonate
14. PFOSA perfluorooctane sulfonamide

C. PFC Contamination at the Washington County Closed Landfill

1. Scope of PFC Investigation

The Washington County Landfill is a closed landfill which received municipal and industrial wastes from 1969 through 1975. During that period 3M deposited a variety of industrial wastes at the landfill including solvents and PFC wastes. Volatile organic hydrocarbon and metals contamination of groundwater below and downgradient of the site was discovered in 1981. A pump and treat system and groundwater gradient control system was installed in 1983. The treatment consists of a spray irrigation system which strips VOCs into the atmosphere. Downgradient residential wells were also found to be contaminated and residents were placed on alternate water supplies.

PFC compounds were detected in the ground water monitoring system at the landfill site during an MPCA investigation in 2004. PFOA was found to exceed the MDH Health Based Value or drinking water standard of 7.0 ug/l (ppb) at well nest E, the treatment area where the spray irrigation system is used (TA-1), nest V and well Z. The average PFOA concentration in well E, treatment area TA-1, nest V, and well Z was 11.1 ppb, 13.5 ppb, 45.7 ppb, and 9.3 ppb, respectively. PFOA was found in the gradient control well at a concentration of 16 ppb. The presence of PFCs in the groundwater caused serious concerns by the MPCA staff who proposed to initiate a feasibility study regarding treatment of these chemicals.

This phase I investigation indicates that the groundwater is contaminated at the landfill site with several other PFCs in addition to PFOA. The concentrations of PFOS at 2.69 ppb and PFOA at 41.6 ppb exceed the HBV for drinking water established by the MDH at 1.0 ppb and 7.0 ppb, respectively. A very high concentration of PFBA (perfluorobutanoic acid) at 1170 ppb was also found in the downgradient groundwater well at the site. There is no HBV or drinking water standard established yet for PFBA. The groundwater remediation system at Washington County Landfill may need to be to be upgraded to treat these compounds. Evaluation is currently underway to determine the effectiveness of an activated carbon system to treat the groundwater.

Residential wells downgradient of the landfill were sampled by the MDH during 2004. Thirty two residences were sampled downgradient of the landfill and two residences were sampled upgradient as control wells. Sampling of the downgradient residences were completed in June and July 2004. The results of downgradient sampling indicated that PFOA was present in 7 residential wells. It should be noted that only PFOA and PFOS were selected to be analyzed in the above residential wells. Since the additive effects of all PFCs (total PFCs) are unknown, it may be prudent to analyze wells for additional PFCs. Other PFCs may be present; for example 8 other PFCs were found in the downgradient monitoring well of the landfill site in this study, including PFBA at very high levels.

An expanded residential well monitoring program for PFC contamination (only C-8 compounds: PFOS and PFOA) "downgradient" of the landfill in the Lake Elmo area was conducted in March and April 2005 by the MDH which discovered that a number of additional residential wells were contaminated with PFCs. PFOS was found to exceed the MDH HBV (health based value) or drinking water standard of 1.0 ug/l (ppb) at a number of wells. Expanded monitoring of residential wells has continued with a number of additional residential wells found contaminated with PFOS and PFOA. Bottled water has been provided to these residences since, and recently, a number of activated carbon treatment systems have been installed at affected residences. To date over 238 residential wells have been tested (only for PFOA and PFOS) in the Lake Elmo area downgradient of the landfill, and 77 wells sampled show PFOS and/or PFOA contamination. 11 wells have levels of PFOS above the MDH Health-Based Value (HBV) of 1.0 ppb and 7 wells have PFOS and PFOA that, when their potential health effects are looked at in combination (Hazard Index), are above health-based exposure limits. 57 wells have either PFOS or PFOA (or both) at levels below the HBVs, and 160 wells did not show detectable PFCs. It is important to note that the HBV for PFOA and PFOS were developed for adults only, which may not necessarily be protective of sensitive population such as children and pregnant women.

2. Sampling Strategy

The PFC sampling in Washington County Landfill was conducted to begin an initial assessment of the extent of PFC contamination in the soils and groundwater because 3M had deposited PFC wastes at this site and downgradient residential wells were found to be contaminated with PFCs. Results from this sampling study may be used to more fully characterize the extent of PFC contamination and help to evaluate if any further remedial actions are needed. This PFC investigation in Washington County Landfill evaluates 13 PFC compounds which have not been previously studied at the site. In addition to soils and groundwater, this study also evaluates the extent of PFC contamination in surface water "ponded" at the site as a result of the spray irrigation system, which may relate to any PFCs potentially released to the atmosphere.

PFC sampling conducted at the Washington County Landfill included water samples from two groundwater monitoring wells (J and V2) located at the site, water samples from surface water ponded at the site, soil (sediment) samples from the surface below ponded water, soil samples from soil borings conducted, and background soil samples from soil borings. Soil borings were completed to assess the depth of penetration or mobility of the PFCs through the landfill site, caused by water movement through the soils from the landfill spray irrigation treatment system. A soil boring was also completed upgradient of the site to determine background PFC levels.

3. Sampling Results

Studies of PFCs in landfills are very limited. Most of these studies have focused solely on the concentrations of PFCs in landfill leachates generated. The Washington County Landfill is not lined and does not have a leachate collection system. The groundwater PFC

contamination is likely to be much more significant at unlined landfills such as Washington County Landfill when compared with lined landfills with a leachate collection system.

Groundwater Contamination - The downgradient groundwater monitoring well indicates that groundwater beneath the site has been contaminated with a total of 10 PFCs, some at relatively high levels. As shown in Table 1, the total PFCs concentration was about 1280 ppb. PFBA was found at a very high level of 1,170 ppb, while PFPeA and PFHxA were found at levels of 43.1 ppb and 15.6 ppb, respectively. These lower fluorinated compounds (C-4 to C-6) are more volatile than higher fluorinated ones (C-8 to C-13), and thus to some extent can be evaporated and released to the air. The two commonly measured C-8 compounds, PFOA and PFOS were found at 41.6 ppb and 2.69 ppb, respectively. These levels again demonstrate the mobility of the PFCs traveling through the soils at this site.

Table 1- PFC levels in Groundwater at Washington County Landfill (ng/ml or ppb)

PFCs	Washington Co. Well J (upgradient well)	Washington Co. Well V2 (downgradient well)
PFBA	<0.110	1170
PFPeA	<0.0205	43.1
PFHxA	<0.0037	15.6
PFHpA	<0.0044	2.38
PFOA	<0.0027	41.6
PFNA	0.001	0.012
PFDA	<0.0015	0.006
PFUnA	<0.0009	<0.0039
PFDoA	0.002	<0.0032
PFTA	<0.0005	<0.0020
PFBS	<0.0201	1.31
PFHxS	<0.0257	1.77
PFOS	<0.0030	2.69
Total PFCs	**0.003**	**1278.468**

Ponded Water and Sediment Contamination - Samples of water "ponded" at the site, resulting in puddles ("ponds") from the spray irrigation system, contained 10 PFCs, similar to those found in the groundwater sample. As shown in Table 2 the total PFCs were calculated to be about 396-380 ppb. PFBA had the highest levels of 371-352 ppb, followed by PFOA at levels of 15.2-10.9 ppb.

Table 2 - PFC levels in Water Samples Ponded at the Site (ng/ml or ppb)

PFCs	Wash -CL-water #1	Wash-CL-water #2
PFBA	371	352
PFPeA	7.98	6.89
PFHxA	3.36	3.28
PFHpA	0.582	0.659
PFOA	10.9	15.2
PFNA	0.009	0.006
PFDA	<0.0156	0.027
PFUnA	<0.0068	0.016
PFDoA	<0.0142	0.016
PFTA	<0.0202	<0.0103
PFBS	<0.333	<0.252
PFHxS	<0.422	<0.300
PFOS	1.35	1.67
Total PFCs	**395.18**	**379.76**

Sediments (soils) collected under this "ponded" water sample also contained relatively high levels of 8 PFCs. The total PFCs were calculated at levels of 51 to 76 ppb. As shown in Table 3, PFOA had the highest levels (22.3-31.1 ppb) followed by PFBA (13.5-22.9 ppb) and PFOS (10-14.6 ppb). It should be noted that C-8 compounds (PFOA and PFOA) appear to have much higher affinity to bond to the solid phase (sediment/soil) as compared to PFBA, which has a higher affinity to partition into the aqueous phase (water). Accordingly PFBA may be more likely to be "stripped" into the atmosphere, although this would need to be evaluated further by conducting air monitoring at the site.

Table 3 - PFC levels in Soil (sediment) Samples below Ponded Water (ng/g or ppb)

PFCs	Wash-CL-sediment #1	Wash-CL-sediment #2
PFBA	13.5	22.9
PFPeA	1.27	2.64
PFHxA	2.54	3.66
PFHpA	0.669	0.858
PFOA	22.3	31.1
PFNA	<0.331	<0.350
PFDA	0.4	0.545
PFUnA	<0.317	<0.335
PFDoA	<0.315	<0.333
PFBS	<0.314	<0.332
PFHxS	0.355	<0.333
PFOS	10	14.6
PFOSA	<0.309	<0.327
Total PFCs	**51.034**	**76.303**

Soil Profile Contamination - PFC results of this study demonstrate that many PFCs have been mobilized and penetrate the soils under the site. The PFCs likely mobilized further down the

soil profile as a result of the site's groundwater treatment system. The landfill uses a pumpout system to pumpout groundwater beneath the site, contaminated with VOCs (volatile organic compounds). The groundwater removed via this pumping system is subsequently sprayed into the atmosphere above the site to volatilize, strip off, or remove the VOCs. The VOCs are transferred into the atmosphere. The VOCs in the groundwater are at levels which made this remediation technology acceptable. As a result groundwater pumped has been continually recirculated at the site, percolating back into the soils. This percolation likely accelerated the movement of PFCs through the soils.

As shown in Table 4, up to 7 PFCs were detected in the soil profiles from surface level down to the end of boring depth of 26 ft. Total PFCs were calculated for each increment ranging from 34.2-0.87 ppb. The highest total PFC levels (34.2 ppb) were found in the boring depth of 12.5 ft.

Table 4 - PFC Levels in Soil Profile (at depth increments) at Treatment Area (ng/g or ppb)

PFCs	(0-1ft)	(1-2ft)	(4.5ft)	(5.5ft)	(7.5ft)	(9.5ft)	(12.5ft)
% MOISTURE	12.5	8.6	12.1	7.69	12.3	9.31	8.6
PFBA	5.49	2.68	3.67	3.33	3.01	1.45	3.06
PFPeA	0.471	<0.209	0.328	0.375	<0.233	0.226	0.299
PFHxA	0.702	0.375	0.405	0.465	0.58	0.416	0.495
PFHpA	0.223	<0.206	<0.223	<0.203	0.247	<0.207	0.293
PFOA	10.5	3.59	2.66	8.51	5.42	4.28	21.6
PFNA	<0.230	<0.220	<0.238	<0.217	<0.245	<0.221	<0.222
PFDA	0.24	<0.212	<0.230	<0.209	<0.237	<0.214	<0.214
PFUnA	<0.220	<0.210	<0.227	<0.207	<0.234	<0.212	<0.212
PFDoA	<0.218	<0.209	<0.226	<0.206	<0.233	<0.211	<0.211
PFBS	<0.218	<0.208	<0.225	<0.205	<0.232	<0.210	<0.210
PFHxS	<0.218	<0.209	<0.226	<0.206	<0.233	<0.211	<0.211
PFOS	7.83	2.43	0.719	4.19	3.41	3.59	8.41
PFOSA	<0.214	<0.205	<0.222	<0.202	<0.228	<0.207	<0.207
Total PFCs	**25.456**	**9.075**	**7.782**	**16.87**	**12.667**	**9.962**	**34.157**

PFCs	(13.5ft)	(16ft)	(18ft)	(20ft)	(22ft)	(24ft)	(26ft)
% MOISTURE	7.57	6.92	13.8	3.07	3.42	3.54	5.99
PFBA	2.38	2.9	3.87	0.874	1.01	1.63	2.64
PFPeA	<0.219	0.291	0.427	<0.216	<0.208	<0.209	<0.209
PFHxA	0.426	0.296	0.526	<0.209	<0.202	0.233	0.387
PFHpA	0.239	<0.207	0.245	<0.212	<0.204	<0.205	<0.206
PFOA	21.7	1.89	7.94	<0.208	1.43	1.24	9.58
PFNA	<0.230	<0.221	<0.245	<0.226	<0.218	<0.219	<0.220
PFDA	<0.222	<0.214	<0.237	<0.219	<0.211	<0.211	<0.212
PFUnA	<0.220	<0.212	<0.234	<0.216	<0.209	<0.209	<0.210
PFDoA	<0.219	<0.210	<0.233	<0.215	<0.207	<0.208	<0.209
PFBS	<0.218	<0.209	<0.232	<0.214	<0.207	<0.207	<0.208
PFHxS	<0.219	<0.210	<0.233	<0.215	<0.207	<0.208	<0.209
PFOS	6.1	1.51	1.54	<0.218	<0.210	<0.211	1.48
PFOSA	<0.215	<0.206	<0.228	<0.211	<0.203	<0.204	<0.205
Total PFCs	**30.845**	**6.887**	**14.548**	**0.874**	**2.44**	**3.103**	**14.087**

PFOA and PFOS were even found at the end of boring depth of 26 ft. PFOA was found at almost all depth increments, consistent with its greater water solubility. The highest levels of PFOA were found at the depth of 12 to 14 ft (21.7), followed by PFOA at the surface level of the soil (10.5 ppb), and the deepest soil level of 26 ft. (9.6 ppb). PFBA (perfluorobutanoic acid) and PFHxA (perfluorohexanoic acid) were also found throughout the soil profile and at the terminal depth of 26 ft. The highest levels of PFBA (5.5 ppb) and PFHxA (0.7 ppb) were found at the surface level of the soil. PFPeA and PFHpA were found down to the depth 18 ft. PFDA was detected at the top surface layer of the soil. It is likely that the PFCs move through the soil in various "plugs" depending upon the concentrations in the spray water and other conditions. The presence of seven PFCs throughout the soil profile depth studied demonstrates that these compounds can be relatively mobile and contaminate groundwater at unprotected locations.

PFOS, PFOA, and PFBA were found in the background soils which may indicate these compounds "drifted" to the soils in the background area tested as a result of adherence to spray droplets (aerosols) (see Table 5). The background soils are soils sampled from an area upgradient of the groundwater direction of flow and out of the direct influence of the area where groundwater is spray irrigated. It is also possible that more volatile precursors present in the spray subsequently degraded to PFOS and/or PFOA; however, this is only a theoretical possibility that needs further investigation. It should be noted that the highest PFOA levels (4.9 ppb) were found at the deepest level of the background soil sample (8 ft.), again demonstrating its mobility.

Table 5 - PFC Levels in Background Soil Boring (ng/g or ppb)

PFCs	Background soil surface	Background Soil -4ft	Background Soil-6ft	Background Soil-8ft
% MOISTURE	12.2	4.96	19.7	4.53
PFBA	0.6	<0.217	<0.243	<0.202
PFPeA	<0.233	<0.214	<0.239	<0.200
PFHxA	<0.226	<0.208	<0.232	<0.194
PFHpA	<0.229	<0.210	<0.235	<0.196
PFOA	1.28	4.25	2.52	4.87
PFNA	<0.244	<0.224	<0.251	<0.209
PFDA	<0.236	<0.217	<0.243	<0.202
PFUnA	<0.234	<0.215	<0.240	<0.200
PFDoA	<0.232	<0.213	<0.239	<0.199
PFBS	<0.231	<0.213	<0.238	<0.198
PFHxS	<0.232	<0.213	<0.239	<0.199
PFOS	1.66	0.309	<0.242	<0.202
PFOSA	<0.228	<0.209	<0.234	<0.195
Total	**3.54**	**4.559**	**2.52**	**4.87**

4. Summary Report

- PFCs were found in the downgradient groundwater monitoring well at the site. PFOS and PFOA levels significantly exceed the MDH Health Based Values of 1.0 ppb and 7.0 ppb, respectively

- PFBA was found at a significantly high level of 1170 ppb in the groundwater of the downgradient monitoring well. An HBV or drinking water standard has not been developed for PFBA.

- Many of the PFCs have mobilized through the soils at the site, likely accelerated due to the use of the spray irrigation system.

- PFOS and PFOA were found in the depth increments tested throughout the soil boring depth to the terminal depth of 26 ft.

- PFOA appears to be more mobile as indicated by its higher concentrations at lower depths, and its concentration in background soils.

- PFOS, PFOA and PFBA were found in the soils samples of the background soil boring, suggesting that these PFCs, or PFC precursors, may have been carried in aerosol drift from the spray irrigation system.

5. Future Needs for PFC Investigation at Washington County Closed Landfill

- Spray irrigation or stripping of groundwater pumped out at any site known to contain PFCs should be reviewed with respect to impacts and transport via air.

