MPCA PFC Investigation
June 30, 2005

The MPCA investigation described in this sampling report consists of sampling and subsequent analysis of perfluorocarbon compounds (PFCs) in various environmental media. This sampling study was undertaken in order to begin to determine the presence and extent of contamination of PFCs in the Minnesota environment, to enhance and complement other PFC characterization studies underway, and to begin to study the behavior of these compounds in various environmental media. The MPCA sampling program was conducted by the following MPCA staff: Fardin Oliaei, Joe Julik, Ingrid Verhagen, Katrina Kessler, Enrique Gentzsch, Harold Wiegner, and Don Kriens. Minnesota Department of Natural Resources staff collected all fish for PFC analyses in this study. This report was prepared by the above noted MPCA staff. This report provides only a brief analysis and discussion of sampling procedures and quality assurance program items.

This sampling report discusses the PFC study projects undertaken by MPCA staff, during the fall 2004 and spring/summer 2005 to date, to assess PFC contamination. This sampling report is divided into subsections, including sampling efforts at the Mississippi River, the 3M Cottage Grove wastewater treatment plant, the Washington County Landfill, the Pine Bend Landfill, the MCES Metro wastewater treatment plant, and fish sampling/collection on the Mississippi River. Each subsection discusses the project basis for sampling at that site, any specific sampling QA/QC, and also provides for attachments for each sampling project. The attachments include a table which describes each sample, laboratory ID, date of sampling, brief sample description or type, analytical parameters, and specific sample locations including GPS coordinates where applicable. Maps are also provided in some cases. Chain of custody forms are provided for each project. Additional attachments may be added at a later date to provide more complete information.

A final data assessment report is anticipated to be prepared for this work summarizing the results and findings, technical issues and chemistry regarding these finding, and further MPCA PFC study requirements based on these findings.

This MPCA PFC sampling effort is intended as a first phase study and is intended to be independent of, but complementary to, the 3M Weston PFC study. It also provides for a much more complete evaluation of the PFC compounds in the media studied, since 12 individual PFC compounds are analyzed as a part of the MPCA studies versus the 4 PFCs proposed in the 3M Weston study. If any intermediate study results elucidate improved understanding of the behavior of the PFC compounds in environmental media, find unexpected PFC concentrations, or otherwise provide useful information, recommendations may be made regarding sampling techniques, locations, media, etc to others conducting PFC studies.

MPCA staff undertook this sampling program due to the relative ubiquitous nature of PFC contamination in the environment. In addition this sampling program was undertaken as a result of studies completed to date which demonstrate the toxicity and extreme persistence of these compounds, the high degree of bioaccumulation, the widespread presence of concentrations of certain PFC compounds found in human blood, the presence in Minnesota of the 3M Cottage Grove plant which produced PFCs, and the known presence of these compounds at specific contaminated sites and the discharge from the 3M Cottage Grove plant. It would have been useful to have initiated this sampling effort earlier when significantly greater concentrations of PFC compounds were discharged from the 3M Cottage Grove plant. Furthermore, earlier assessment of PFC contamination in groundwater and wells would have allowed prior notification. However, these studies will provide useful data for any further assessments by MPCA staff and other entities.

Background on the Perfluorochemical Problem

The 3M plant at Cottage Grove produced perfluorochemical compounds (PFCs) for several decades. As a result of the PFC production processes, wastewater, fluorocarbon production wastes and byproducts, and sludges were generated. Wastewater was discharged from the 3M Cottage Grove wastewater treatment plant to the Mississippi River. Limited analyses of the discharged wastewater show that PFCs were discharged at high concentrations in the past. PFC concentrations in the discharge may have contaminated river sediments and resulted in bioaccumulation of these compounds in aquatic organisms and fish.

In addition, PFC wastes from the production processes were deposited at several sites at the 3M plant site and other locations. PFC disposal at the 3M site has caused PFC contamination of groundwater beneath the 3M Cottage Grove site. Two notable PFC waste deposit locations off site include the Oakdale Dump and the Washington County Landfill. PFC waste deposits at these sites have resulted in the contamination of groundwater with PFCs under and downgradient of these sites. Residential wells and drinking water supplies at certain locations have now been found to be contaminated with certain PFCs tested. Some of the residential wells contain levels of PFOS (perfluorooctane sulfonate) that exceed the drinking water standard or HBV (health based value) recently established by the Minnesota Department of Health. The extent of PFC contamination at these sites is unknown and is under investigation.

The PFC family is characterized by chains of carbon atoms of varying lengths, to which fluorine atoms are strongly bonded, producing extremely stable chemicals that until recently were thought to be biologically inert. PFCs have been shown to cause specific toxicity in several biological systems, and are extremely persistent chemicals that contaminate human blood and wildlife. Certain PFCs bioaccumulate readily up the food chain. Scientists have been especially concerned because unlike many other toxic chemicals, the most pervasive and toxic members of the PFC family (PFOS and PFOA) are not known to degrade in the environment. PFOS and PFOA were designed to not degrade and may persist on the order of centuries.