- The technology needed for removal of PFCs from pumped out groundwater at the Washington County Landfill site should be evaluated. A system may need to be implemented for PFC removal from the groundwater pumpout, perhaps granular activated carbon.

- Extensive monitoring of the levels of PFCs in groundwater and other media, including ambient air during spray irrigation operation, should be done.

- Residents affected by the contamination have been supplied with bottled water and/or home activated carbon treatment systems. The City of Lake Elmo is constructing a new water supply system for the area.

- Analysis of wells for other PFCs should be considered, given the finding of 10 PFCs in this study in the downgradient well at the site, and the unexpected finding of a very high level for PFBA. Other products or degradation products might also be present at unexpectedly high levels. 3M also apparently made perfluoroethylcyclohexane sulfonic acid, trifluoromethylperfluorocyclohexane sulfonate, perfluoroheptane sulfonate, perfluorononane sulfonic acid, perfluoropentane sulfonic acid, perfluorocyclohexane sulfonate, which does not appear to have been monitored by anyone at any site in any study, and perfluorodecane sulfonate, which has been found at significant levels, when analyzed for in other studies in other regions.

- The substances tested for are ultimate degradation products or byproducts of many different ultimate products and intermediates that were more likely disposed than the fluorinated acids monitored for. The practicality of monitoring for such precursors should be evaluated.

- The MDH should consider development of HBVs (health base values) for PFOS and PFOA for the sensitive population (pregnant women and children). The MDH stated in its document determining the HBV values for PFOS and PFOA that the HBVs for sensitive populations, pregnant women and children, are likely 3 to 4 times more restrictive. Accordingly, the HBV for PFOS may be about 0.25 ppb, rendering additional residential wells tested to be unacceptable. Similarly, the need for evaluation of any HBVs for other PFCs found in well water should be assessed.

- PFC monitoring should be expanded in phase two of this investigation to the particulate and vapor phases of the ambient air, if spray irrigation is continued.

D. PFC Contamination at 3M Cottage Grove Wastewater Treatment Plant

1. Scope of PFC Investigation

The 3M Cottage Grove facility is a diverse facility that manufactures a number of products including organic chemicals, polymers, adhesives, thermoplastic resins, phenolic resins, fine chemicals, polyester resins, epoxy resins, urethanes, curative organic compounds, ceramic solutions, abrasives, glass beads, toners, pressure sensitive tapes, polymeric films, extrusions, automotive products, and fluorochemicals. The facility also conducts "pilot" or research operations for the development of new products. The 3M hazardous waste incinerator is located at the Cottage Grove facility and incinerates hazardous waste from other 3M plants around the U.S.

3M Cottage Grove Wastewater Treatment Plant (WWTP) - The 3M Cottage Grove wastewater treatment plant (WWTP) treats process wastewater generated from the production facilities, scrubber wastewater from the incinerator, "pilot" production wastewaters, and sanitary wastewaters. The WWTP consists of 3 separate treatment trains, phase 1, phase 2, and phase 3, with a separate treatment system for cooling water. The phase 1 system primarily treats inorganic process wastewater constituents by chemical precipitation and settling. The phase 2 system treats process wastewaters of primarily consisting of organic constituents and sanitary wastewater by an activated sludge system. The effluent from the phase 2 system is discharged to the phase 1 system and the combined phase 1 and 2 effluents are directed to a granular activated carbon treatment system prior to discharge. The phase 3 treatment system treats the 3M hazardous waste incinerator scrubber wastewaters and consists of chemical precipitation and settling. After this system the phase 3 wastewater is directed to a separate (phase 3) activated carbon system prior to discharge. The phase 1, 2 and phase 3 effluents from the activated carbon systems are discharged to the Mississippi River at a common discharge outfall, designated in the NPDES permit as SD001 (surface discharge 001).

The 3M facility uses cooling water for cooling equipment in processes at the plant. Cooling water is supplied from production wells underlying the plant and also from the 3M Woodbury groundwater remediation pump-out system (barrier well system). Groundwater is pumped out under the 3M Woodbury site in order to contain the spread of VOC (volatile organic carbons) contaminants at that site. (Some "lower level" PFC contamination has also been found in groundwater under the 3M Woodbury site). The 3M Woodbury groundwater pump-out water is piped to the 3M Cottage Grove plant cooling water system. Cooling water at the 3M plant is once-through and no treatment is required other than temperature reduction via a cooling pond and dechlorination. Some stormwater runoff water may also be directed to the cooling water retention pond. Cooling water from the 3M plant is discharged to the Mississippi River via NPDES discharge outfall SD002.

Sludge produced during the wastewater treatment processes are treated in thickeners and belt presses prior to final disposal. Final disposal of sludge generated in the phase 1 and 2 systems is disposed of at a non-hazardous waste landfill. Phase 3 sludge is incinerated and then disposed at a hazardous waste disposal facility.

3M Cottage Grove Plant NPDES Permit Requirement - As a result of PFC production at the plant since about 1950, wastewater discharged from the plant to the river likely contained relatively high levels of PFCs. This discharge of PFCs continued during the decades of perfluorochemical production at the plant. Beginning in 2000 the 3M plant began its phase-out of production of PFOA and any PFOS-related perfluorochemicals. This phase-out was completed by the end of 2002. PFC production at the plant now consists of one PFBS (perfluorobutane sulfonate) product, the 4-carbon substitute for the prior PFOS based production, and some pilot level production of PFBS based PFCs. PFOA is no longer produced. Data for PFC concentrations in the 3M discharge prior to the phase-out is very limited since 3M did not routinely monitor for these PFC compounds. Beginning in December 2002, 3M was required to routinely monitor 5 PFC compounds pursuant to the 3M Cottage Grove plant NPDES permit.

PFCs Discharge Levels to Mississippi River - 3M analyzed its discharge for 5 PFCs during a Jan-March 2000 period. This limited historical data allows some estimate of the mass of PFCs that may have been discharged prior to the production phase-out. Based on the Jan-March 2000 discharge data, which includes analysis of 5 PFC compounds, 3M could potentially have discharged about 50,000 lbs per year of PFC compounds to the Mississippi River. Calculations based solely on this Jan-March 2000 discharge concentration data using average river flows for a nominal 20 year period of calculation (using river flows during 1980 through 2000), show that the total PFC mixed river concentration (throughout the river after lock and dam # 2) could have averaged about 1880 ng/l (parts per trillion). This was for a 20 year period of calculation only, completed for the purpose of determining mixed river PFC concentrations, which assumes that PFCs were discharged to the river at similar concentrations throughout this period. This may not have been the case. It is possible that lower or even higher concentrations were discharged. Using these concentrations the mixed river concentration of the individual PFOS compound may have averaged about 550 ppt during this 20 year nominal period used for the purpose of this calculation. Based on this calculation the mixed river concentration of PFOS would have at times, during low flow

years, exceeded the recently established PFOS drinking water "standard" by the Minnesota Department of Health of 1.0 ppb (or 1000 ppt).

Groundwater PFC Contamination Beneath 3M Plant - 3M disposed of PFC tar residues, wastes, and sludges at several locations at the 3M Cottage Grove plant site in the past. As a result of this practice groundwater beneath the 3M plant was found to be contaminated with PFCs. Deeper production wells at the site, previously used as a drinking water source for plant employees, were also found to be contaminated in excess of the MDH health based value (HBV) for PFOS. The PFC contamination sites at the 3M plant are being evaluated and groundwater is being remediated, in part, by wells pumping out PFC contaminated water. PFCs contained in the plant pumpout water and production wells, along with relatively low level PFCs contained in the Woodbury pumpout water, are sources of PFCs contained in the 3M plant discharge to the river.

Granular Activated Carbon (GAC) Treatment System - In January 2004 3M completed installation and began operation of a granular activated carbon treatment system for treatment of the phase 1 and 2 wastewater, pursuant to a requirement of the 3M Cottage Grove NPDES permit, followed shortly thereafter with completion of a granular activated carbon treatment system for treatment of the phase 3 incinerator wastewater. The activated carbon systems were installed primarily to remove alkyl phenol ethoxylate compounds in the 3M discharge, which had been determined to be causing acute toxicity to aquatic organisms, and to enhance wastewater treatment in order to meet federal discharge standards. In addition, MPCA staff had been recommending installation of activated carbon treatment at the 3M plant in order to remove unknown or uncharacterized organic compounds that may be present in the 3M discharge. Operation of pilot projects at the 3M plant subjected the pre-existing treatment systems and the discharge to variable and unknown organic compound composition. These varying organic pollutants were potentially not removable, or were inadequately treated, without activated carbon treatment.

The activated carbon systems installed also serve to remove PFCs in the wastewater discharged. The activated carbon systems represent the best technology available for removal of most organic compounds, including PFCs, from wastewater effluents. Since beginning operation of the activated carbon treatment systems in January 2004 the PFC discharge concentrations have dropped, although individual PFCs in the discharge continue. The discharge levels of PFOS dropped from the pre-activated carbon treatment system levels of 103 ppb average for the period December 2002 to December 2003, to 6.6 ppb average for the period January 2004 to April 2005. This decrease represents a 94% reduction in the concentration of PFOS discharged. The other PFCs analyzed by 3M have shown the following reductions in concentrations for the same period evaluated: PFHS 5.7 ppb to 1.4 ppb – 76% reduction, PFHA 22 ppb to 10 ppb – 54% reduction, PFBS 676 ppb to 193 ppb – 71% reduction, and PFOA 83 ppb to 45 ppb – 46% reduction.

Although the activated carbon system is working well to remove PFOS at an approximate 94% removal rate, PFOA is not removed as efficiently on a consistent basis, based on PFOA discharge levels reported and comparing the periods before and after activated carbon treatment. It appears that that the activated carbon treatment system may not be as effective

in removal of carboxylic acid PFCs, although a full assessment is needed to make definitive conclusions. After PFOA and PFOS related perfluorochemical production was terminated by the end of 2002, the levels of PFOS and PFOA were expected to drop to levels lower than those that have been found in routine monitoring by 3M. It is possible that contaminated groundwater may be a contributing source of the higher than expected levels of PFOA, PFBS, and, to some extent, PFOS in the 3M discharge. This requires further assessment. The continuing levels of PFBS in the discharge may be related, in part, to the current PFBS based production at the 3M plant, although the contributions from this process to wastewater have not been determined.

2. Sampling Strategy

As part of this phase I study sampling was conducted at the 3M Cottage Grove WWTP on June 27, 2005. Samples were collected at five locations: influent wastewater to the WWTP (influent), influent to the Phase 1 and 2 granular activated carbon system (GAC influent), effluent from the Phase 1 and 2 granular activated carbon system (GAC effluent), combined effluent from Phase 1, 2, and 3 treatment systems at the parshall flume (effluent), and effluent from the cooling water system (cooling water). The 3M incinerator was out of service on the day of sampling. Therefore, the phase 3 activated carbon system was not in operation and no treated wastewater was being discharged from the phase 3 system.

As stated above, wastewater samples were obtained from various locations within the 3M Cottage Grove WWTP. A dedicated sampler, used by 3M for its influent sample collections, was used to collect the influent sample. The sampler consisted of a polypropylene sampling beaker of about 1000 ml capacity attached to a metal chain approximately 10 feet in length. The sampler was thoroughly flushed and rinsed several times before use. The GAC influent and GAC effluent samples were collected directly from sampling ports off lines that respectively feed influent and effluent to the Phase 1 and 2 granular activated carbon treatment system. The effluent sample was collected by dipping the sample containers directly into the effluent flow at the parshall flume. The cooling water sample was collected using a dedicated sampler that 3M uses to collect cooling water effluent samples. The sampler consisted of a polypropylene bucket attached to a metal chain which was lowered into the stream to collect samples. The sampler was thoroughly flushed several times before sample collection. The sample was taken directly from a sampling port off a line feeding sludge cake to the fluidized bed incinerator in operation.

All wastewater samples collected at the 3M WWTP were analyzed for 12 PFCs.

3. Sampling Results

PFC Levels from Wastewater Treatment Plant (WWTP) Influent - As shown in Table 6, the WWTP influent sample (influent wastewater to the WWTP after pH adjustment) contained detectable levels of seven of the 12 analyzed PFCs. The total PFC levels were calculated at 202,850 ppt. Of the compounds detected in the WWTP influent sample, PFBA (Pentafluorobenzoic Acid) was found at the highest concentration, 178,000 ppt. The second highest PFC was PFHxS (Perfluorohexanesulfonate) at a level of 11,000 ppt. PFOA and

PFOS were detected at 3,740 and 3,170 ppt, respectively. The other PFCs detected included PFPeA (Perfluoro-n-pentanoic acid), PFHxA (perfluorohexanoic acid), PFBS (perfluorobutane Sulfonate) at levels of 1,920 ppt, 1,720 ppt, and 3,300 ppt, respectively.

PFC Levels at Granular Activated Carbon (GAC) Influent - The GAC influent sample (influent to the Phase 1 and 2 granular activated carbon system before treatment) contained detectable levels of the same seven PFCs detected in the WWTP influent sample (Table 6). The total PFC levels were calculated at 173,110 ppt. Like the WWTP influent sample, the highest concentration detected was of PFBA at 100,000 ppt, followed by PFBS at 26100 ppt. PFOA and PFOS were detected at 7,760 and 24,800 ppt, respectively. It is important to note that the PFOS concentration in the GAC influent was greater than ten times the concentration in the treatment plant influent, and the PFBS levels were 8 times higher.

The concentration of PFOA was also higher in the GAC influent than in the WWTP influent sample. This may be due to the aerobic biodegradation of precursor PFC compounds to PFOS and PFOA by microorganisms. Biodegradation of fluorochemical precursors to PFOA and PFOS has been found to occur, as described in the literature, and may also be due to recycle of waste activated sludge. The other detected PFCs were PFPeA, PFHxA, and PFHxS at levels of 2,350 ppt, 2,100 ppt, and 10,000 ppt, respectively.

Table 6 - PFC levels in Influent and Effluent at the 3M Cottage Grove WWTP (ng/l or ppt)

PFCs	WWTP influent	GAC influent	GAC effluent	SD001 effluent	SD002 effluent
PFBA	178000	100000	58100	80600	6740
PFPeA	1920	2350	3130	9960	1110
PFHxA	1720	2100	3760	9270	1320
PFHpA	<1240	<1240	1090	2350	437
PFOA	3740	7760	1670	62400	4010
PFNA	<1330	<1330	<884	<882	<53.6
PFDA	<1280	<1280	<855	<852	<51.8
PFUnA	<1270	<1270	<847	<844	<51.3
PFDoA	<1260	<1260	<842	<839	<51.0
PFBS	3300	26100	169000	104000	3870
PFHxS	11000	10000	1160	3480	11300
PFOS	3170	24800	1330	19200	1670
PFOSA	<1240	<1240	<825	<822	<50.0
Total PFCs	**202850**	**173110**	**239240**	**291260**	**30457**

1. WWTP influent is influent wastewater to the WWTP after pH adjustment.
2. GAC influent is influent to the Phase 1 and 2 granular activated carbon system before treatment.
3. GAC effluent is effluent from the Phase 1 and 2 granular activated carbon system after treatment.
4. SD001 effluent is combined effluent from Phase 1, 2, and 3 treatment systems.
5. SD002 effluent is effluent from the cooling water system.

PFC Levels at Granular Activated Carbon (GAC) Effluent - The GAC effluent sample (effluent from the Phase 1 and 2 granular activated carbon system after treatment) contained

detectable levels of eight of the 12 analyzed PFCs (Table 6). The total PFC levels were calculated at 239,240 ppt. In addition to the seven PFCs detected in the WWTP and GAC influent samples, the GAC effluent sample contained detectable PFHpA (Perfluoroheptanoic acid) at 1,090 ppt. PFBS was detected at the highest concentration in the GAC effluent sample, at 169,000 ppt. This concentration is six times greater than the concentration of PFBS detected in the GAC influent sample. This increase through the activated carbon system is currently unexplainable, and more evaluation would be needed to understand the capability of the activated carbon systems to remove PFBS. It is possible that a time lag in sampling the influent versus effluent wastewater, due to the hydraulic retention time of the system, may account for some, but likely not all, of this increase.

PFBA was the second highest detected PFC in the GAC effluent at a level of 58,000 ppt, which represents a 48 % reduction in PFBA through the activated carbon system. PFOA and PFOS were detected in the GAC effluent sample at 1,670 ppt and 1,330 ppt, respectively. This represents a 79 % reduction in PFOA and a 95 % reduction in PFOS through the activated carbon system. The other detected PFCs were PFPeA, PFHxA, and PFHxS at relatively low levels of 3,310 ppt, 3,760 ppt, and 1,160 ppt, respectively.