PFOS (perfluorooctane sulfonate) is a member of a large family of sulfonated perfluoro-chemicals produced by 3M, which were used during the last 50 years in a wide variety of industrial, commercial, and consumer products. These chemicals are a component of soil and stain-resistant coatings for fabrics, leather, furniture, and carpets (under the 3M Scotchgard line); used in fire-fighting foams, commercial and consumer floor polishes, cleaning products, and as a surfactant in other specialty applications. Although, final formulations for these uses contain less than 1% of the PFOS, all sulfonated perfluoro-chemicals have the potential to degrade back to PFOS which does not appear to degrade further.

According to EPA, PFOS is of significant concern on the basis of evidence of widespread human exposure and indications of toxicity.....These chemicals "combine persistence, bioaccumulation, and toxicity properties to an extraordinary degree." In May 16, 2000, following negotiations with EPA, 3M announced that it would voluntarily phase out perfluorooctanyl sulfonate (PFOS) chemistry by year 2002. This negotiation began as a result of data 3M supplied to the EPA which indicated that these chemicals are very persistent in the environment and have a strong tendency to accumulate in human and animal tissues and could potentially pose a risk to human health and the environment over the long term (EPA-OPPT: AR226-0629).

3M Corporation is the sole US manufacturer of the PFOS family of chemicals, and appears to be the dominant producer in the world. In the 50 years between the start of commercial production and the phase out announcement, many millions of pounds of PFOS chemicals have entered the environment and now contaminate the blood of people and wildlife to an extraordinary extent. PFOS has been found widely in human blood samples (ppm levels in manufacturing workers, and ppb levels in non-exposed workers and in blood bank samples). PFOS has also been found in the wildlife species across the US (especially in fish eating birds). PFOS accumulates to a high degree in humans and animals. It has an estimated half-life of 4-8 years in humans.

Although research is still evolving, PFOS is known to damage the liver and to produce birth defects in lab animals, among other health effects. PFOS caused postnatal deaths and other developmental effects in offspring in a 2-generation reproductive effects study done on rats (NOAEL-no observable adverse effect level of 0.1 mg/kg/day and LOAEL-lowest observable adverse effect level of 0.4 mg/kg/day). At higher doses in this study, all progeny in first generation died while at the LOAEL many of the progeny from the second generation died, a very unusual second generation effects. Based on the evidence of widespread human exposure and indications of toxicity in a 2 generation rat study, EPA considers PFOS a significant environmental contaminant of concern. In the preliminary risk assessment conducted by EPA, margins of exposure (MOEs) for workers and possibly the general population were recommended.

After 3M "announced its phase out of the perfluorooctanyl chemistry (8 carbon or C-8 chain fluorocarbons) 3M derived perfluorobutane sulfonate (PFBS) as an alternative. The C-8 perfluorocarbon production phase-out began in 2000 and was completed by the

end of 2002. The PFBS is a four-carbon cousin of the chemical in the old Scotchgard, and is the building block for Scotchgard's new generation. 3M received EPA approval for, and is manufacturing, 18 new fluorochemicals. These new fluorinated compounds are based on this 4 carbon (C-4) PFBS compound, and thus serve as substitutes for the 8 carbon chain perfluorinated chemicals associated with PFOS, PFOA, etc. Although there are significant uncertainties surrounding the behavior of fluorocarbon compounds in general in the environment in the areas of partitioning behavior, degradation, chronic toxicity and bioaccumulation, 3M conducted some 40 toxicity and other tests to demonstrate the relative non-toxicity of these PFBS-based fluorochemicals.

The significance for bioaccumulation and toxicity of the PFBS substitute for C-8 fluorocarbon production has not been completely evaluated at this time. However, PFBS and related C-4 fluorochemicals will remain very persistent in the environment since they are relatively non-biodegradable, by design, and it is anticipated that concentrations of PFBS will "accumulate" in blood of humans. The PFBS levels in blood are expected in part due to the ubiquitous nature of the PFBS based fluorochemical products and also likely due to a relatively higher volatility versus PFOS, PFOA, etc.

There is some information that suggests that the half life of the shorter perfluorinated compounds is longer than C-8 based compounds in humans. Although a very brief review of tests completed by 3M appears to demonstrate the relative non-toxicity of PFBS, any long term or chronic effects of these new fluorochemicals are of course unknown. Because of the heightened sensitivity and awareness of the toxicities associated with PFOS, PFOA, and related higher chain fluorochemical compounds, it may be prudent to begin some evaluation of the new C-4 PFBS chemicals, in order to respond in an informed fashion to any inquiries.

The MPCA requires monitoring for PFBS monthly in the 3M Cottage Grove wastewater treatment plant discharge, pursuant to the NPDES permit, but little monitoring for PFBS in other media and locations has been completed to date.

MPCA Mississippi River PFC Sampling

Sampling was conducted on the Mississippi River in pool 2 above, below, and proximate to the 3M Cottage Grove facility. 3M 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 prior to discharge to the Mississippi River. Water and sediment samples were taken upstream (above) and downstream (below) of the 3M discharge point (cove area) in the Mississippi River, and within the cove. Water and sediment samples were taken at 5 separate locations including: a water and sediment sample just upstream of the 3M discharge (cove) and the MCES Eagle Point WWTP discharge, water and sediment samples for 3 separate downstream locations (number # 1, # 2, and # 3 downstream), and water and sediment samples of the cove area. See the attached map and description, including GIS coordinates, for samples taken in the Mississippi River and in the cove. All sampling for this project occurred between about 11AM and 8PM on May 20, 2005.

Basis for Sampling

The basis for collection of samples in the Mississippi River is related to the decades of discharge of fluorocarbons into the river from the 3M Cottage Grove wastewater treatment plant (WWTP). Beginning in 2000 3M began its phase-out of production of perfluorooctanyl or C-8 (8 carbon chain PFC) compounds, substituting with 4 carbon chain based fluorocarbon (C-4) compounds. Phase-out was completed by the end of 2002. Limited data was available for PFCs discharged to the river in the WWTP effluent since 3M did not routinely monitor these compounds prior to and during the phase-out. PFC concentration data for the WWTP discharge for a Jan-March 2000 period, conducted by 3M, was available and likely represents PFC concentrations in the 3M discharge prior to the C-8 production phase-out beginning in 2000. Based on the Jan-March 2000 WWTP discharge PFC data, which includes analysis of only 5 PFC compounds, 3M discharged about 50,000 lbs per year of PFC compounds to the Mississippi River. Preliminary calculations, based on the Jan-March 2000 WWTP discharge concentration data and using average river flows for a period of 1980 through 2000, show that the total PFC mixed river concentration (all of the river) would have averaged about 1.88 ug/l. The mixed river concentration of the individual PFOS compound would have averaged about .55 ug/l. At times, especially in low flow years, the mixed river concentration of PFOS (perfluorooctane sulfonate) may have exceeded the recently established PFOS drinking water standard of 1.0 ug/l. Given the probable high mass of PFCs discharged to the river and the significant mixed river PFC concentrations, the long term persistence of these compounds in the environment, the extreme bioaccumulative nature of certain PFCs, and the known toxicity associated with these compounds, this study was warranted as an initial assessment of the impact of these compounds on the aquatic environment proximate to the 3M discharge.

It would have been useful to have been able to monitor the impact of the 3M PFC discharge on the river before or during the 3M production phase-out, in order to more fully assess the impact of these PFCs when very high PFC and PFOS concentrations were

discharged. Beginning in December 2002 3M was required to monitor for 5 PFC compounds in its discharge pursuant to the 3M NPDES (National Pollutant Discharge Elimination System) permit. Since the PFC C-8 production was phased-out by the end of 2002, PFOS concentration levels in the 3M discharge have diminished significantly. Other individual PFCs also show reductions, but to a lesser degree. PFBS (perfluorocarbon butane sulfonate), a C-4 fluorochemical, increased in concentration in the 3M discharge after 2002 due to the change in production from C-8 based fluorochemicals to C-4 based fluorochemicals. In January 2004 3M completed installation of a new granular activated carbon system to treat the discharge. The activated carbon system was required pursuant to the NPDES permit issued February 1, 2003. The activated carbon system has provided for a significant reduction in PFOS discharge concentrations and also reduced other PFC concentrations, but to a lesser extent, based on the 5 PFCs analyzed pursuant to the NPDES permit.

Although generally highly water soluble, PFCs may have been attached, in part, to the suspended solids material discharged from the 3M WWTP (biological activated sludge system). Although operation of the activated carbon system has provided for a reduction of PFCs discharged, especially PFOS, it is possible that adsorption and attenuation of PFCs to sediments may have occurred because of the high PFC mass previously discharged. Some of the PFC attached solids may have deposited in the river discharge area (river cove) and the river downstream of the 3M discharge. Sampling in the river environment is very complicated by the fluvial mechanics and geomorphology of the river, sediment grain size and organic content affecting the affinity for organic compound adsorption, and other factors which will cause significant variances in organic contaminant concentrations in sediments. Flood conditions and changing flows would also affect sediment transport. This assessment is not intended to determine the differential deposition of sediments over time or the differential concentrations of PFCs according to depth. Only the top 10 cm of the cores were submitted for analysis. Four sampling locations were used to obtain a composite to minimize variables in PFS sediment distribution. This limited number of samples using surficial cores will not fully characterize PFC concentrations deposited in sediments proximate to the 3M plant, and is intended only as an initial examination.

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 to attempt to acquire somewhat older sediment cores where potential deposition of 3M discharge solids may have occurred. No assessment was made to evaluate the plume location for the 3M discharge but it is expected under typical river flow conditions to track 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 3M discharge flow would be expected to be relatively fully mixed within the river. It is unknown whether suspended solids discharged from 3M would deposit prior to lock and dam # 2, which contributes to the preliminary nature of this assessment.