PFC Levels at Treated Processed Wastewater Effluent (SD001) - The SD001 effluent sample from the combined phase 1, 2, and 3 treatment systems contained detectable levels of the same eight PFCs detected in the GAC effluent sample (Table 6). The total PFC levels were calculated at 291,260 ppt, the highest levels of all five selected influents and effluents sampling locations. Similar to the GAC effluent sample the PFC detected at the highest concentration in the combined effluent sample was PFBS at 104,000 ppt, followed with PFBA at 80,600 ppt. PFOA and PFOS were detected in the combined SD001 effluent at concentrations of 62,400 ppt and 19,200 ppt, respectively. It is important to note that these concentrations represent a significant increase in both PFOA and PFOS from the GAC effluent to the combined final effluent (SD001 effluent). No further wastewater treatment is accomplished, or required, between the activated carbon system and the SD001 final discharge. These concentration increases may be due to the retention time of the system at the final discharge polishing pond receiving the activated carbon effluent, such that the sample of water collected at the GAC effluent was not in the same "batch" of water sampled at the combined SD001 effluent. However, further study and mass balance assessment would be needed to determine the mechanism or reasons for this change. Notably, PFBS did decrease from the GAC effluent to the SD001 discharge. The other detected PFCs were PFPeA, PFHxA, PFHpA, and PFHxS at levels of 9,960 ppt, 9,270 ppt, 2,350 ppt, and 3,840 ppt, respectively.

PFC Levels at Cooling Water Effluent (SD002) - The cooling water effluent sample (SD002 effluent) contained detectable levels of the same eight PFCs detected in the GAC effluent and combined SD001 effluent samples. As shown in Table 6, the total PFC levels were calculated at 30,457 ppt. PFHxS was detected at the highest concentration in the cooling water at 11,300 ppt. PFBA had the second highest level at 6,740 ppt. PFOA and PFOS were detected in the cooling water SD002 effluent at relatively low level concentrations of 4,010 and 1,670 ppt, respectively. The other detected PFCs were PFPeA, PFHxA, PFHpA, and PFBS at relatively low levels of 1,110 ppt, 1,320 ppt, 437 ppt, and 3,870 ppt, respectively.

Effectiveness of GAC System and Evaluation of Fluorochemical Precursor Degradation

From the concentrations reported above it is evident that the granular activated carbon (GAC) system at the 3M Cottage Grove WWTP is somewhat effective at reducing the concentration of PFOA, and much more effective at reducing the concentration of PFOS in the wastewater. This is not the case for all the PFCs analyzed during this limited study. Of the 12 PFCs examined PFPeA, PFHxA, and PFBS exhibited higher concentrations in the GAC effluent samples than the GAC influent samples. Based only on this one sampling event, it appears that the granular activated carbon (GAC) system has varied effectiveness in removing individual PFCs from wastewater. Understanding the fate of PFCs subject to granular activated carbon systems is an area that would require further study.

As previously discussed, the concentration of PFOS and PFOA in the GAC influent samples were higher than the levels detected in the influent to the plant (WWTP influent). This is consistent with the observations of Schulz et al (2005) during their study of wastewater treatment influent and effluent PFC levels at 9 U.S. WWTPs. This study found that in 9 out of 10 plants sampled, at least one class of PFCs showed an increase in the effluent as compared to the influent concentrations. One mechanism for an increase in PFCs in the effluent versus the influent is degradation of PFC precursor compounds in the treatment system to PFOS, PFOA, and other PFCs.

Higher concentrations of PFCs in the effluent may be due, in part, to the recycle of waste activated sludge solids containing adsorbed PFCs. Recycling a portion of the waste stream within the plant may promote biological degradation of parent fluorochemicals into the chemicals analyzed in this study and may explain part of the increase in effluent (GAC influent in this case) versus influent concentrations. Fluorochemical telomer alcohols, if present, have been found to biodegrade to PFOA when exposed to wastewater aerobic microbes. Understanding the formation of PFCs in wastewater treatment unit operations, and evaluation of fluorochemical precursor biodegradation mechanisms is an area that would require further research.

Current Mass of PFCs Discharged from 3M Plant via SD001 and SD002

Based on the sample results of this study, the mass of total PFCs currently discharged by 3M from its treated process wastewater to the Mississippi River, using a nominal flow rate of 3.5 million gallons per day (MGD) is about 8.5 lbs/day, or an annual rate of 3100 lbs/year. Based on this study's samples, the mass of total PFCs discharged from the cooling water discharge at SD0002 to the Mississippi River, using a nominal flow rate of about 4 MGD, is about 1.0 lbs/day, or an annual rate of 365 lbs/year. Based on this study's samples, the total PFCs currently discharged from the 3M plant to the Mississippi River is about 3465 lbs/year. Note that this mass calculation does not include any PFCs discharged from the incinerator wastewater system, out of service for maintenance during this sampling.

4. Summary Report

- Eight of the 12 PFCs analyzed in this study were detected and quantified in the activated carbon effluent and discharge, and the cooling water discharge, to the Mississippi River.

- PFOS was being removed efficiently through the activated carbon system at about 95%, based on this one sampling event

- PFOA was being removed through the activated carbon system at about 79% based on this one sampling event.

- The GAC system may be somewhat less effective, or less consistent, in removal of carboxylic acid PFCs.

- PFBS remains in the discharge at relatively high levels. It is uncertain if this is related to the current production of one PFBS product and some pilot level production. The efficiency for removal of PFBS through the system needs to be evaluated.

- The total PFC concentration discharged to the river from this sampling is 321,730 ppt, which includes 291,260 ppt from effluent of the phase 1, 2 activated carbon system and 30,460 ppt from the cooling water discharge. The total estimated PFCs discharged to the river, based on this study's sampling of the 3M discharges, is about 3465 lbs/year.

- PFHxS (perfluorohexane sulfonate) was found at an unexpected level of 11,300 ppt in the cooling water discharge.

5. Future Need for PFC Investigation at 3M Cottage Grove WWTP

- A better understanding of the fate and transport of PFCs, in particular PFOS and PFOA, within biological wastewater treatment plants would be useful.

- Further review of available research and understanding of the potential biodegradation pathways of PFCs in wastewater treatment processes is needed.

- PFBA, found at relatively high concentrations in our study, should be tested for in routine monthly monitoring by 3M. Monitoring of PFBA is not currently required by the NPDES permit.

- The impact of the discharge of any groundwater pump-out water from the 3M site and discharged to the cooling water system should be evaluated. The need for activated carbon treatment of cooling water containing PFCs, currently discharged to the river, should be assessed.

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- Development of discharge standards for PFOS, PFOA, and perhaps other PFCs is needed determine the acceptable discharge concentrations for these contaminants.

- The continuing presence and origin of PFOS, PFOA, and other PFCs related to prior production processes, now phased-out, should be assessed.

- Further evaluations should be completed to understand the sources of all PFCs introduced to the wastewater treatment plant, and mass balance assessments should be done to allow a clearer understanding of the removal efficiency of the individual PFC compounds.

- The contribution of PFCs from the phase 3 incinerator activated carbon system needs to be assessed. This system was out of service during this sampling.

- A complete assessment should be completed by 3M to determine the efficiency for removal for all individual PFC compounds through the activated carbon treatment system.

- The need to analyze for other PFCs that could be present should be discussed and evaluated.

E. PFC Contamination at Pine Bend Landfill

1. Scope of PFC Investigation

PFC sampling was conducted at the Pine Bend Landfill on April 27, 2005. The Pine Bend Landfill received wastewater sludges from the 3M Cottage Grove plant beginning in about 1975. 3M wastewater sludges deposited were generated from the 3M plant's phase 1 and 2 wastewater treatment system and would have contained PFCs. The extent of PFC concentrations in the 3M sludges deposited at the Pine Bend Landfill is unknown since 3M did not monitor PFCs in its sludges.

The Pine Bend Landfill site is located in Inver Grove Heights, Dakota County, Minnesota, and is the largest open landfill in Minnesota. The active landfill encompasses 220 acres, 52 of which are lined. The landfill is an operating, mixed-municipal solid waste facility. The site was first issued a permit to operate by the MPCA on September 7, 1971. The landfill has both unlined and lined portions. The unlined portions of the landfill received final cover during 1995-1996.

Areas of the landfill that are lined use a liner consisting of 2 ft. of compacted clay and a 60 mil synthetic liner. The liner system is overlaid with a 1 ft sand drainage layer. The drainage layer serves to collect and transport leachate that is generated in the solid waste. Leachate is generated and collected from both lined and unlined areas. The leachate collection system includes 10,014 liner feet of pipe. The facility has the capacity to store up to 121,000 gallons of leachate at the site. Leachate is stored in 2 tanks, the east and west storage tanks. Leachate is transported to MCES wastewater treatment system for treatment. Finished areas of the landfill are capped with at least 1 ft buffer soils, a 40 mil synthetic liner, a 6 inch drainage layer, 12 inches of general soils, and 6 inches of topsoil.

The landfill has an active gas collection system which includes 150 extraction wells and 36,500 linear feet of gas collection piping. Landfill gas is tied into a gas-to-energy conversion plant, and is used for electrical energy production, with an output of up to 13.8 megawatts. Landfill gas collection produces a condensate which is transported and treated at the MCES wastewater treatment system.

Groundwater under and near the landfill is monitored through a system of 56 groundwater monitoring wells. Four stormwater retention ponds are also maintained at the site for collection and treatment of stormwater runoff.

2. Sampling Strategy

Because of the active disposal of 3M sludges at the landfill containing PFCs, this study was done to determine the extent of PFC concentrations in leachate generated at the landfill, to determine the levels of PFCs, if any, in groundwater monitoring wells at the site, and to determine the levels of PFCs is gas condensate generated at the site. This study provides an initial assessment of the extent of PFC levels in the leachate, and the mass loadings of PFCs in leachate directed to the MCES wastewater treatment plant.

The gas condensate sample was collected since it may offer some insight into the potential levels of PFCs contained in the recovered gas and potentially discharged to the atmosphere. No (air) gas emission sample was available or collected.

Leachate samples were collected from east and west leachate storage tanks since they represent the total collected leachate from the landfill leachate collection system. Leachate was also collected from the dual landfill gas and leachate extraction wells. Samples were taken from the #15 unlined and #219 lined areas. The gas condensate sample was collected from the landfill gas collection system. Water samples were obtained from groundwater monitoring wells at the site; wells 11A and 26 were sampled. Well 11A is an upgradient well at the site that has not demonstrated contamination of previously analyzed parameters. Well 26 is a downgradient well that demonstrates contamination by previously analyzed parameters.

All samples were analyzed for the 12 PFCs.

3. Sampling Results

PFC Levels in the Leachates - Sampling demonstrates that 10 PFCs are contained in the leachate. As shown in Table 7, PFOA was found in the highest concentrations of any PFCs at an average of 61.65 ppb, consistent with its apparent greater mobility through solid matrices. PFHxA, a 6 carbon PFC carboxylic acid similar to the 8 carbon PFOA, was found in the next highest concentration at an average of 24.95 ppb, which may be also related to greater mobility, particularly in the landfill's more acidic environment. PFOS was found at an average of 19.79 ppb in the leachate.

Table 7 - Sampling Results in Leachate and Gas Condensate Samples (ng/ml or ppb)

PFCs	West tank	East tank	West & East tank Average	#15 Unlined	# 219 Lined	Gas Condensate
PFBA	1.62	2.2	1.91	1.4	1.6	4.57
PFPeA	7.71	5.02	6.37	9.23	2.71	5.48
PFHxA	21.6	28.9	24.95	16.9	13.1	37.9
PFHpA	7.5	14.7	11.10	4.27	3.99	15.1
PFOA	41.5	81.8	61.65	29.8	14.2	83.8
PFNA	0.381	0.884	0.63	0.235	0.243	0.788
PFDA	0.109	0.335	0.22	0.07	<0.0420	0.214
PFUnA	<0.0483	0.053	0.053	<0.0475	<0.0433	0.056
PFDoA	<0.0459	<0.0455	<0.0455	0.278	<0.0411	0.125
PFBS	2.57	4.78	3.68	1.89	1.82	6.3
PFHxS	4.28	7.44	5.86	2.18	4.39	9.48
PFOS	8.18	31.4	19.79	4.04	3.14	29.9
Total PFCs	**95.45**	**177.512**	**136.16**	**70.293**	**45.193**	**193.713**

There is very limited data available to date for studies of PFCs in landfill leachates. The 3M Multi-City Study (2001) analyzed 3 PFCs, PFOS, PFOA, and FOSA (perfluorooctane sulfonamide), in landfill leachates at 4 of the 5 cities sampled in this study. The highest levels were found in landfill leachate from the Decatur, Alabama Morgan County Landfill with PFOS at 52.7 ppb, PFOA at 47.5 ppb, and FOSA at .25 ppb. The 3M fluorochemical production plant in Decatur, Alabama disposed of its wastewater treatment plant sludge at the Morgan County, Alabama landfill until 1998. (Leachate from the Morgan County, Alabama is sent to the Decatur, Alabama wastewater treatment plant.) PFOS was not detected in 3 of the cities studied, and at less than 1.0 ppb in one city. PFOA was not detected in 2 of the cities studied and at less than 1.0 ppb in 2 cities studied. FOSA was no detected in any cities in this study other than Decatur, Alabama. (Note that FOSA was not analyzed in this phase I MPCA study).

A study by Berger et al, “Perfluorinated Alkylated Substances in the European Nordic Environment” conducted limited landfill leachate analyses for PFCs. This study found a median level of PFOA in landfill effluent (leachate) at 0.3 ppb and a median level of PFOS in landfill effluent (leachate) at 0.66 ppb. The sum of PFCs analyzed in landfill leachate in this study was 1.54 ppb.

The sources of the PFCs in the Pine Bend Landfill may not be wholly originated from the 3M sludge. Based on review of the limited studies in the literature and PFCs in leachates determined at other landfills by the MPCA, however, it appears that the primary source of PFCs in the Pine Bend Landfill leachate is related to the deposition of the 3M sludge and not consumer products containing PFCs. The Pine Bend Landfill leachate contains relatively high levels of PFCs comparable to the Decatur, Alabama landfill leachate which received 3M sludge from the 3M fluorochemical plant in Decatur.

PFC Levels in Gas Condensate - There is a lack of information in the literature available for PFCs in gas condensates from municipal mixed waste landfills. Gas condensate is common at landfills which generate and collect gas, and is derived from the condensation of water vapor in the gas. Landfill gas is typically combusted and energy may be captured from this combustion. Gas condensate is typically discharged and treated at the same source as the landfill leachate generated. In this case gas condensate is collected in tanks, and subsequently transported and treated at the MCES wastewater treatment plant. This phase I study is apparently the first study that has analyzed landfill gas condensate for PFCs. As shown in Table 7, gas condensate in this study contained relatively high levels of PFCs with PFOA at 75.3 ppb, PFHxA at 35.9 ppb, and PFOS at 26.4 ppb. No samples were analyzed for PFCs in the gas emitted to the atmosphere from the gas to energy system at the landfill. It is possible that some PFCs may be emitted into the atmosphere given their presence at relatively high concentrations in the gas condensate. However, further study would be required to determine if any PFC air emissions occur.

The Pine Bend Landfill leachate is transported and treated at the MCES wastewater treatment plant. The landfill generates an average of about 6.23 million gallons per year of leachate requiring treatment. Based on the average total PFCs in leachate determined in this study, this represents about 7.14 lbs/year of PFCs, or about 0.02 lbs/day of PFCs directed to the MCES wastewater treatment plant for treatment. As determined in this phase I study at the Metro wastewater treatment plant, the total mass of PFCs in the influent to the MCES wastewater treatment plant is about 0.217 lbs/day. Although based on limited analysis, the contribution of .02 lbs/day of PFCs from the Pine Bend Landfill leachate would represent about 10 % of the PFC loading to the MCES plant. This assessment is complicated by PFC chemistry since the MCES plant PFC influent loading calculation, as well as the Pine bend Landfill leachate PFC loading, does not include analysis for precursor PFCs in the influent MCES wastewater. These PFC precursors, not analyzed, may later degrade through the treatment plant into non-biodegradable PFOS and PFOA.

PFC Levels in Groundwater - Groundwater samples at the site (upgradient well #11A and downgradient well #26) demonstrate that PFCs have entered the groundwater (Table 8). Although PFCs are present in groundwater (even in the upgradient well # 11A), the levels found are well below the applicable HBVs (health based values) or drinking water standards for PFOS and PFOA.