The MPCA has not derived discharge limitations or criterion for PFOS or other PFC compounds, with respect to aquatic toxicity or human health. Acute toxicity data available through testing conducted by 3M contractors indicate that the discharge would not have been acutely toxic to aquatic life tested. However, the discharge may have caused chronic toxicity effects in the past. For example, the 42 day NOEC (no observable effect concentration-survival) for PFOS for fathead minnows was determined to be 300 ug/l. The Jan-March 2000 3M analysis of the WWTP discharge, likely representative of the pre-production phase-out concentrations, determined a PFOS concentration in the 3M discharge at 1403 ug/l. Other PFOS data completed during the PFOS production phase-out also demonstrate high PFOS discharge levels in excess of the NOEC for fathead minnows. Therefore, the 3M discharge may have had chronic impacts on aquatic life on at least portions of the river near the discharge.

Sampling and QA/QC

Water samples from the river and cove locations were obtained by a direct method through direct insertion of the sample container in the river by hand to a depth 2 ft below the surface. This was accomplished by inserting the bottle downward, maintaining an air gap, until a depth 2 ft depth was reached. The bottle was inverted facing upstream at the 2 ft depth to collect the sample. Sample containers consisted of polypropylene bottles with screw cap lids. Sample bottles were prepared by the laboratory (methanol rinsed, deionized water, air dried) and were maintained in a sealed condition at all times until use. New nitrile gloves were used for each water sample collection. Once filled, water sample bottles were sealed individually in a zip lock bag and stored in a cooler at 4 degrees C. In addition to the 2 ft below depth sample, a surface water sample from the cove area was collected. This was obtained by direct skimming of the sample container at the surface of the cove water. The use of Kemmerer water sampling or sampling via other sampling equipment such as peristaltic pump was avoided to minimize potential cross contamination problems.

Sediment samples were collected at each of the water sample locations and were obtained by compositing 4 separate sediment cores. All 4 separate sediment core locations were generally within 100 ft from one to the next. 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. The first location of the 4 core composite for river samples corresponded to location for the water sample. All sediment cores were obtained using a MPCA core sampler with a stainless steel core tube. The top 10 cm (surface to 10 cm below) was extruded from the top of the core tube. These 4 surficial sediment subsamples were thoroughly mixed together to form the composite sample in a precleaned and methanol rinsed stainless steel bowl using a precleaned and methanol rinsed stainless steel spatula for mixing. The core tube, mixing bowl and spatula were cleaned by brushing with non phosphate detergent and site water, multiple rinses with site water, and thorough rinsing with methanol prior to sampling the composite locations. Cleaning was not done between each individual core since the core subsamples were composited for the analytical sample. Sample containers for the composited sediments consisted of

polypropylene bottles with screw cap lids. Sample bottles were pre-cleaned by the laboratory (methanol rinsed, deionized water, air dried) and were maintained in a sealed condition at all times until use. New nitrile gloves were used for each sediment sample collection. Once filled, sediment sample bottles were sealed individually in a zip lock bag and stored in a cooler at 4 degrees C.

Sediments collected had similar grain size distribution consisting predominantly of silts, with some clays and fine sandy loams, based on visual/textural analysis.

In addition to the water and sediment samples, a sample was taken of algae material from the cove area. Significant amounts of algae masses were observed at the cove. Algal material was obtained by direct and repeated skimming of a sample container on the water surface, collecting the algae. QA/QC procedures noted above for water sampling were followed.

One algal material sample, 6 water samples, and 5 sediment composite samples were obtained. See the attached Mississippi River PFC Sampling table which describes the sample location, matrix or type, date and time of collection, laboratory ID number, sample collection description, GPS coordinates where applicable, and parameters. All field data was recorded by hand in tablet, and records were maintained.

Analysis will be completed on all samples for the following PFC compounds: PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFBS, PFHxS, and PFOS.

In addition to the above noted specific procedures, all general QA/QC procedures for PFC sample collection were followed for all media sample collections. These include QA/QC procedures such as field personnel wearing only multiple washed clothing, no water resistant clothing or materials, no tyvek materials, use of nitrile or polypropylene gloves worn at all times during collection and handling of samples, replacement of gloves for each sampling, avoidance of any food wrappings, precleaning of all sampling equipment, no post it notes, avoidance of any microwave popcorn, no aluminum foil, no teflon materials used, and so on. MPCA staff in general followed QAP procedures used by 3M for prior investigations except that Kimwipes or similar lab wipe materials used in prior investigations were not used because of the MPCA contract laboratory (Axys Laboratory) finding that these materials subject samples to PFC contamination. (3M was advised of this finding.)