Table 8 - Water Samples from Groundwater Monitoring Wells (ng/ml, or ppb)

PFCs	Well #11 A) (upgradient well)	Well # 26 (downgradient well)
PFBA	0.006	4.97
PFPeA	<0.0041	1.39
PFHxA	<0.0041	1.18
PFHpA	<0.0042	0.317
PFOA	0.008	1.6
PFNA	<0.0042	<0.0043
PFDA	<0.0040	<0.0041
PFUnA	<0.0042	<0.0042
PFDoA	<0.0040	<0.0040
PFBS	<0.0023	0.069
PFHxS	<0.0044	0.051
PFOS	<0.0043	0.114
Total PFCs	**0.014**	**9.691**

4. Summary Report

- There is very limited information in the literature available for PFCs contained in landfill leachates.
- The Pine Bend Landfill leachate contains PFCs at relatively high levels, comparable to those found at a Decatur, Alabama landfill that also received wastewater sludges containing PFCs.
- Based on very limited data, PFCs in the Pine Bend Landfill leachate represent about 10 % of the total PFC mass load to the MCES wastewater treatment plant.
- This is the only known study which has evaluated PFCs in condensates from gas generated at landfills. Analysis of condensate of gas generated at the Pine Bend Landfill contains relatively high levels of PFCs.
- Analysis of air emitted from combustion of landfill gas for PFCs was not completed in this study.

5. Future Need for PFC Investigation at Pine Bend Landfill

- Gas emitted from the gas to energy system should be analyzed for PFCs.
- Groundwater should continue to be periodically monitored for PFCs.
- Further sampling and a mass balance assessment should be developed to assess the loading of leachates containing PFCs on wastewater treatment plants receiving these

leachates, and whether this poses an acceptable impact with respect to wastewater treatment plant effluents and sludges generated.

F. PFC Contamination at MCES Metro Wastewater Treatment Plant

1. Scope of PFC Investigation

The Metropolitan Council of Environmental Services (MCES) main metro wastewater treatment plant (metro WWTP) located in St. Paul, Minnesota, is one of the largest wastewater treatment plants in the U.S. and treats an average of 215 million gallons per day (MGD) of wastewater from approximately 62 communities and 800 industries. The metro WWTP treats about 75% of the wastewater generated in the metro region. The plant has an average treatment capacity of 251 MGD. The facility utilizes an activated-sludge process for treating wastewater to an advanced secondary treatment level prior to discharge to the Mississippi River. High levels of ammonia and conventional pollutants are removed during the critical summer period. Biological phosphorus is also removed. Sludge generated is processed by thickening, chemical and/or thermal conditioning and high pressure or centrifugal dewatering prior to incineration. Ash from incineration is transferred off-site. Energy recovered as steam in the waste-heat boilers is used to heat buildings, to thermally condition sludge, or to power steam turbines. The metro WWTP discharges to the Mississippi River.

As part of this multi-media Phase I PFC study sampling was conducted at the metro WWTP on April 25, 2005. Samples were collected at five locations within the WWTP: influent wastewater after the primary screens (influent), final treated effluent prior to disinfection (effluent), primary sludge solids, secondary sludge solids, and dewatered sludge (biosolids) prior to incineration.

PFC sampling was done at the metro WWTP to ascertain levels of PFCs at a municipal WWTP where, although specific PFC production processes are not discharged to the system, PFCs contained in some products or wastes from domestic and industrial sources may be introduced into the sewer system. At least 2 instances of discrete PFC industrial contributions to Metro WWTP are known. Leachate generated at the Pine Bend Landfill and other landfills is transported to the metro WWTP for disposal and treatment. The Pine Bend Landfill leachate has been found to contain PFCs pursuant to this study, and therefore contributes PFCs to the metro WWTP. In addition, the Oakdale Dump groundwater remediation pumpout system contains elevated levels of PFCs and is discharged to the Metro sewer system and wastewater treatment plant. This study was also completed to determine the concentration of PFCs in sludge generated from municipal wastewater treatment.

2. PFCs Found in Wastewater Discharges in Other Studies

Several studies have been done on the pervasiveness of PFCs in wastewater discharges. Studies done in the U.S. and in other countries have documented high PFC concentration

directly downstream of the effluent discharge from industrial wastewater treatment facilities associated with a PFC production facility. Fewer studies have focused on the levels of PFCs discharged from municipally owned treatment works. At least one study identified comparatively high concentrations of PFOS and PFOA in the effluent and sludge from wastewater treatment plants located in municipalities where PFC production/manufacturing facilities were located.

A study by Saito et al, "Perfluorooctanoate and Perfluorooctane Sulfonate Concentrations in Surface Water in Japan", found PFOA in samples collected at the mouth of the Ai River, the location of the Aigawa Ryuiki industrial wastewater disposal site at a level of 67,000 ng/l (ppt). The 67,000 ppt level in the mouth of the Ai River is consistent with PFOA levels determined by 3M at times in monitoring their Cottage Grove wastewater treatment plant discharge.

In 2001 3M published the results of a "Multi-City Study" which analyzed PFOS, PFOA, and FOSA (n-alkylperfluorooctanesulfonamide) in a variety of media including Publicly Owned Treatment Works (POTW) effluent and POTW sludge (3M Multi-City Study). The 3M Multi-City Study looked at POTWs in four cities known to have a PFC manufacturing facility (Decatur, Alabama) or industrial use or supply chain use of PFCs (Mobile, Alabama; Columbus, Georgia; and Pensacola, Florida) and two cities of similar geographic location that did not have an industrial source of PFCs contributing to a POTW (Cleveland, Tennessee and Port Lucie, Florida). The highest concentrations of the PFCs analyzed were observed in samples from the POTW effluent and sludge in Decatur, Alabama. Decatur is one of the two 3M manufacturing facilities in the U.S that produces PFCs. POTW effluent from Decatur contained PFOS of up to 5290 ppt, PFOA up to 2420 ppt, and FOSA at 56 ppt. The wastewater sludge from the Decatur POTW contained PFOS, PFOA, and FSOA concentrations up to 2,840, 244, and 107 ppb (parts per billion) respectively.

The industrial sources of PFCs in Columbus, Georgia; Mobile, Alabama; and Pensacola, Florida are, respectively, various textile industries, a paper mill, and a carpet manufacturing facility. These industries used 3M PFCs in the manufacturing processes for their products. PFOS was detected in the effluent from POTWs in these cities at levels between 41 and 959 ppt. PFOA was detected in the effluent from these facilities at levels between 67 and 147 ppt. FOSA was detected in the effluent from the Columbus POTW at a concentration of 85 ppt, and was detected below the quantifiable level in the effluent samples from Mobile and Pensacola. The wastewater sludge sampled at these facilities contained PFOS at concentrations ranging from 57.7 to 159 ppb. PFOA was detected in the sludge from the Columbus and Pensacola POTWs at levels between 2.4 and 16.5 ppb. PFOA was not detected at a quantifiable level in the effluent or sludge from the Mobile POTW. FOSA was detected in the sludge from Columbus and Pensacola at concentrations between 1.27 and 43.4 ppb and below the quantifiable level in the effluent from the Mobile POTW.

Wastewater effluent from the POTW in Cleveland, Tennessee (the city that was used as the non-PFC producing geographic equivalent to Decatur) had PFOS concentrations up to 454 ppt and PFOA concentrations up to 674 ppt. FOSA was detected, but below the quantifiable level in the effluent from the Cleveland POTW. The wastewater sludge from the Cleveland

POTW contained PFOS, PFOA, and FOSA respectively, at concentrations up to 130, 3.11, and 1.7 ppb. The wastewater effluent from the POTW located in the other "control" city in the study, Port St. Lucie, Florida, contained PFOS at concentrations between 48 and 486 ppt and PFOA between 40 and 44 ppt. Sludge from this facility had levels of PFOS between 60.2 and 62.9 ppb, and PFOA was below the quantifiable level.

The publication by Berger et al, "Perfluorinated Alkylated Substances (PFAS) in the European Nordic Environment" examined sediment, sewage sludge, water, and biota from participating Nordic countries and found PFCs in wastewater effluents at levels in the range of 20 ppt. The study found high variability in the concentration of PFAS in sewage sludge, with results ranging from 0.15 ppb in a sample from a Finnish POTW to 3.8 ppb in a sample from a Swedish wastewater treatment plant. Berger et al found PFOS and PFOA to be the dominating perfluorochemical in sewage sludge.

PFOS, PFOA, and related PFCs may have been discharged directly from wastewater treatment plants associated with the industrial production facilities, such as paper mills or textile mills, or indirectly from municipally owned plants that receive waste streams from any number industries including carpets producers, paper mills, textile factories, or producers of other fire resistant materials. As part of his research in 2002 on "Biological and Chemical Conversion of Nylon 6, 6 for Remediation and Recovery", Mark Eiteman of the University of Georgia found that more than four billion pounds of pre and post consumer carpet waste enter the municipal waste stream (solid waste) each year. Even though the presence of PFCs in industrial and municipal wastewater treatment plants has been studied, very little is known about the fate and transport of PFCs that enter municipal wastewater treatment plants by other routes, such as mixed source waste streams.

As a result of extensive use of PFCs in consumer products, these PFCs may be released to municipal wastewater treatment plants via domestic wastewater. In a study by Melissa Schultz et al, 2005, of Oregon State University, effluents and influents at 10 U.S. wastewater treatment plants in the U.S. were analyzed to better understand the behavior of fluorochemicals during wastewater treatment. Schulz found PFCs in all of the wastewater influents and effluents of these plants, and each wastewater plant exhibited a "fingerprint" of PFCs, despite similar treatment processes. This study found that in 9 out of 10 plants sampled, at least one class of PFCs showed an increase in the effluent as compared to the influent concentrations. One mechanism for an increase in PFCs in the effluent versus the influent is possible degradation of PFC precursor compounds in the treatment system to PFOS, PFOA, and other PFCs. This study demonstrates that wastewater treatment plant effluents are a potential point source of PFCs to the environment.

According to the 3M Multi-City Study PFOS readily adsorbs to soil/sediment/sludge matrices and due to the acidic nature of PFOS, once adsorbed, it forms strong bonds with sludge particles and does not readily desorb. This chemical interaction or partitioning to solids in wastewaters is typical of many organic contaminants and may explain the higher levels of PFOS in wastewater sludge, compared to the concentration of PFOS in the wastewater at the same plant.

Telomer alcohols are polyfluorinated compounds that are primarily used as an intermediate in the production of fluorinated surfactants and polymers, used widely in textile, paper, and carpet industries. A paper published by Lange in 2002 reported that fluorochemical telomer alcohols biodegrade to PFOA when exposed to municipal wastewater treatment sludge. This biodegradation pathway as well as others yet-to-be-documented may help explain the detection of PFOA in municipal wastewater sludge in POTWs without a direct discharge from a PFOA production source. Another paper by Dinglasan et al (2005) described a study which demonstrates the biodegradation of telomer alcohols into PFOA.

It is likely that a number of PFC compounds present in consumer products degrade to PFOS and PFOA in wastewater treatment plants, and therefore are a source of PFOS and PFOA in wastewater treatment plant effluents. A paper by Rhoads et al (2005) describes at study in the microbial transformation of N-ethyl-N-(2-hydroxyethyl) perfluorooctanesulfonamide (N-EtFOSE). N-EtFOSE was used in oil and water repellant coatings for paper and packaging products (foods). N-EtFOSE was exposed to microbial activity by activated sludge wastewater cultures to determine if it biodegrades, and into what compounds. This study found that N-EtFOSE was degraded by microbial aerobic transformation to the eventual stable end products of PFOS and PFOA.

3. Sampling Strategy

As previously stated, wastewater samples and sludge samples were obtained from various locations within the metro WWTP. A portable sampler, used by MCES for its sample collections, was used to collect influent and effluent water samples. Primary and secondary sludge samples were collected at the sludge processing building. Primary sludge was taken directly from a line off the primary sludge underflow and contained about 5-6% solids. Secondary sludge was taken directly from the dissolved air flotation thickener and contained about 3-4% solids. Samples were collected directly into the sample containers. The biosolids sample was collected from the incinerator building. The biosolids sample contained about 35% solids.

All wastewater and sludge samples collected at the metro WWTP were analyzed for 12 PFCs.

4. Sampling Results

PFC Levels in Influent and Effluent of Metro WWTP - As previously noted, wastewater samples in this study were obtained from the metro WWTP influent after primary screens (influent) and the effluent prior to disinfection (effluent).

The influent sample contained detectable levels five of the 12 analyzed PFCs. Of the compounds detected in the influent sample PFOS and PFOA were found at the highest concentrations. The influent sample contained 53 ppt PFOS and 46 ppt PFOA. PFPeA (Perfluoro-n-pentanoic acid), PFHxA (perfluorohexanoic acid), and PFHxS (perfluorohexane sulfonate) were detected in the influent at levels ranging from 6 to 15 ppt (Table 9).

Table 9 - PFC Levels in Influent and Effluent of Metro Wastewater Treatment Plant (ng/l or ppt)

PFCs	Metro Influent	Metro Effluent
PFPeA	6, 12	14
PFHxA	10,15	22
PFHpA	<4.3	7
PFOA	46	78
PFNA	<4.3	<4.2
PFDA	<4.1	<4.0
PFUnA	<4.2	<4.2
PFDoA	<4.0	<3.9
PFBS	<2.4	<2.3
PFHxS	<4.4, 7	<4.4
PFOS	53	81
Total PFCs	121	202

Similar to the influent sample, the effluent sample contained detectable levels of five of the 12 analyzed PFCs. Four of the five PFCs detected in the influent sample were also detected in the effluent sample. PFHxS was detected in the influent sample but not in the effluent sample, while PFHpA (perfluoroheptanoic acid) was detected in the effluent sample but not the influent sample. These compounds were detected in the respective samples at 7 ppt.

PFOS and PFOA were detected at the highest concentrations of the five PFCs detected in the effluent sample. The effluent contained PFOS and PFOA at 81 and 78 ppt, respectively. The concentrations of PFOS at 81 ppt and PFOA at 78 ppt observed in the effluent at the metro WWTP are on the same order of magnitude as those seen in the 3M Multi-City Study at all of the POTWs except the Decatur, Alabama plant, which had PFOS effluent levels up to 5290 ppt and PFOA effluent levels up to 2420 ppt.

All of the PFCs were detected at higher concentrations in samples from the effluent than from the influent. This result is consistent with the observations of Schulz et al (2005) during their study of wastewater treatment influent and effluent PFC levels at 9 U.S. WWTPs. As discussed above higher levels of PFOS and PFOA in the effluent versus influent may be explained, in part, by degradation of precursor perfluorochemicals such as N-EtFOSE into PFOS and PFOA. Higher concentrations of PFCs in the Metro effluent may also be due, in part, to the retention of solids in the treatment system, where recycling a portion of the waste stream within the plant promotes biological degradation of precursor fluorochemicals into the chemicals analyzed in this study. The formation of PFCs in wastewater treatment unit operations and the evaluation of other potential PFC biodegradation mechanisms is an area that requires further research.

Based on this study's sample results the total mass of PFCs discharged from the MCES Metro wastewater treatment plant to the Mississippi River is about 0.362 lbs/day, using a nominal discharge flow rate of 215 million gallons per day, which calculates to an annual mass discharge of about 132 lbs/year.

PFC Levels in Sludges of Metro WWTP - In this study sludge samples were obtained from the metro WWTP primary sludge solids, the secondary sludge solids, and the dewatered sludge prior to incineration (biosolids). As previously noted, primary sludge contained between 5-6% solids, secondary sludge contained 3-4% solids, and the biosolids contained approximately 35% solids. Percent solid is a measure of the water content. For example 3% solid indicates that the sample contains 97% water.

Table 10 - PFC Levels in Sludges of at Metro Wastewater Treatment Plant (ng/g dry weight basis or ppb)

Sample ID	Primary Sludge	Secondary Sludge	Biosolid
PFHxA	2.37	4.09	3.65
PFHpA	<0.863	2.21	<0.492
PFOA	3.79	21.5	11.1
PFNA	1.92	10.4	5.63
PFDA	3.34	39.5	17
PFHxS	<0.876	10.3	6.35
PFOS	25.9	309	79.7
Total PFCs	**37.32**	**397**	**123.43**

As shown in Table 10, five PFCs were detected in the primary sludge sample. PFOS and PFOA were detected at 25.9 and 3.79 ppb, respectively, with other PFCs at less than detectable levels.

The sample from the secondary sludge had detectable levels of seven PFCs. PFOS was detected at a concentration of 309 ppb, PFOA was detected at a concentration of 21.5 ppb, PFDA at 39.5 ppb, PFUnA at 22.3 ppb, PFDoA at 25.8 ppb, PFHxS at 10.3 ppb, and PFNA at 10.4 ppb. Other PFCs were detected at levels from non-detect to 4.09 ppb (Table 10).

Biosolids from the metro WWTP were found to contain PFOS at 79.7 ppb, PFOA at 11.1 ppb, PFDA at 17 ppb, PFBS at 8.41 ppb, PFHxS at 6.35 ppb, PFNA at 5.63 ppb with other PFCs at levels less than 5 ppb (Table 10).

The concentrations of PFOS observed in the secondary sludge and biosolid samples collected at the metro WWTP are comparable to the levels of those compounds seen in sewage sludge collected as part of the 3M Multi-City Study at all of the POTWs, except the Decatur, Alabama plant. The concentration of PFOS in the secondary sludge from the metro WWTP, 309 ppb, is slightly higher than the levels detected in the sludge from Cleveland, Mobile, Columbus, Pensacola, and Port St. Lucie POTWs, 116, 60, 159, 125, and 62.9 ppb, respectively, and less than the level of PFOS at the Decatur POTW, 3120 ppb. Unfortunately the exact sludge sampling location within the POTWs included in the Multi-City Study is not known, however, it is assumed that samples represent secondary sludge or biosolids.

The levels of PFCs in sewage sludge at the metro WWTP observed during this study are higher than those reported by Berger et al in the European Nordic Environment study. Berger et al found high variability in the concentration of PFAS in sewage sludge with results ranging from 0.15 ppb in a sample from a Finnish POTW to 3.8 ppb in a sample from a Swedish treatment plant. The finding of higher concentrations of PFOS and PFOA in the sewage sludge versus wastewater at the metro WWTP is supported by the findings of Berger et al. Berger et al found PFOS and PFOA to be the dominating PFAS compounds in sewage sludge and found PFCs at ppb levels in sewage sludge, while the highest concentration in wastewater observed in that study was 20 ppt.

The relatively higher concentrations of PFCs found in the Metro secondary sludge versus those found in other studies for plants not exposed to PFC industrial contributions may be explained, in part, by local PFC contributions (landfill leachates containing PFCs and Oakdale Dump pumpout discharge). However, this is based on very limited data and more evaluation and mass balance calculations would be required to determine whether these sources have any significant impact on the Metro wastewater treatment plant sludge PFC concentrations.

The higher concentrations of PFCs in the samples from the secondary sludge versus the primary sludge at the metro WWTP is consistent with efficient design and operation of the treatment plant. Primary sludge predominately consists of inorganic solids and larger particles that readily settle out due to gravitational forces, while secondary sludge is generally characterized by more organic material. The secondary sludge or "waste activated sludge" is collected from the activated sludge basin which is designed to significantly reduce the organic load through the treatment plant. Additionally, as waste activated sludge is regularly recycled in a treatment plant, it makes sense that secondary sludge would exhibit higher concentrations of PFCs.

The higher levels of PFCs in secondary sludge and biosolids from the metro WWTP correlates well with the results of previous research. As discussed above, PFCs readily adsorb to sludge particles. The 3M Multi-City Study reported that high levels of PFOS can be expected in sewage sludge due to the acidic properties of the chemical. Schulz et al (2005) estimated that a significant percent of the PFCs that enter a wastewater treatment plan end up in the biosolids. Furthermore biodegradation of PFC parent compounds by microorganisms in the waste activated sludge may account for the appearance of new and higher concentrations of certain PFCs in secondary sludge and biosolids.

5. Summary Report

- PFOS and PFOA were found at 81 and 78 ppt in the effluent with other PFCs at lower levels to non-detect. These levels do not appear especially high and are comparable to those concentrations found in other studies related to POTW effluents that may contain PFCs.

- Respectively, PFOS and PFOA were found at 53 and 46 ppt in influent samples with other PFCs at lower levels to non-detect.

- Higher influent PFC concentrations versus effluent PFC concentrations are consistent with a previous study done on PFCs in wastewater treatment plants, explained by the biodegradation of PFC precursors into PFOS and PFOA through the WWTP. Higher effluent versus influent PFC concentrations may also be due, in part, to the retention time through the system and the recycle of waste activated sludge. PFOS and PFOA have not been shown to further biodegrade, and persist for extremely long periods.

- Primary sludge exhibited PFOS at 25.9 ppb and PFOA at 3.79 ppb, with other PFCs at low ppb to non-detect levels.

- Much higher concentrations of PFCs were found in the secondary sludge (waste activated sludge) with PFOS at 309 ppb, PFOA at 21.5 ppb, PFDA at 39.5 ppb, PFUnA at 22.3 ppb, PFDoA at 25.8 ppb, PFHxS at 10.3 ppb, PFNA at 10.4 ppb, with other PFCs at lower ppb levels to non-detect. The relatively higher concentrations of PFCs found in the Metro secondary sludge versus those found in other studies for plants not exposed to PFC industrial contributions may be explained, in part, by local PFC contributions (landfill leachates containing PFCs and Oakdale Dump pumpout discharge).

- Biosolids were found to contain PFCs with PFOS at 79.7 ppb, PFOA at 11.1 ppb, PFDA at 17 ppb, PFBS at 8.41, PFHxS at 6.35 ppb, PFNA at 5.63 ppb with other PFCs at lower levels (less than 5 ppb).

- Higher levels of PFCs in secondary sludge and biosolids is consistent with normal operation of a WWTP which relies on the removal of the majority of organic compounds in the secondary or waste activated sludge processes.

- The removal of individual PFCs is expected to vary according to the individual PFC compound chemistry.

- At a discharge flow rate of about 200 million gallons per day the Metro plant discharges about 0.132 lbs/day of PFOS and 0.127 lbs/day of PFOA, with annual discharges estimated at 48 lbs/year PFOS and 46 lbs/year PFOA, based on this effluent sampling. Based on this one sampling event, the total discharge of PFCs annually is about 123 lbs/year.

6. Future Need for PFC Investigation at MCES Metro Plant

- A more extensive study of the fate and transport of PFCs, in particular PFOS and PFOA, and the potential biodegradation pathways of PFCs within wastewater treatment plants would be useful.

- The potential repercussions of PFOS and PFOA in beneficially used biosolids should be examined.

- The prevalence of domestic and commercial sources of PFCs to POTWs should be examined further.

- The impacts of the disposal sanitary landfill leachates and other discrete discharge sources containing PFOS, PFOA, and related PFCs on wastewater treatment plant effluents and sludges should be evaluated.

- It may be prudent to test the effluents or discharges at other municipal and industrial wastewater treatment plants for PFCs.

- It needs to be determined if the concentration levels of PFCs discharged from municipally owned treatment plants, like the Metro WWTP, are acceptable with respect to impacts, as currently there are no PFC wastewater treatment plant discharge standards.

G. PFC Contamination in Mississippi River Water and Sediment

1. Scope of PFC Investigation

The PFC river water and sediment study was begun to determine the impact of past and present PFC discharges on Mississippi River water and sediment. PFCs from the 3M Cottage Grove plant were discharged to the river since the early 1950s. As discussed in the introduction section, the 3M Cottage Grove production plant is one of the 3M PFC production facilities in the U.S. that produced 8-carbon PFCs. The other 3M fluorochemical production plant in the U.S. is located in Decatur, Alabama. In the recent past the 3M Cottage Grove plant primarily produced PFOA. However PFOS-related fluorochemicals were also produced at the Cottage Grove plant during the 1950s and 1960s, and continued to be produced after that in pilot scale projects. These fluorochemical production processes and formulation steps are the sources of the PFCs in the discharge from the 3M Cottage Grove plant, and the origin of fluorochemical wastes that have caused contamination at certain Minnesota sites. Beginning in the 1960s the 3M Decatur plant produced most of the 3M PFOS-related fluorochemicals made by 3M in the U.S. Like the Cottage Grove Plant, the 3M Decatur plant, which discharges wastewater to the Tennessee River, terminated all production of 8-carbon PFCs by the end of 2002, and PFC production at that plant is also now based on the 4-carbon PFC perfluorobutane sulfonate (PFBS). PFC production at the other 3M fluorochemical plant in Antwerp, Belgium is also now based on the 4-carbon PFC PFBS.

Because of the extremely long term persistence of PFOS and PFOA and the fact that these compounds do not degrade in the environment we expect that these compounds may reside in river sediments and other environmental media for an indefinitely long period. In addition, PFOS has been found to significantly bioconcentrate in aquatic organisms from water containing PFOS. PFOS biomagnifies in higher trophic-level organisms such as fish, and wildlife that may feed on contaminated fish. This phase I study of PFC concentrations in the Mississippi River water and sediment will be examined in conjunction with PFC levels in

fish analyzed. The data will further be analyzed to determine if levels in sediments are a concern over the long term with respect to uptake by aquatic organisms, fish, and wildlife. In addition, river water and sediment analyses will assist in possible determination of any risk potentially imposed by human consumption of any contaminated fish or wildlife.

2. Historical Discharges of PFC Contaminants from 3M Cottage Grove Wastewater Treatment Plants into Mississippi River

Limited data is available for PFCs discharged to the Mississippi River from the 3M wastewater treatment plant effluent prior to 2002. 3M did not routinely monitor these compounds in their discharge to the river. Beginning in December 2002, 3M was required to routinely monitor 5 PFC compounds pursuant to the 3M Cottage Grove plant NPDES permit. 3M also completed limited analysis of its discharge for 5 PFCs during a Jan-March 2000 sampling period. This historical data allows at least some limited estimate of the mass of PFCs that may have been discharged prior to the production phase-out. Based on the 3M Jan-March 2000 discharge data, for analysis of only 5 PFC compounds, 3M could potentially have discharged about 50,000 lbs per year of PFC compounds to the Mississippi River. Calculations based solely on this Jan-March 2000 discharge concentration data, using average river flows for a nominal 20 year period of calculation (using average river flows from 1980 through 2000), show that the total PFC mixed river concentration throughout the river (after lock and dam # 2) would have averaged about 1880 ng/l (parts per trillion). This was for a 20 year period of calculation only, completed for the purpose of determining mixed river PFC concentrations, and assumes that PFCs were discharged to the river at similar concentrations throughout this period. This may not have been the case. It is possible that lower or even higher concentrations were discharged. Using these concentrations the mixed river concentration of the individual PFOS compound may have averaged about 550 ppt during this 20 year nominal period of calculation. At times, during low flow periods, the total mixed river concentration of PFOS at the lock and dam # 2 area would have exceeded the recently established PFOS drinking water "standard" by the Minnesota Department of Health of 1.0 ppb (or 1000 ppt).

As discussed previously, in 2000 3M began its phase-out of production of PFOS-related PFC compounds at its plants, PFOA, and other 3M manufactured precursor PFCs that eventually break down to PFOS and PFOA. Phase-out of PFOS-related PFCs and PFOA was completed by the end of 2002. Current production at the 3M Cottage Grove Center is limited to PFBS and one flame retardant product, with some pilot scale production of PFBS based PFCs. PFOA is no longer produced by 3M. In hindsight it would have been valuable to have been able to monitor the impact of the 3M PFC discharge on the river before or during the 3M PFOS-related PFC and PFOA phase-out, in order to more fully assess the impact of these PFCs on the environment when considerably higher concentrations of PFOA, PFOS, and related PFCs were discharged from the 3M plant. As previously stated, beginning in December 2002 3M was required to monitor for 5 PFC compounds in its discharge pursuant to its NPDES (National Pollutant Discharge Elimination System) permit.

Pursuant to the NPDES permit 3M installed a granular activated carbon system to treat its wastewater treatment plant discharge. Installation of the activated carbon system was

completed in January 2003. Analysis of monthly discharge data submitted to the MPCA as part of the NPDES permit shows that the activated carbon system has resulted in a significant reduction in PFOS discharge concentrations. The activated carbon system has also reduced other PFC concentrations, but to a lesser extent. PFOA and other carboxylic acid PFCs may not be removed by the activated carbon system to the extent anticipated, however a full evaluation of the efficiency of removal of the individual PFC compounds through the activated carbon system is needed in order to make any definitive conclusions regarding efficiency.

Since the PFOS-related and PFOA production was phased-out in 2002, and after operation of the activated carbon treatment system, PFOS concentration levels in the 3M discharge have dropped significantly. Other individual PFC compounds show significant reductions in the discharge, but generally to a lesser degree than PFOS. PFBS (perfluorobutane sulfonate), the 4-carbon PFC now used in production, continues to be discharged. Although the PFC production is currently limited to PFBS, PFOS, PFOA, and other PFCs related to past 8-carbon production continue to be discharged to the Mississippi River. In part this is due to the fact that 3M pumps contaminated groundwater from several wells at the 3M Cottage Grove site which eventually is discharged to the plant cooling and wastewater systems. The origins of the continued presence of PFOS, PFOA, and other compounds related to past 8-carbon PFC production in the 3M discharge has not been fully characterized and needs to be assessed.

Based on samples collected at the 3M wastewater treatment plant in this phase I study (see the 3M Cottage Grove Plant PFC study section of this report) on June 27, 2005, the total PFCs in the discharge to the Mississippi River from the 3M treated process wastewater and cooling water discharges are about 291,000 ppt (part per trillion) and 30,457 ppt, respectively. Using a nominal discharge flow rate of 3.5 million gallons per day (MGD) for the 3M process discharge and 4.0 MGD for the 3M cooling water discharge this is equivalent to about 8.5 lbs/day PFCs discharged, or about 3465 lbs/year PFCs currently discharged based on this sampling event.

3. Sampling Strategy

This is the only study in Minnesota to date that included analyses of water and sediment samples for a complement of 12 individual PFC compounds. Samples were collected in the river area of pool #2, above Lock and Dam #2. The results of this study will be evaluated in conjunction with recent studies of the 3M fluorochemical wastewater to the Mississippi River, the Metropolitan Council of Environmental Services (MCES) Metro wastewater treatment plant discharge and sludge, fish impacted by 3M PFC discharges, and landfill leachate contributions.

The 3M Cottage Grove plant discharges its treated wastewater into a ravine where it combines with an intermittently flowing natural stream. The ravine widens into a relatively quiescent “cove” area of the Mississippi River prior to discharge to the main river body. Water and sediment samples were taken in the river upstream (above) and downstream (below) the 3M discharge point (cove area) in the river, and within the river cove. Individual

water and sediment samples were taken at 5 separate locations including: a water and sediment sample just upstream of the 3M discharge location (cove) and the MCES Eagle Point wastewater treatment plant discharge, water and sediment samples for 3 separate downstream locations (number # 1, # 2, and # 3 downstream), and water and sediment samples of the river cove area. Global Positioning System (GPS) coordinates were taken to locate the exact position of samples taken in the Mississippi River and in the cove. All sampling for this project occurred on May 20, 2005.

PFC compounds have varying degrees of water solubility. The PFOS salt form is relatively water soluble. Individual PFC compounds may elicit different chemical characteristics with respect to their eventual behavior in the water environment and their attachment to sediments. We expect that some PFCs may have been attached to the suspended solids material discharged from the 3M wastewater treatment plant (biological activated sludge system). The exact nature and extent of PFCs partitioned to these discharge solids and their disposition in the river is unknown. It is likely that a significant amount of the PFCs discharged from 3M have been deposited in river sediments. However, since some PFCs tend to concentrate on the water surface microlayer (top of water surface) due to their surface active properties, not all of the PFCs discharged at the Cottage Grove wastewater treatment plant end up attached to sediment. This surface adhesion property may have allowed some portion of the discharged PFCs, along with those attached to suspended river solids, to be carried for some distances downstream.

Sampling in the river environment is further complicated by the fluvial mechanics and geomorphology of the river. Flood conditions and changing intensity of river flow also affect how sediments are transported downstream. Sediment grain size and organic content and other physical and chemical factors affect the affinity for certain organic compounds to adsorb onto river solids, and may cause significant variances in organic contaminant concentrations in sediments.

Sedimentation of suspended solids in the river occurs continuously, and sediment scouring and resuspension may also occur depending on flow conditions, and the geomorphology of the river. Sediment is deposited in the river over time, and at variable rates depending on several conditions including location, and may be resuspended and moved at times during high flow conditions. In some areas, for example, sediments may accumulate at a rate of 2-4 cm per year, or more. As a result, deeper sediments may be correlated with past solids deposited that were discharged to the river from point sources and deposited at a certain point in time.

Because of the 40-50 years of potential discharge of PFCs from the 3M Cottage Grove plant, it is possible that many of the past PFCs discharged are contained in deeper sediments. This Phase I initial assessment was not intended to determine the differential deposition of sediments over time. Only the top 10 cm of the cores were submitted for analysis in this study, which may represent only the past few years of sedimentation in the river. Therefore, the top 10 cm sampled may only be representative of recent years of the 3M discharge, and likely predominantly during the period when reduced masses of PFCs were discharged after the PFOS-related and PFOA production terminated by the end of 2002. This study did not

evaluate the river sedimentation rate in the area sampled or correlate the 10 cm core depth with specific dates.

Water and sediment samples were taken in the river at locations outside of the river channel, which were to the east of the channel for the upstream and # 1 and #2 downstream locations, and to the west of the channel for the #3 downstream location. These locations were chosen to avoid channel influences and scouring areas. No assessment was made to evaluate the exact plume location for the 3M discharge but it is expected under typical river flow conditions to track on the east side of the river. Lock and Dam #2 lies approximately 1-1.5 miles downstream of the 3M discharge. After Lock and Dam # 2 the discharge from the 3M plant would be expected to be relatively well mixed within the river.