Equipment: MPCA sampling boat, MPCA core sampler with stainless steel core tube, GPS equipment, stainless spatulas-bowls, nitrile gloves, decontamination equipment and solvents, waste bags, coolers, ice, pre-prepared sample bottles and blanks, plastic zip lock bags, field data sheets, chain of custody forms, safety equipment, rinse bottles, GPS hand held, hip boots and waders, petite ponar dredge (not used), etc.

Specific Attachments for MPCA Mississippi River PFC Sampling: Mississippi River PFC Sampling Table, Map of samples on river with GPS data, including boat travel log,

Chain of Custody, General map of river area with channel locations, 3M Monthly PFC Discharge Data for SD001

Common Attachments: Axys Laboratory sheet for Collection and Handling of Samples for Analysis of PFOA, PFOS, and Other Fluorinated Compounds, Quality Assurance Project Plan for Empirical Human Exposure Assessment Multi-City Study Sampling Task (Battelle QAP)

MPCA Mississippi River PFC Sampling

Sample Location	Matrix	Date	Axys ID	description	GIS coordinates	Parameters
river upstream of 3M	water	5/20/2005	L7835-8	surface 2ft below	attached sheets	12 PFCs
river upstream	sediment	5/20/2005	L7835-14	4 sample composite, 10 cm depths	attached sheets	12 PFCs
river cove	water	5/20/2005	L7835-9	surface 2 ft below	attached sheets	12 PFCs
river cove	water	5/20/2005	L7835-10	surface top	attached sheets	12 PFCs
river cove	algal material	5/20/2005	L7835-3	surface	attached sheets	12 PFCs
river cove sediment	sediment	5/20/2005	L7835-15	4 sample composite, 10 cm depths	attached sheets	12 PFCs
#1 river downstream of 3M	water	5/20/2005	L7835-11	surface 2ft below	attached sheets	12 PFCs
#1 river downstream of 3M	sediment	5/20/2005	L7835-5	4 sample composite, 10 cm depths	attached sheets	12 PFCs
#2 river downstream of 3M	water	5/20/2005	L7835-4	surface 2 ft below	attached sheets	12 PFCs
#2 river downstream of 3M	sediment	5/20/2005	L7835-6	4 sample composite, 10 cm depths	attached sheets	12 PFCs
#3 river downstream of 3M	water	5/20/2005	L7835-2	surface 2 ft below	attached sheets	12 PFCs
#3 river downstream of 3M	sediment	5/20/2005	L7835-7	4 sample composite, 10 cm depths	attached sheets	12 PFCs
field blank	water	5/20/2005	L7835-12			
natural spring water-blank	water	5/20/2005	L7835-13			

MPCA 3M Cottage Grove Plant PFC Sampling

PFC sampling was conducted at the 3M Cottage Grove plant on June 27, 2005. Samples were collected from the treated process wastewater discharge SD001, the cooling water discharge SD002, the wastewater treatment plant influent (Phase 1 and 2), and the influent and effluent of the Phase 1 and 2 granular activated carbon treatment system. PFC sampling was conducted at the plant at these locations as a normal part of the NPDES program, to more fully characterize the PFC compounds discharged by analyzing 12 PFCs versus the 5 PFCs typically analyzed, to determine the performance of the wastewater treatment plant and the Phase 1 and 2 activated carbon treatment system on the day of sampling, and to determine the extent of PFC compounds in the SD002 cooling water on the day of sampling. All samples for PFC analysis were collected on June 27, 2005.

Basis for Sampling

3M operates a wastewater treatment plant (WWTP) which treats all production process wastewater generated from the plant and discharges treated wastewater to the Mississippi River, pursuant to authorization by NPDES Permit MN0001449. The wastewater treatment system is separated into 3 phases. Phase 1 wastewater contains primarily inorganic constituents and is treated primarily by pH adjustment, neutralization, and clarification. Phase 2 wastewater contains primarily organic constituents and is treated primarily by equalization, activated sludge system, and clarification. Clarified effluent from Phase 2 is further treated through the Phase 1 pH adjustment and clarification system. The combined Phase 1 and 2 are directed to a granular activated carbon treatment system prior to discharge into SD001. The Phase 3 system treats wastewater from the plant's hazardous waste incinerator which contains primarily inorganic soot, ash, and acids scrubbed from the incinerator air emission. Phase 3 scrubber wastewater also contains metals and is treated by pH adjustment, metals precipitation, and clarification. After pH adjustment, metals precipitation, and clarification the Phase 3 wastewater is directed to the Phase 3 granular activated carbon treatment system prior to discharge into SD001. SD001 (surface discharge 001) contains the treated effluents after activated carbon treatment from Phase 1, 2 and 3. SD001 typically discharges at a rate of about 4 million gallons per day (MGD).

The plant uses cooling water for once through cooling purposes at the plant. Cooling water is supplied from plant production wells underlying the 3M Cottage Grove plant and is also supplied from pump-out water from a ground water barrier control system at a Woodbury site. Groundwater is pumped at the 3M Woodbury site to control spread of contaminants from a former 3M disposal site in Woodbury, MN. 3M Woodbury pump-out water is piped to the 3M Cottage Grove plant cooling water system. Cooling water used at the plant is once through and no treatment has been required. Cooling water is discharged from the 3M Cottage Grove plant via SD002.