4. Sampling Results

PFC Contamination in Mississippi River Water - All river water samples were taken at a depth of 2 ft below the river surface. A cove water was also taken at the top surface. As shown in Table 11 the river cove water, where 3M discharges its treated wastewater treatment plant effluent, contained levels of many PFCs in the high part per trillion (ppt) concentrations range. PFOS was found at 10,800 and 18,200 ppt, PFOA at 3,200 and 3,600 ppt, and PFHxS (perfluorohexane sulfonate) at 8,200 and 9,700 ppt. PFBS was found at a higher concentration, 84,800 and 89,800 ppt. These concentrations in the high ppt range are consistent with the PFC concentrations measured in the 3M wastewater treatment plant discharge (effluent).

River water PFC concentrations were found in the lower parts per trillion (ppt) concentration range. The only PFCs found in the river were PFOS and PFOA. PFOS was found in the river water immediately downstream of the 3M discharge at a level of 14.5 ppt at location #1, at a level of 6 ppt at downstream location #2, and non-detect at downstream location #3. Downstream location #3 is in a relatively quiescent area of the river likely not “exposed” to the 3M discharge. PFOA was found in the river water immediately downstream at location #1 at a level of 35.3 ppt, and was not detected at the other downstream locations. The diminishing downstream PFOS and PFOA river water concentration is primarily due to the dilution of the 3M discharge with the river flow. River water samples were collected below the surface and may not fully characterize the river water concentrations of PFCs due to their surface active properties (may concentrate more on the water surface).

Although PFBS was found in the cove water at relatively high concentrations its absence in river water may be due to its potential to adhere to the surface micro layer, or to differences in volatility. The exact mechanism is not understood at this point.

The river water collected upstream of the 3M discharge showed a PFOS concentration of 5.14 ppt. No other PFC compounds were detected in the upstream river water. The upstream PFOS concentration can be deemed “background” for the 3M discharge, and represents upstream PFOS contributions likely occurring as a result of other wastewater discharges or sources. Although groundwater under the 3M Cottage Grove plant is contaminated with PFCs and PFOS and this groundwater flows towards the river, it is unlikely that the upstream

sampling location used in this study was influenced to a significant extent by any 3M contaminated groundwater discharge to the river, although this was not quantified. The 5.14 ppt PFOS is comparable to background PFOS levels found in other studies, as discussed below.

PFC Analysis of Floating Algae - This study also collected floating algae from the river cove that receives the 3M Cottage Grove wastewater treatment plant discharge. PFOS was found at 264 ppb in the algae. The PFOS algae concentration may be used to assist in derivation of bioconcentration factors as more data is generated. The algae PFOS concentration of 264 ppb indicates that bioconcentration of PFOS from the water column, determined in the river cove water at the surface at 18.2 ppb, is occurring from water to algae.

Table 11 - PFC Concentrations in Mississippi River Water (ng/l or ppt) and Duckweed Samples (ng/g or ppb)

PFCs	Miss-up	Miss-down #1	Miss-down #2	Miss-down #3	Cove Water	Cove Water Top Surface	Duckweed (Lemna minor)
PFBA	<12.8	<12.7	<12.9	<12.8	5000.00	5530.00	Not Reported
PFPeA	<12.6	<12.5	<12.7	<12.6	1320.00	1560.00	Not Reported
PFHxA	<4.90	<4.87	<4.93	<4.92	1780.00	1970.00	< 5.69
PFHpA	<4.96	<4.93	<4.99	<4.98	<251	<251	< 5.75
PFOA	<4.88	35.30	<4.91	<4.90	3250.00	3650.00	18.10
PFNA	<5.30	<5.26	<5.33	<5.31	<268	<268	< 2.46
PFDA	<5.12	<5.09	<5.15	<5.13	<259	<259	5.21
PFUnA	<5.07	<5.04	<5.10	<5.08	<257	<257	< 2.36
PFDoA	<5.04	<5.01	<5.07	<5.05	<255	<255	3.25
PFBS	<5.02	<4.99	<5.05	<5.03	84800.00	89800.00	68.80
PFHxS	<5.04	<5.01	<5.07	<5.05	8230.00	9720.00	21.20
PFOS	5.14	14.50	6.00	<5.11	10800.00	18200.00	264.00
PFOSA	<5.10	<5.07	<5.13	<5.11	<258	<258	24.90
Total PFCs	**5.14**	**49.80**	**6.00**	**0.00**	**107080.00**	**121370.00**	**405.46**

Mississippi River Water PFC Concentrations and Comparison with Other Studies - River water and sediment samples associated with this study were collected during the on-going production of 4-carbon PFBS based PFCs at 3M, when PFOA and any PFOS-related production had been terminated. However, levels of PFOS, PFOA and other 8-carbon PFCs representative of past discharges continue to be present in the 3M plant discharge. It is possible that the presence of these chemicals is associated in part with 8-carbon groundwater contamination sources at the 3M plant. The relative sources of continuing contributions of 8-carbon fluorocarbons such as PFOS and PFOA in the 3M influent wastewaters and discharge remains to be determined.

A number of studies have been conducted worldwide to determine the levels of PFCs in surface waters. One paper titled “Perfluorooctanoic Acid and Perfluorooctanoic sulfonate in Michigan and New York Waters”, by Sinclair et al describes a study done on water samples collected in Michigan Great Lakes in 2001 and inland waters of New York in 2003 and 2004.

Sinclair et al found PFOS in 89% of Michigan water samples. Background water concentrations were found to be between 2 and 5 ng/l (ppt) for PFOS and between <8 and 16 ng/l (ppt) for PFOA. The maximum concentrations found in this study, PFOS at 29 ppt and PFOA at 36 ppt, were at locations influenced by industrial discharges that may have used some PFC compounds in their process (pulp and paper mills).

The range of PFCs in Michigan waters was similar to that found in Japanese surface waters. A study by Saito et al, titled "Perfluorooctanoate and Perfluorooctane Sulfonate Concentrations in Surface Water in Japan" found PFOS and PFOA levels in the 1-5 ppt range. The Saito study found two highly contaminated areas; the mouth of the Ai River and portions of the Kanzaki Rivers. PFOA was found in samples collected at the mouth of the Ai River, the location of the Aigawa Ryuiki industrial wastewater disposal site at a level of 67,000 ng/l (ppt). The 67,000 ppt level in the mouth of the Ai River is consistent with PFOA levels determined by 3M, at times, in monitoring their wastewater treatment plant discharge. The Saito et al study also found relatively high PFOS levels, up to 86 ppt, in an area of the Kanzaki River in Japan. Interestingly, the Saito study also found low ppt levels of PFOS and PFOA in drinking (tap) water at several locations, with PFOA up to 40 ppt and PFOS up to 12 ppt. PFOS contamination in the Kanzaki River is believed to have been caused from runoff of fire fighting foam containing PFOS from the Osaka International Airport (Yamashita et al, 2004).

A PFC study published by Berger et al, entitled, "Perfluorinated Alkylated Substances (PFAS) in the European Nordic Environment", examined sediment, sewage sludge, water, and biota from participating Nordic countries and found median levels of PFOA of 5.2 ppt for seawater and 7.8 ppt for lake waters. This study also found median levels of 20.5 ppt PFOA in sewage effluent (discharge), 13.1 ppt in rainwater, and 297 ppt in landfill effluent (leachate). Although this study found PFOS to be the most prominent residue in solid abiotic samples, the median PFOS levels in water samples were less than 1 ppt for seawater, less than 1 ppt for lake waters, less than 1 ppt for rainwater, 12.7 ppt for sewage effluent, and 65.8 ppt for landfill effluent. This was believed to be due to the lower water solubility of PFOS compared to the carboxylic acid PFCs (PFOA). PFOA represented the predominant PFC in water samples in this study, followed by PFHxA.

A study by Taniyasu et al, titled "Perfluorinated Carboxylates and Sulfonates in Open Ocean Waters of the Pacific and Atlantic Oceans" found very high concentrations of PFOS and PFOA in Tokyo Bay waters, with PFOS ranging from 0.338 ppt to 57.7 ppt, and PFOA ranging from 1.8 ppt to 192 ppt. These concentrations are likely associated with industrial discharges and PFC manufacturing industries in the Tokyo area. This study also found samples from the mid-Atlantic ocean to contain very low ppt levels of PFCs, with PFOS at 0.037 to 0.073 ppt and PFOA at 0.1 to .439 ppt. These levels are comparable to the levels found in the South China and Sulu Seas. Taniyasu et al found PFOS and PFOA in the central to eastern Pacific Ocean at concentrations of 0.015 to 0.062 ppt and 0.001 to 0.002 ppt, respectively. The report suggests that these levels appear to be indicative of background values for remote marine waters far from local sources. Interestingly, this study sampled deep sea water (1000 m to 3000 meters) and found trace PFC levels ranging from less than

0.017 to 0.024 ppt for PFOS, and 0.076 ppt to .117 ppt for PFOA. PFOA appears to be more ubiquitous than PFOS in this study.

Hansen et al (2002) studied PFOS in surface water samples collected from the Tennessee River upstream and downstream of the 3M fluorochemical manufacturing plant in Decatur, Alabama, which discharges into the Tennessee River. This study found relatively high concentrations of PFOS in river water downstream of the 3M Decatur, Alabama. The downstream PFOS concentrations were observed to increase at a point approximately 6 miles below the 3M discharge; the average PFOS concentration from that point downstream was 114 ± 19 ppt.

Our current study of the Mississippi River found a background PFOS level of about 5 ppt. This concentration compares with the general background PFOS levels found in other studies. The PFOS and PFOA concentrations detected in Mississippi River water (downstream samples 1, 2, and 3) downstream of the 3M discharge are not surprising, and correlate with levels found in other studies proximate to PFC contamination sources.

Table 12 - PFC Concentrations in Mississippi River Sediment Samples (ng/g dry weight or ppb)

PFCs	Sediment upstream	Sed-Miss-down #1	Sed-Miss-down #2	Sed-Miss-down #3	Sediment Cove
PFPeA	<0.308	0.966	<0.320	<0.312	1.21
PFHxA	<0.299	0.755	<0.311	<0.302	2.28
PFHpA	<0.302	0.262	<0.315	<0.306	0.758
PFOA	<0.298	6.62	1.31	<0.301	18
PFNA	<0.323	0.333	<0.336	<0.327	0.671
PFDA	<0.312	1.13	0.49	<0.316	2.93
PFUnA	<0.309	0.437	<0.322	<0.313	1.73
PFDoA	<0.307	0.281	0.365	<0.311	2.47
PFBS	<0.306	1.74	<0.318	<0.310	49.8
PFHxS	<0.307	1.54	<0.320	<0.311	9.24
PFOS	1.57	27.9	8.26	1.69	99.4
Total PFC	**1.57**	**41.964**	**10.425**	**1.69**	**188.489**

PFC Contamination in Mississippi River Sediment - Mississippi River sediment core samples were collected at each of the previously described water sample locations. Sediment samples were obtained by compositing 4 separate sediment cores from each sample location. Efforts were made to collect the four individual sediment core (used to make up each composite sample) within 100 ft of each other. All sediment cores were obtained at a depth of 10 cm below the river bottom. Global Positioning System (GPS) waypoints for each river core location were recorded with a boat mounted WAAS capable GPS receiver. Waypoints for the cove area sediment composite were recorded with a hand held non-WAAS capable GPS receiver. Sediments collected had similar grain size distribution consisting predominantly of silts, with some clays and fine sandy loams, based on visual textural analysis.

As shown in Table 12, similar to the river water samples, PFC contamination in sediment was found at the highest concentrations in the sample from the river cove receiving the 3M discharge. PFOS was found at a concentration of 99.4 ng/g (ppb), PFBS at 49.8 ppb, PFOA at 18 ppb, PFHxS at 9.24 ppb, and other PFCs at lower ppb levels. Analysis of river sediment at location #1, immediately downstream of the cove and the 3M discharge, contained PFOS at 27.9 ppb, PFOA at 6.62 ppb, with other PFCs also present but in the 1.0 ppb or less range. River sediment at downstream location # 2 found diminishing PFC concentrations with PFOS at 8.26 ppb, PFOA at 1.31 ppb, PFDA at 0.49 ppb, PFDoA at 0.365 ppb, with other PFCs were non-detect. Analysis of river sediment at downstream location #3, a quiescent area likely not appreciably impacted by the 3M discharge, showed PFOS at 1.69 ppb with all other PFC compounds non-detect.

Mississippi River Sediment PFC Concentrations and Comparison with Other Studies - There is limited information available regarding PFC contamination of surface water sediments. 3M analyzed PFOS, PFOA, and FOSA in Publicly Owned Treatment Works (POTW) effluent, POTW sludge, landfill leachate, sediment, surface water, and drinking water in 6 cities (3M Multi-City Study). The 3M study found that sediments in surface water contained non-detect to 1.75 ppb PFOA, non-detect to 1.13 ppb PFOS, and non-detect to 0.54 ppb FOSA. It should be noted that the 3M sediments samples in the 3M Multi-City Study appear to have been taken, for the most part, upstream of POTW discharges and would not be representative of impacts from PFC discharges from POTWs, or industrial PFC sources. Accordingly, the sediment PFC levels found in the 3M study would be more likely representative of background.

The publication by Berger et al, "Perfluorinated Alkylated Substances (PFAS) in the European Nordic Environment" examined sediment from participating Nordic countries and found PFCs in sediments at low levels likely indicative of background. The highest concentration of PFCs was found in a Finnish sediment. The Finnish sample was characterized by a PFC concentration of 1.15 ppb. Sediment samples from Sweden, Iceland, and the Faeroe Islands hardly contained detectable PFCs, and Finnish sediment was dominated by PFOS and Norwegian samples by PFOS and PFOA.

A study by Giesy et al of PFOS of surface water, sediments, clams, and fish collected from locations upstream and downstream of the 3M facility at Decatur, Alabama, found very high levels of PFOS in surface water sediment in the Tennessee River receiving water, downstream of the 3M Decatur plant. The nearest 2 downstream locations contained sediment PFOS contamination at 5930 ppb and 1299 ppb wet weight, compared to upstream levels of 0.18 ppb and 0.98 ppb.

When compared to literature values, the PFC concentration levels found in Mississippi River sediments appear relatively high. One important difference between the literature and the current study is that PFCs observed in Mississippi River sediment samples during this study are uniquely associated with a PFC production facility discharge source. The sediment PFC levels determined in this study are considerably lower than those found in Tennessee River sediments downstream of the 3M Decatur, Alabama plant. It is important to note that both

the current Mississippi River study and the Giesy Tennessee River study are ongoing and the amount of sediment data available at this time from both studies is limited.

5. Summary Report

- The upstream or background river water sample result of PFOS at about 5 ppt is typical of background PFOS concentrations found in other studies worldwide.

- PFOS and PFOA were found in river water downstream of the 3M discharge (PFOS at 14 ppt and PFOA at 35 ppt). These levels are comparable to those concentrations found in other studies related to industrial discharges that may contain PFCs.

- The PFOS and PFOA river concentrations are more reflective of the current 3M 4-carbon PFBS based production, and are not representative of past very high concentrations when PFOA and PFOS-related PFCs were produced at the 3M Cottage Grove plant.

- PFOA river water concentrations are higher than PFOS. This is probably due to its greater water solubility.

- The concentrations of PFCs in samples taken from the river cove water which receives the 3M discharge are in the very high ppt ranges, and are approximately 1000 times higher than PFOS concentrations found in the main river body. These concentrations are comparable to the concentrations from fluorochemical plant discharges, and to the PFC concentrations routinely monitored in the 3M discharge. The high PFC concentrations in the river cove water are quickly diluted by the large river flow.

- Although the 3M activated carbon system is relatively effective at removing PFCs, its effectiveness is not uniform and consistent.

- It is likely that some PFCs in the water concentrate on the water surface micro layer, due to their surface active properties. Therefore, concentrations of PFCs may be higher in the very top or micro surface layer of the water. This study did not evaluate this aspect.

- The sediments from the river cove receiving the 3M discharge are heavily contaminated with several PFC compounds at higher ppb levels.

- The concentrations of PFCs found in river sediments are relatively high compared to background, correlate with a PFC production facility discharge, and are comparable to levels found in other studies with PFC contamination sources. The levels of PFCs found in downstream sediments in this study, based on very limited samples at relatively shallow depths (10 cm), are considerably lower than those found to date in the Tennessee River downstream of the 3M Decatur, Alabama discharge.

- Background PFOS in sediment samples taken upstream of the 3M discharge is consistent with background PFOS found in other studies.

- The 10 cm sediment cores analyzed in this study are most likely representative of the past 3-4 years of river sedimentation. However evaluation has not been made to determine the period of time that correlates with these 10 cm sediment cores. Likewise, the sediment concentrations observed within these cores are more likely representative of the past few years of discharge from 3M, during which time less PFCs were discharged versus the years and decades before.