SD001 (treated process wastewaters) and SD002 (cooling waters) are discharged to a ravine located proximate to the site which widens into a cove, discharging into the Mississippi River. The combined SD001 and SD002 are designated as SD003.

As a result of fluorochemical production at the plant, the SD001 discharge has historically contained very high levels of PFCs discharging to the river. The discharge of PFC compounds has occurred for decades from the plant into the river. Beginning in 2000 3M began its phase-out of production of perfluorooctanyl or C-8 (8 carbon chain PFC) compounds, substituting the C-8 compounds with 4 carbon chain based fluorocarbon (C-4) compounds. Phase-out was completed by the end of 2002. Prior to and during the C-8 fluorocarbon production phase-out limited data was available for PFCs discharged to the river in the WWTP effluent since 3M did not routinely monitor for these compounds. PFC concentration data for the WWTP discharge for a Jan-March 2000 period, conducted by 3M, is available and likely represents PFC concentrations in the 3M discharge prior to the C-8 production phase-out beginning in 2000. Based on the Jan-March 2000 WWTP discharge PFC data, which includes analysis of only 5 PFC compounds, 3M discharged about 50,000 lbs per year of PFC compounds to the Mississippi River before the phase-out. Preliminary calculations by MPCA staff, based on the Jan-March 2000 WWTP discharge concentration data and using average river flows for a period of 1980 through 2000, show that the total PFC mixed river concentration (all of the river) would have averaged about 1.88 ug/l prior to the production phase-out. The mixed river concentration of the individual PFOS compound would have averaged about .55 ug/l. At times, especially in low flow years, the mixed river concentration of PFOS (perfluorooctane sulfonate) may have exceeded the recently established PFOS drinking water standard of 1.0 ug/l.

The C-8 fluorocarbon phase-out, which was complete by the end of 2002, resulted in a reduction of the concentration of PFOS and other fluorocarbons discharged. (PFBS (perfluorocarbon butane sulfonate), a C-4 fluorochemical, increased in concentration in the 3M discharge after 2002 due to the change in production from C-8 based fluorochemicals to C-4 based fluorochemicals.)

In January 2004 3M completed installation and began operation of a granular activated carbon treatment system for the Phase 1 and 2 wastewater, required pursuant to the NPDES permit. The activated carbon system was installed primarily to remove alkyl phenol ethoxylate compounds which had previously caused acute aquatic toxicity and to provide for removal of organic compounds to meet federal discharge limitations. In addition, the MPCA sought installation of the activated carbon system to remove unknown or uncharacterized organic compounds that may be present in the 3M discharge. The operation of temporary production pilot projects at the plant means that the discharge is subject to changing organic composition.

The activated carbon treatment system was expected to reduce PFC concentrations in the discharge to very low levels or non-detect concentrations. Since the initiation of operation of the activated carbon system in January 2004 PFC concentrations in the discharge have dropped, although concentrations of individual PFCs in the discharge

persist. The levels of PFOS have dropped from pre-carbon treatment concentrations of 103 ug/l for the period December 2002 to December 2003, to 6.6 ug/l for the period January 2004 to present during which the discharge received activated carbon treatment. This decrease in concentration represents a 94% reduction in PFOS. The other PFCs analyzed routinely pursuant to the NPDES permit have shown the following reductions in concentrations for the same periods: PFHS 5.7 ug/l to 1.4 ug/l – 76% reduction, PFBS 676 ug/l to 193 ug/l – 71% reduction, PFOA 82.5 ug/l to 44.6 ug/l – 46% reduction, and PFHA 22 ug/l to 10 ug/l – 54% reduction. PFOA is not being removed as well as anticipated.

During the June 27, 20005 sampling effort samples were obtained at SD001 since it is routinely monitored by 3M, and will provide a check and comparison with NPDES data. SD002 was also sampled since it contains PFCs due to the contaminated Woodbury pump-out water. Sampling of SD001 and SD002 will allow a determination of that day's PFC contribution to the river. The influent and effluent of the Phase 1 and 2 activated carbon system will allow some brief assessment of the performance for removal of PFCs through the activated carbon system. The wastewater treatment plant influent was collected in order to assess the total influent PFCs to the wastewater treatment system and will also provide a brief assessment of the PFC removal performance of wastewater treatment plant before activated carbon, since the influent activated carbon sample may be used as an effluent sample for the wastewater treatment system (activated sludge system) before carbon treatment.