- Deeper sediments (deeper than the top 10 cm) may contain a "reservoir" of PFCs adsorbed to solids deposited from past years and decades of discharge from 3M.

6. Future Need for PFC Investigation in Mississippi River

- A more extensive collection of river sediment cores is needed to characterize the levels of PFC contamination in the river sediments and the river cove sediments.

- Deeper sediment cores need to be collected and analyzed with sediment dating techniques, to assess past the PFC contaminant load within the river corresponding to past decades of PFCs discharged.

- PFC sediment core analysis is needed further downstream of the 3M discharge, and at Lake Pepin. Lake Pepin serves as a "sink" for sedimentation of upstream Mississippi River suspended solids. PFCs may reside in Lake Pepin sediments due to this sedimentation effect.

- The extent of PFC contamination in the river cove needs to be assessed. An evaluation should be done to decide whether river cove sediments represent a continuing source of PFC discharge and contamination to the Mississippi River, and whether cove sediments should be remediated or removed (dredged) to eliminate this high PFC contamination source.

- The bioavailability of PFC contaminated sediment needs to be understood and evaluated, to determine potential continuing impacts to aquatic life and wildlife. It needs to be determined whether PFCs in sediment pose a continuing risk and source for aquatic life bioaccumulation.

- More river water samples need to be taken, especially at the water surface or micro layer to determine PFC concentrations in this layer, consistent with PFC chemistry.

- The acceptable PFC discharge and river water concentrations need to be understood. Although the PFC levels in the water do not presently pose acute toxicity to aquatic life, it needs to be determined whether or not they pose a problem with respect to continuing uptake and bioconcentration in aquatic organisms and fish, biomagnify in

higher trophic levels such as fish, and accordingly pose any health risk due to wildlife and humans consuming these fish.

H. PFC Contamination in Mississippi River Fish

1. Concerns about Fish Contamination with PFOS and other PFC Compounds

Persistence - PFOS is a persistent organic pollutant that is extremely resistant to environmental degradation. Once PFOS precursors degrade to PFOS, PFOS will remain in the environment since there are no known degradation mechanisms. Once PFOS is in the environment it is often bioavailable and may enter the food chain. It can be transferred from one media to other (i.e. from water to air, sediment and aquatic biota) and can be transported over a long range, or further distributed at a distance from its source. A number of studies have quantified PFOS and other PFC compounds in a wide range of animals and aquatic life across the world. Some of these studies have found significant levels of PFOS and other PFCs in animals located in very remote areas distant from any PFOS source, such as in the Arctic. This suggests that either PFOS or its precursors undergo long-range transport. PFOS is often the most common PFC compound found in these studies. Other PFC precursors related to the PFOS chemistry eventually degrade to PFOS. Wildlife species from a number of sites in the U.S. have shown widespread distribution of PFOS in tissues, and PFOS was detected in the ppb range in the blood plasma of several species including eagles, wild birds, and fish. Fish eating birds such as eagles, and fish eating mammals such as mink, have been found to contain some of the highest PFOS levels reported.

PFC compounds preferentially distribute and accumulate in livers and blood in animals, including humans. No further metabolism by PFOS in animals is expected. Elimination is slow and the elimination half-life of PFOS differs from species to species. Unlike other persistent organic pollutants, such as dioxins and PCBs, PFOS does not accumulate in fat tissue of organisms. This is because PFOS is both hydrophobic and lipophilic. PFOS therefore binds to proteins in the blood and liver.

As previously described, PFC compounds and PFOS have been found in animals and abiotic samples in very remote regions of the world, demonstrating properties for long range transport for PFOS. The exact mechanism for long-range transport is unknown. Although PFOS is relatively non-volatile it may be transported in the atmosphere via adsorption particles and/or as metabolic precursors such as the FOSE alcohols, which are relatively volatile and have been found in air. These precursors may evaporate into the atmosphere, remain in a gas phase, condense on atmospheric particles present and subsequently be carried away for long distances or settle out with them, or later be washed out with rain. PFOS precursors degrade to PFOS in the environment and/or are metabolized to PFOS in organisms consuming the precursors.

Bioaccumulation - PFOS has been shown to bioconcentrate in fish. Bioconcentration is the specific bioaccumulation process by which the concentration of a chemical in an organism becomes higher than its concentration in the air or the water around the organism. Although the process is the same for both natural and manmade chemicals, the term bioconcentration

usually refers to chemicals foreign to the organism. For fish and other aquatic animals, bioconcentration may be the result of uptake through the gills, in addition to uptake through the food chain. Laboratory bioconcentration studies in fish have shown that significant PFOS bioconcentration occurs. Studies on the bluegill sunfish found a bioconcentration factor (BCF) of 2796 for PFOS. A PFOS bioconcentration factor of 1100 for whole fish, 5400 for liver, and 4300 for blood has been reported for rainbow trout (Martin et al, 2003). Bioconcentration studies based on environmental sampling have also demonstrated PFOS bioconcentration in other aquatic organisms. Kannan et al (2005) found that the concentration of PFOS in benthic invertebrates such as amphipods and zebra mussels were approximately 1000 times greater than the PFOS levels in the surrounding water.

PFOS bioaccumulate in fish and other animals. Bioaccumulation is an increase in the concentration of a chemical in an organism over time, compared to the chemical's concentration in the environment. Bioaccumulation includes uptake from all routes of exposure, not just from the external media. Usually the most important exposure other than external media is food. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted. Understanding the dynamic process of bioaccumulation is very important in protecting humans and other organisms from the adverse effects of chemical exposure, and it has become a critical consideration in the regulation of chemicals. Giesy and Kannan (2005) estimated bioaccumulation factors ranging from 830 to 26,000 for PFOS for channel catfish and largemouth bass, respectively.

PFOS also significantly biomagnifies up the food chain. Biomagnification describes a process that results in the accumulation of a chemical in an organism at higher levels than are found in its food. It occurs when a chemical becomes more and more concentrated as it moves up through a food chain, the dietary linkages between single-celled plants all the way up through increasingly larger animal species. For example, the PFOS concentrations in predatory fishes are often 10 to 20 times greater than those in their prey species. Bioaccumulation and biomagnification of PFC levels in fish occurs when the fish consume organisms characterized by persistent levels of PFCs.

A major route for PFOS into the food chain affecting and causing human PFOS blood contamination may be through eating PFC contaminated fish. Together with the fact that PFOS is found in many water sources, eating contaminated fish may explain why studies have seen higher levels of PFOS in blood from humans that consume higher amounts of fish. A study done in Sweden found that PFOS levels in blood from females with a high consumption of fish were much higher (PFOS average 27.2 ppb) than females in the general Swedish population (PFOS average 17.9 ppb).

Toxicity - In addition to animal laboratory studies showing that PFOS causes certain toxicity endpoints, including the initiation of certain cancers, the toxicity of PFOS has been studied in a variety of aquatic and terrestrial species, including aquatic plants, invertebrates and vertebrates and terrestrial invertebrates, birds and mammals. Toxicity data is primarily limited to the PFOS perfluorochemical compound. Adverse animal effects range from

growth inhibition, histopathological effects, atrophied thymus, change in species diversity in a microcosm, and mortality.

In general the PFOS levels found in most discharges have not been shown to subject fish to acute toxicity. The most sensitive aquatic toxicity endpoint occurred in a study on the bluegill which found no significant mortality at a PFOS exposure concentration of 86 ppb over 62 days of uptake, but significant mortality after a 35 day exposure to 870 ppb. The lowest definitive no observed effect concentration (NOEC) of 300 ppb PFOS was determined for the fathead minnow. The NOEC level is applicable to both survival and growth endpoints.

A recent study by Hoff et al (2005) of 3 freshwater fish species in Belgium found a strong correlation between liver PFOS concentrations and blood serum ALT (alanine aminotransferase) in the eel and carp, and suggest that PFOS may induce liver damage at certain concentrations in freshwater fish under field conditions. The ALT test detects liver injury. ALT values are usually compared to the levels of other enzymes, such as alkaline phosphatase (ALP) and aspartate aminotransferase (AST), to help determine which form of liver disease is present. This study also found a significant relationship between the hepatic PFOS concentration and the serum chloride, sodium, and calcium concentrations in carp, and suggest that PFOS could induce ion regulatory distress by disrupting membrane structure and/or function of the gill cells which play a key role in osmoregulation and regulation of ion homeostasis. The fish evaluated in this study demonstrating these impacts contained high PFOS levels with carp at 11.3 to 1822 ppb PFOS, and eel at 17.3 to 9031 ppb PFOS. Some of the fish in this study were collected from surface waters proximate to a fluorochemical plant discharge in Antwerp, Belgium and are among the highest reported wildlife liver PFOS concentrations.

2. Scope of PFC Investigation

The objective of the fish collection and PFC analysis is to determine the extent of PFC contamination in fish in the Mississippi River, and to better understand the bioavailability of PFCs that accumulated over the approximate last 50 years in the Mississippi River sediment. Determination of PFCs in fish will also help to determine the metabolic uptake of PFCs by fish species representing different trophic levels and ecological groups (benthivorous and piscivorous), and to begin to assess the ecological and human health impacts of these contaminants. Fish in the river may be exposed to PFCs dissolved in the river water column, and/or by ingesting other aquatic organisms that were previously exposed to PFCs as a result of bioconcentration of PFCs in the river water.

This phase I PFC study is intended to provide an initial assessment of the levels of PFC contamination in Mississippi River fish. Fish PFC data collected to date, and data yet to be collected, will be used to discern trends between fish and other aquatic sampling media such as water and sediment, and will be used to develop a model for PFC bioaccumulation. As other PFC data for fish in the river are acquired the PFC data can be used to assess whether the PFC levels observed in the Mississippi River fish pose a risk for wildlife and human

consumption. Accordingly the fish PFC data may be used to evaluate the need for any consumption advisory related to PFC contamination of fish.

3. Sampling Strategy

Fish were collected for this study by the Minnesota Department of Natural Resources in the Mississippi River in the immediate vicinity of the 3M Cottage Grove discharge, and from the downstream river in the Lake Pepin area. During mid August 2004, a total of twenty fish samples from four different species (small mouth bass, white bass, common carp, and walleye) were collected from the vicinity of the 3M Cottage Grove discharge. In order to adequately determine the PFC levels in Mississippi River fish exposed to PFCs discharged from the 3M Cottage Grove plant, additional fish were collected on October 3, 2005 in pool #2 of the Mississippi River downstream and proximate to the 3M Cottage Grove plant discharge. More than 100 fish from seven different species (small mouth bass, white bass, common carp, walleye, small mouth buffalo, gizzard shad, and emerald shiner) were collected. In addition, approximately 100 fish samples from six different species (small mouth bass, white bass, common carp, walleye, gizzard shad, and emerald shiner) were also collected in October 4-5, 2005 from the Lake Pepin area. Samples were collected from two distinct ecological groups (benthivorous and piscivorous) and different trophic levels from the study areas.

Fish from the Lake Pepin area were chosen for collection, in addition to fish collected from pool #2, in order to assess PFC contamination in fish residing in the river at distal locations from the 3M discharge. In addition, Lake Pepin serves as a depository for suspended solids carried by the river upstream, and therefore Lake Pepin sediments may contain PFCs available for aquatic food chain uptake.

Fish collected during mid August 2004 were analyzed to determine PFC levels in the fish livers (all fish collected in 2004 were analyzed) and tissue (fillet) for a few selected 2004 fish specimens. All samples were analyzed for 12 individual PFC compounds. The October 3, 2005 pool #2 Mississippi River fish were analyzed for PFC concentration levels in blood, obtained by caudal blood extraction. These blood samples, for which analysis and data is complete, included 21 fish (6 small mouth bass, 5 white bass, 5 common carp, 4 walleye, and one small mouth buffalo). The October 3, 2005 pool #2 Mississippi River fish were immediately frozen after blood extraction, and are awaiting analysis for 12 or more PFCs in fish tissue (fillet), fish liver, and whole fish analysis after determination of their sex and their age. Fillet PFC analysis is required in order to allow an assessment of the potential risk to humans consuming these fish. PFC analysis is required on whole fish in order to assess the risk and impact on wildlife consuming these fish. The fish collected in October 4-5, 2005 from the Mississippi River Lake Pepin area are also awaiting analysis of PFCs in fillet, liver, and whole fish after determination of their sex and their age. It is important that the October 3, 2005 pool #2 Mississippi River fish and the October 4-5, 2005 fish from the Mississippi River Lake Pepin area are analyzed in order to adequately assess the levels of risk to human health and wildlife consuming these fish, in accordance with the objections of this study.

Criteria for Fish Species Collection - The primary criteria for collecting these target species are:

- The species are commonly consumed in the area and are of commercial and recreational fishing value.
- The species have the potential to bioaccumulate PFC contaminants.
- The species have a wide geographic distribution and are easy to identify taxonomically.
- The species represent two distinct ecological groups of benthivorous (bottom feeders) and piscivorous (predators) species.

The decision to collect species from two different ecological groups was made because it allows for monitoring of distinct habitats, feeding strategies, and physiological factors that might results in differences in bioaccumulation of different PFC contaminants. Benthivors (i.e. Common carp) are generally found closer to the bottom of the water column and may accumulate PFC contaminants from direct physical contact with contaminated sediment and/or by consuming benthic invertebrates and epibenthic organisms that live in contaminated sediment. Piscivors (i.e. Walleye and bass) can be found throughout the water column and are good indicator of PFC contamination that may be biomagnified through several trophic levels of the food web. Gizzard shad and emerald shiner, which represent the lower trophic level, were collected to better understand bioaccumulation and biomagnification of PFCs throughout the aquatic food chain.

4. Sampling Results

PFC Contamination of Fish Liver Samples - This Phase I study found that all of the 12 PFC compounds analyzed were present in the fish livers of the 2004 Mississippi River pool #2 fish tested, with the exception of PFBA (perfluorobutanoic acid). Some fish (the same age) were composited by species for liver PFC analyses. As shown in Table 13, PFOS was the dominant PFC found in all fish livers tested in this study. PFOS was highest in the smallmouth bass livers, with a range of 597 ppb to 6350 ppb. In carp livers PFOS ranged from 130 ppb to 309 ppb, averaging 210 ppb. PFOS concentrations in the 2 white bass liver composites were 305 and 1120 ppb. PFOS concentrations in the two walleye livers were 184 and 371 ppb. PFOSA was found at 58.3 ppb in the smallmouth bass liver that contained the high 6350 ppb PFOS concentration. PFOSA was not found in the other fish livers.

In general the PFOS levels found in the fish livers for the 2004 fish collected during our study appear higher than concentration levels determined in fish liver at other locations worldwide, with the exception of certain individual fish in some studies and the Belgium fish liver study. Contamination of PFCs in these fish livers is almost certainly the result of exposure to PFCs discharged from the 3M Cottage Grove plant. PFOS levels in fish livers in this study appear to correlate with those found in fish livers at other locations where PFC contamination sources are present (Tokyo Bay, Belgium).

The 6350 ppb concentration of PFOS found in the one smallmouth bass liver in our study was extremely high, and to our knowledge based on a review of the literature, is comparable to the highest PFOS levels found in fish liver worldwide.

Table 13 – PFC Contamination Levels in Fish Liver Samples from Mississippi River
August 2004 (ng/g wet weight = ppb)

Fish species	SMB #1	SMB#2a,#2b,#2c,#2d	SMB#3,#4	SMB#5	WB #1	WB#2,#3,#4,#5
sex/age	1F/8 y	1F & 3M/2y	2F/3y	1F/4 y	1F/7y	3F & 1M/6y
PFBA	<3.70	<3.76	<3.76	<3.88	<3.92	<3.88
PFHxA	10.4	<0.360	20.2	<0.371	<0.376	<0.371
PFHpA	1.49	<0.365	<0.365	4.17	6.32	1.1
PFOA	0.489	0.551	<0.359	<0.370	<0.374	1.27
PFNA	0.635	<0.390	<0.390	<0.401	3.17	4.26
PFDA	63	13.1	25.5	18.1	11.2	19.4
PFUnA	31.2	26.1	34.5	21.2	5.03	6.95
PFDoA	84.7	25.9	21.9	21.4	4.6	4.15
PFTA	44.6	14	4.32	5.1	0.828	6.67
PFHxS	<0.364	<0.371	<0.371	<0.382	3.16	<0.382
PFOS	6350	1030	597	717	305	1120
PFOSA	58.3	<0.363	<0.363	<0.374	<0.379	<0.374
Total PFCs	**6644.81**	**1109.651**	**703.42**	**786.97**	**339.308**	**1163.8**

Fish Species	Carp #2,#4,#5	Carp #3	Carp #1	WE #2	WE #1
sex/age	2F & 1M/6y	1F/7y	1F/8 y	1M/4y	1F/9 y
PFBA	<3.70	<3.83	<3.62	<3.81	<3.74
PFHxA	<0.354	2.91	<0.346	<0.365	<0.358
PFHpA	0.969	<0.371	<0.351	<0.369	3.17
PFOA	0.662	<0.365	<0.345	0.651	<0.357
PFNA	1.5	0.89	0.817	<0.394	2.91
PFDA	6.54	4.99	2.86	13.6	8.41
PFUnA	1.66	3.21	3.18	5.5	3.17
PFDoA	1.73	1.82	1.14	2.29	<0.368
PFTA	5.39	0.455	0.408	3.31	2.17
PFHxS	<0.364	<0.377	0.88	<0.375	<0.368
PFOS	309	130	202	371	184
PFOSA	<0.357	<0.370	<0.349	<0.368	<0.361
Total PFCs	**327.451**	**144.275**	**211.285**	**396.351**	**203.83**

SMB = smallmouth bass
WB = white bass
Carp = common carp
WE = walleye

Levels of PFC Contamination in Mississippi River Fish Livers Compared to Other Studies

Fish livers have been tested for PFOS and related PFCs in a number of studies worldwide. In a study of fish from the Michigan waters of the Great Lakes by Kannan et al the following PFOS concentrations were found in fish liver:

Chinook Salmon – 32-173 ppb (average 100 ppb)
Lake Whitefish – 33-81 ppb (average 67 ppb)

Brown Trout – range <17-26 ppb
Various species – range <7.7-120 ppb (average 43 ppb)

The Kannan study noted that Brown Trout livers had significantly lower PFOS levels. Brown trout mainly feed on zooplankton and less on small fish or invertebrates which may explain the lower bioaccumulation of PFOS in Brown Trout liver, and exemplifies the species differences in bioaccumulation of PFOS. The Brown Trout in this study were also collected in Lake Superior which is believed to be relatively less polluted than the other great lakes with respect to PFCs.