Sampling and QA/QC

The water sample from SD002 was obtained by using the plant's sample collection container at the SD002 sampling station. This PVC container is normally used by 3M for collection of PFC samples. The PVC sample container is connected via metal chain and is dipped into the SD002 parshall flume approximately 10 ft below. During the June 27, 2005 sampling effort the container was thoroughly flushed a couple times before sample collection. Samples were collected in the PVC container by 3M staff and poured directly into the PFC sample bottles. The water sample for SD001 was obtained by direct insertion of the sample bottle into the SD001 discharge parshall flume. No intermediate sampling device was used for SD001 sample collection. The 3M composite sampler for SD001 was not used due to the presence of teflon tape on portions of the sampler. The influent and effluent activated carbon treatment samples were collected by direct discharge of water into the sample bottles from sampling taps for these sources located on the influent and effluent ends of the Phase 1, 2 granular activated carbon treatment system. No intermediate sampling devices were used for the influent and effluent activated carbon treatment samples. The wastewater treatment plant (WWTP) influent was collected at the head of the wastewater treatment system after pH adjustment. The WWTP influent sample was collected by use of the PVC sample container at the WWTP influent channel. The sample container was flushed thoroughly before sample collection by insertion in the influent and discharging. Samples were collected in the container by 3M staff and poured directly into the PFC sample bottles.

Sample bottles for analyses consisted of 1 liter polypropylene bottles with screw cap lids. Two samples were collected at each location. Sample bottles were prepared by the laboratory (methanol rinsed, deionized water, air dried) and were maintained in a sealed condition at all times until use. New nitrile gloves were used for each water sample collection. Once filled, water sample bottles were sealed individually in a zip lock bag and stored in a cooler at 4 degrees C. The use of Kemmerer water sampling or sampling via other sampling equipment such as peristaltic pump was avoided to minimize potential cross contamination problems.

It should be noted that the activated carbon treatment system for Phase 3 wastewater was not in operation at the time of sampling due to change-out of the activated carbon for the Phase 3 system.

In addition to the above noted specific procedures, all general QA/QC procedures for PFC sample collection were followed for wastewater sample collection. These include QA/QC procedures such as field personnel wearing only multiple washed clothing, no water resistant clothing or materials, no tyvek materials, use of nitrile or polypropylene gloves worn at all times during collection and handling of samples, replacement of gloves for each sampling, avoidance of any food wrappings, precleaning of all sampling equipment, and so on. MPCA staff in general followed QAP procedures used by 3M for prior investigations except that Kimwipes or similar lab wipe materials used in prior investigations were not used because of the MPCA contract laboratory (Axys Laboratory) finding that these materials subject samples to PFC contamination. (3M was advised of this finding.)

Analysis will be completed on all samples for the following PFC compounds: PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFBS, PFHxS, and PFOS.

See the attached MPCA 3M Cottage Grove Plant PFC Sampling table for table for sample location, type, date, laboratory ID number, and parameters analyzed.

Equipment: Nitrile gloves, a trash receptacle, coolers, ice, pre-prepared sample bottles and blanks, plastic zip lock bags, field data sheets, chain of custody forms, safety equipment, rinse bottles, coolers, etc.

Specific Attachments for MPCA Mississippi River PFC Sampling: MPCA 3M Cottage Grove Plant PFC Sampling table, Chain of Custody

Common Attachments: Axys Laboratory sheet for Collection and Handling of Samples for Analysis of PFOA, PFOS, and Other Fluorinated Compounds, Quality Assurance Project Plan for Empirical Human Exposure Assessment Multi-City Study Sampling Task (Battelle QAP). MPCA also used portions of the sampling protocol described in the Proposed Quality Assurance Project Plan/Work Plan for the Polybrominated Diphenyl Ethers: Emerging Contaminants in Lake Superior (GL2002-184), where applicable for PFC sampling. See attached document.

MPCA 3M Cottage Grove Plant PFC Sampling

Sample Location	Matrix	Date	Axys ID	description	Parameters
WWTP influent	wastewater	6/27/2005	to be issued	raw untreated influent ww to phase 1,2 systems	12 PFCs
GAC influent	treated wastewater	6/27/2005	to be issued	influent ww to Phase 1, 2 GAC system	12 PFCs
GAC effluent	treated wastewater	6/27/2005	to be issued	effluent from Phase 1, 2 GAC system	12 PFCs
SD001	wastewater effluent	6/27/2005	to be issued	Treated process ww discharge, after GAC systems	12 PFCs
SD002	cooling water effluent	6/27/2005	to be issued	cooling water discharge	12 PFCs

MPCA Washington County Landfill PFC Sampling

PFC sampling was conducted at the Washington County Landfill and included water samples from groundwater monitoring wells (J and V2) located at the site, soil samples from soil borings conducted, water samples from surface water ponded at the site, soil samples from the surface below ponded water, and background soil from soil borings conducted were obtained. See the Washington County Landfill PFC Sampling Table for a description of samples, laboratory ID, date, and sample type.

Basis for Sampling

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 and residents were placed on alternate water supplies.