A study of fish in Tokyo Bay, Japan found PFOS in fish liver at a range of 62 to 198 ppb. Tokyo Bay water has been found to have very high levels of PFOS ranging from 338 ppt to 57,700 ppt and PFOA ranging from 1,800 ppt to 192,000 ppt. These high PFOS and PFOA concentration levels in the bay water are likely related to fluorochemical production sources in the Tokyo Bay area and industrial discharges. PFOS levels in fish liver in fish from Lake Biwa, Japan ranged from 3 to 310 ppb.

As described above, very high PFOS levels were found in fish collected from surface waters in Belgium near a fluorochemical production facility. The Belgium study found PFOS concentration levels in carp liver at 11.3 to 1822 ppb, and eel liver at 17.3 to 9031 ppb. Aside from the Belgium study, a review of the literature indicates that the maximum concentration levels of PFOS found in fish liver is generally about 1000 ppb (OECD Hazard Assessment of PFOS and its Salts – 2002).

A study by Corsolini et al (2004) in Mediterranean organisms found PFOS levels in tuna liver at an average of 39 ppb. Giesy et al (2001) previously found PFOS in bluefin tuna liver of the Mediterranean up to 87 ppb.

In the Great lakes Study by Kannan et al (2004) smallmouth bass tissue (skinless fillets) were analyzed for PFOS with the following results: from the Raison River at a range of 2.0 to 41.3 ppb, from the St. Clair River at a range of <2 to 2.7 ppb, and from the Calumet River at a range of 2.5 to 7.6 ppb.

A study by Oliaei (MPCA) in Lake Superior fish liver composites, including carp and lake trout, found PFOS at 14.6 ppb and 19.4 ppb, and PFOA at 2.47 ppb and 5.76 ppb.

PFC Contamination of Fish Fillet Tissue Samples - PFC analysis of selected fish fillet from the Mississippi River pool #2 fish collected in 2004 show that these fish fillet are contaminated with PFOS at levels ranging from 118 ppb to 985 ppb (Table 14). Although these limited PFC analyses in fillets are not adequate to allow a complete risk assessment to determine whether fish consumption restrictions are needed, the PFOS levels appear high enough to warrant immediate precaution.

Table 14 - PFC Contamination levels in Fish Fillet Tissue Samples from Mississippi River August 2004 (ng/g wet weight basis)

Fish Species	SMB #1-fillet	SMB #2a,#2b,#2c,2d-fillet	WB#2,#3,#4,#5-fillet
Age/Sex	8 year- female	2 year (3male/1female) composite	6 year (3 female/1 male) composite
PFHxA	< 0.558	< 0.650	< 0.767
PFHpA	< 0.491	< 0.803	< 0.750
PFOA	< 0.417	< 0.549	< 0.668
PFNA	< 0.495	< 0.576	< 0.680
PFDA	2.97	2.39	4.32
PFUnA	2.31	2.21	1.58
PFDoA	4.6	2.57	1.62
PFHxS	< 1.47	< 1.27	< 1.24
PFOS	985	118	139
PFOSA	31.3	4.87	3.74
Total	**1026.18**	**130.04**	**150.26**

PFC Contamination of Fish Blood Samples - Analysis of blood from the October 3, 2005 pool #2 Mississippi River fish collected downstream and proximate to the 3M Cottage Grove plant discharge, as shown in Table 15, indicate that the PFOS concentrations found in some fish blood are extremely high. In the White Bass species PFOS in blood ranged from 712 ppb to an extraordinarily high concentration of 29,600 ppb. Small Mouth Bass blood contained very high PFOS levels ranging from 1660 ppb to 4230 ppb. Carp blood contained very high PFOS levels ranging from 865 to 7980 ppb. Walleye blood contained PFOS levels ranging from 136 ppb to a high level of 2670 ppb. The one Small Mouth Buffalo fish blood contained a very high level of PFOS at 5840 ppb. PFOA was non-detect to low level concentrations in the blood of most fish, except for carp. Relatively low levels of PFOA were found in blood of Carp ranging from 0.87 ppb to 15.5 ppb. PFOA was also found in the blood of the Small Mouth Buffalo at 10.4 ppb. PFOSA (perfluorooctane sulfonamide) was also found in the fish blood of all species tested at relatively high levels. Other individual PFC compounds were found at lower concentrations in the fish blood. As shown in the table the cumulative total of PFCs in fish blood demonstrates that many of the fish tested have very high levels of total PFC concentration.

Table 15 - PFC Contamination Levels in Fish Blood Samples from Mississippi River
October 2005 (ng/ml = ppb)

Fish species	SMB1-B	SMB2-B	SMB3-B	SMB4-B	SMB5-B	SMB6-B	WB1-B	WB2-B	WB3-B	WB4-B	WB5-B
Length (mm)	280	264	236	280	229	261	319	380	315	251	362
PFBA	3.58	6.03	2.92	3.64	6.12	4.37	< 0.330	0.66	0.48	5.62	< 0.272
PFPeA	< 0.256	< 0.256	< 0.256	< 0.256	< 1.02	< 0.256	< 0.256	< 0.256	< 0.256	< 0.333	< 0.256
PFHpA	< 0.278	< 0.278	< 0.278	< 0.278	< 1.11	< 0.278	< 0.278	< 0.278	< 0.278	< 0.278	< 0.278
PFOA	0.31	< 0.236	< 0.236	< 0.236	< 0.944	< 0.236	< 0.236	< 0.236	< 0.236	11.30	< 0.236
PFNA	0.62	0.71	< 0.280	0.33	< 1.12	0.59	13.80	6.52	7.82	27.00	5.05
PFDA	51.30	54.80	34.90	46.10	32.90	52.90	75.00	28.90	49.10	210.00	25.30
PFUnA	43.00	35.50	31.50	42.40	25.50	47.70	40.90	13.60	20.20	83.50	10.70
PFDoA	71.30	44.30	29.90	57.80	27.60	48.40	32.90	9.19	18.00	92.10	9.36
PFBS	< 0.504	< 0.504	< 0.504	< 0.504	< 2.02	< 0.504	< 0.504	< 0.504	< 0.504	3.57	< 0.504
PFHxS	1.76	0.95	< 0.579	1.04	< 1.97	< 0.492	2.05	2.05	< 0.515	355.00	< 0.492
PFOS	4060.00	4230.00	1790.00	2640.00	1430.00	1660.00	5960.00	1010.00	2350.00	29600.00	712.00
PFOSA	372.00	294.00	111.00	355.00	70.00	182.00	244.00	96.00	92.20	1860.00	87.20
Total PFC	**4603.87**	**4666.29**	**2000.22**	**3146.31**	**1592.12**	**1995.96**	**6368.65**	**1166.92**	**2537.80**	32248.09	**849.61**

Fish species	WE1-B	WE2-B	WE3-B	WE4-B	CARP1-B	CARP2-B	CARP3-B	CARP4-B	CARP5-B	SM BUF-B
Length (mm)	724	546	490	715	527	572	570	643	671	533
PFBA	2.12	1.82	1.09	1.19	8.92	4.85	2.58	3.93	0.83	10.90
PFPeA	< 0.256	< 0.256	< 0.256	< 0.256	< 0.259	< 0.256	< 0.256	< 0.256	< 0.256	0.52
PFHpA	< 0.278	< 0.278	< 0.278	< 0.278	< 0.278	0.44	< 0.278	< 0.278	< 0.278	< 0.278
PFOA	1.22	< 0.236	2.40	< 0.236	15.50	0.87	6.30	10.30	1.11	10.40
PFNA	0.43	2.46	2.73	1.19	3.87	3.43	4.68	12.40	10.80	1.56
PFDA	2.53	12.70	28.50	8.52	50.10	23.80	27.30	63.10	32.60	37.20
PFUnA	1.36	5.57	13.00	4.88	28.00	9.82	11.10	22.20	13.70	27.80
PFDoA	1.20	5.27	14.60	3.58	31.90	8.00	8.04	16.90	8.52	36.00
PFBS	< 0.504	< 0.504	< 0.504	< 0.504	1.83	< 0.504	< 0.504	0.57	< 0.504	1.72
PFHxS	1.71	0.98	11.90	0.98	30.60	2.16	8.52	34.20	2.83	14.70
PFOS	136.00	860.00	2670.00	385.00	4070.00	865.00	1800.00	7980.00	883.00	5840.00
PFOSA	41.50	109.00	555.00	101.00	292.00	10.70	61.20	104.00	30.70	1150.00
Total PFC	**188.07**	**997.80**	**3299.22**	**506.34**	**4532.72**	**929.07**	**1929.72**	**8247.60**	**984.09**	**7130.80**

SMB-B = Blood sample of smallmouth bass
WB–B = Blood sample of white bass
Carp-B = Blood sample of Common carp
WE-B = Blood sample of small walleye
SM BUP-B = Blood sample of small mouth buffalo

Levels of PFC Contamination in Mississippi River Fish Blood Compared to Other Studies
There is limited information available in the literature for PFCs in fish blood. Based on a review of the literature, the concentrations of PFOS and the other PFC compounds found in fish blood in this study are significantly higher than those found in other studies.

PFOS was found in blood of fishes in a study in Japan at levels ranging from 2 to 834 ppb (Taniyasu et al, 2002). In a study of Mediterranean sea animals by Corsolina and Kannan (2004) PFOS was found in blood of bottlenose dolphins at concentrations ranging from 42 to 210 ppb. PFOA and PFHxS was found in bottlenose dolphin blood at levels of <2.5 ppb to 6.1 ppb. PFOS was found in blood of bluefin tuna and swordfish at levels ranging from 27 ppb to 52 ppb and 4 ppb to 21 ppb, respectively

Most of the PFCs analyses in blood have been done on animals. In the Global Biomonitoring of Perfluorinated Organics study by Giesy et al, 2001, PFOS was found in blood of ringed and grey seals from the Canadian and Norwegian Arctic at levels ranging from 3 to 50 ppb. PFOS concentrations in seals from the Baltic Sea were found at 14 to 230 ppb. PFOS in blood plasma and serum of Layasan and black footed albatrosses contained PFOS at a range of 3 to 26 ppb. The Giesy study found that PFOS concentrations in the blood of cormorants and herring gulls from the North American Great Lakes were about 10 times higher than those found in the albatrosses. The Giesy study found that blood plasma from bald eagle fledglings from the midwestern U.S. contained probably the highest levels of PFOS at 2570 ppb.

To our knowledge based on a review of the currently available literature, the PFOS levels found in the blood of fish collected October 3, 2005 from the Mississippi River pool #2 area in this study are the highest PFOS levels found in any animals tested worldwide.

5. Levels of PFC Contamination in Mississippi River Fish Cause for Immediate Concern

The high concentration levels of PFOS and PFCs found in the livers of fish collected in 2004, and the very high concentration levels of PFOS and other PFCs found in blood of fish collected October 3, 2005 from the Mississippi River pool #2 area are a cause for immediate concern. PFC analysis on fillet and whole fish samples of the October 3, 2005 fish collected from the Mississippi River pool #2 area, and PFC analysis on fillet and whole fish samples of the October 4-5, 2005 fish collected from the Mississippi River Lake Pepin area should be pursued as soon as possible in order to assess risk imposed by humans and wildlife consuming these fish.

The bioavailability of PFOS and other PFCs for accumulation in these fish needs to be understood, and bioavailability will vary dependent upon fish species and habits. PFOS has been found to resist biodegradation in any media including sediments. It needs to be determined if sediments containing PFCs from past discharges serve as a “reservoir” source of contamination exposure to fish through redissolution into the water column, bioconcentration through the food chain, or other mechanisms. Other organic contaminants,

such as PCBs, have continued to pose and cause contamination of fish due to their resistance to biodegradation and long term residence in the aquatic environment, including sediments.

PFC contamination found in the fish collected near the vicinity of the 3M discharge are likely the result of exposure to PFCs discharged from the 3M Cottage Grove plant.

6. Summary Report

- Analysis of fish in the Mississippi River, collected in August 2004 and October 2005, demonstrate that these fish are heavily contaminated with PFC compounds, predominantly PFOS.

- The PFOS concentrations found in fish livers are at high levels and are indicative of exposure to a PFC contamination source, the 3M discharge.

- PFOS levels and its bioaccumulation in these fish are expected to continue for long periods.

- There are differences in the bioaccumulation rate of PFCs in the fish species included in this study.

- Past discharge concentrations of PFOS from the 3M Cottage Grove plant indicate that at times the discharge could have caused toxic effects on fish. This would have occurred prior to the PFOS related and PFOA production phase-out. The limited data available show that the PFOS concentration, at times, could have exceeded the NOEC level for fathead minnows of 300 ppb at the point of discharge.

- PFOS levels in the Mississippi River fish liver are similar to levels studied in Belgium. The high PFOS levels in fish liver collected near a fluorochemical production plant in Belgium were associated with serum ALT activity, a marker for hepatic damage, showing that PFOS may induce liver damage to fish at these levels.

- The PFOA perfluorochemical was found at very low levels or non-detect in fish livers tested, and is consistent with its low bioconcentration rate, and the results of PFOA in other studies.

- The one smallmouth bass for fish collected in 2004 in this study contained a very high level of PFOS in liver, 6350 ppb, and is comparable to the highest PFOS levels found in fish liver to date worldwide, based on our knowledge and review of the literature.

- Young small mouth bass (2 year olds) livers contained relatively high levels of PFOS at 1030 ppb, even though the levels of PFOS and other PFCs in the 3M discharge have been reduced during this 2 year period since termination of PFOA and PFOS related production by the end of 2002. The mechanism of bioavailability for exposure to fish needs to be understood, and whether sediments contaminated with

past PFC discharges continue to be a source for contamination exposure to fish and aquatic life.

- The levels of PFOS found in blood of fish collected on October 3, 2005 from the Mississippi River pool #2, downstream and proximate to the 3M Cottage Grove plant discharge, are extraordinarily high and are the highest in blood of any animals tested worldwide, to our knowledge based on a review of the literature.

- The PFOS and related PFC contamination levels found in fish in this study may pose a risk to humans and wildlife consuming these fish, which requires immediate assessment.

7. Immediate Need for further Investigation of PFC Contamination in Fish from Mississippi River

- Fish collected in October 2005 in the Mississippi River pool #2 and the Mississippi River Lake Pepin should be immediately analyzed for PFCs in fillet and whole fish to determine the risk associated with human and wildlife consumption. These analyses and risk assessment should be done as soon as possible to assess the need for a fish consumption advisory.

- Analysis of more fish may be necessary to be able to adequately characterize PFC contamination levels in Mississippi River fish.

- Other aquatic species including fish from lower trophic levels should be analyzed and a model for bioaccumulation of PFCs should be developed.

- The relationship between PFC levels in Mississippi River water and sediment and availability and bioaccumulation in fish needs to be understood. The mass of PFCs in sediments needs to be assessed for potential as a continuing source for aquatic life exposure.

- It would be prudent to test PFCs in higher trophic levels (wildlife biomonitoring), including mammals and birds, consuming contaminated fish, considering the PFOS contamination levels found in fish blood and liver in this study.

- An analysis of fish contaminant trends and other media analyzed (water and sediment) should be completed.

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