PFC compounds were detected in the ground water monitoring system at the landfill site during 2004. PFOA exceeded the Health Based Value at well nest E, the treatment area (TA-1), nest V and well Z. The average concentration (composite of a nest of wells) respectively was 11.1 micrograms per liter, 13.5 micrograms per liter, 45.7 micrograms per liter and 9.3 micrograms per liter. PFOA was found in the gradient control well at a concentration of 16 micrograms per liter. The presence of PFCs in the ground water caused the MPCA to initiate a feasibility study regarding treatment of these chemicals. The ground water remediation system at Washington County Landfill will have to be upgraded to treat these compounds.

Residential wells downgradient of the landfill were sampled 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.

An expanded residential well monitoring program for PFC contamination "downgradient" of the landfill in the Lake Elmo area was conducted in March April 2005 by the Minnesota Department of Health (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 at a number of wells. Expanded monitoring of residential wells is expected to continue to further determine the extent of fluorochemical contamination from the site.

The MPCA Washington County Landfill PFC Sampling study was completed to begin an initial assessment of the extent of PFC contamination in the soils and groundwater for the obvious reason that 3M had deposited flourochemical 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 study also evaluates 12 PFC compounds which have not been previously studied in the soils and groundwater at the site. 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.

Sampling and QA/QC

A soil boring was completed at a location right at the edge of the landfill treatment area (TA-1). The soil boring was completed to collect soil samples at specific depth increments. A MPCA Geoprobe Model 540B mounted on a Catepillar brand "bobcat" was used to collect soil boring samples. The spray irrigator was shut off immediately prior to sampling. The geoprobe was used to advance a soil core sampler. A PVC liner was placed inside the 2 inch diameter by 3 foot long metal soil core sampler. The core

sampler was advance two feet per sample. After extraction from the borehole, the PVC liner was then removed from the core sampler. A specialized blade was then used cut the liner in half laterally from end to end without disturbing the soil sample. The soil sample was then collected with a small sampling device in such a manner as only soil not in direct contact with the PVC liner were placed in the sample container. A new liner was then placed inside the core sampler for the next sample. This procedure was repeated to a depth of 24 feet at TA-1. The core sampler and liner were cleaned with soap and water and rinsed with lab grade water between each sample.

The geoprobe was then moved to a location ~100 feet northeast of TA-1 and background soil core samples were taken to a depth of 8 ft.

Soil boring core samples were placed in the sample containers. Sample containers consisted of polypropylene bottles with screw cap lids. Sample bottles were prepared by the laboratory (methanol rinsed, deionized water, air dried) and were maintained in a sealed condition at all times until use. Fresh nitrile gloves were used for each sample retrieval and collection. When necessary stainless steel scoops or spatulas were used to fill sample containers, and a stainless steel bowl was used when necessary to mix any soil sample contents. Stainless steel spatulas, scoops, and bowl were cleaned using decontamination procedures after each sample increment was collected. Once filled, sample bottles were sealed individually in a zip lock bag and stored in a cooler at 4 degrees C.

Soil samples were retrieved at specific depth increments within the soil boring as shown in the MPCA Washington County Landfill Sampling Table. Analysis of PFCs will be done at these increments to determine the extent of PFC soil contamination at various depths. The soil boring was completed at the TA-1 location since groundwater monitoring determined contamination of PFCs at this location. A background soil boring was completed in an area outside of the influence of the landfill site contamination. Soil samples were also collected at 4 specific depth increments for the background soil boring.

Two surface sediment or soil samples were collected at 2 areas where water had ponded as a result of the groundwater pump-out spray irrigation system. The ponded water would primarily consist of groundwater pumped out under the site. The sediment/soil samples under the ponded water were collected by stainless steel scoop and spatula precleaned using fluorocarbon decontamination procedures. Three subsamples (3-4 cm depth) were collected from two different sites. A mixing bowl was used to mix the collected three subsamples from each site and transfer into two different sample containers (Sediment #1 and Sediment #2). Sample containers consisted of polypropylene bottles with screw cap lids. Sample bottles were prepared by the laboratory (methanol rinsed, deionized water, air dried) and were maintained in a sealed condition at all times until use. Fresh nitrile gloves were used for each sediment/soil sample retrieval and collection. Stainless steel spatulas, scoops, and bowl were cleaned using decontamination procedures after each sample increment was collected. Once filled, sample bottles were sealed individually in a zip lock bag and stored in a cooler at 4 degrees C.

Ground water samples collected at wells J and V2 were collected during Fall Quarter 2004 sampling of the monitoring system at the landfill. Duplicate samples were collected by the sampling contractor, Interpoll Laboratories. One set was analyzed by MDH Environmental Laboratory and the other set was provided under Chain of Custody procedures to Dr. Oliaei for analysis by Axys Laboratory. These samples were collected following the protocol outlined in *Minnesota Pollution Control Agency Closed Landfill Program Sampling Protocol for Monitoring Wells, updated April 22, 2005.* (The basic protocol is to purge the pump until the well stabilizes with respect to pH +/- 0.1 units, specific conductance +/- 5% and dissolved oxygen +/- 0.5 mg/L). A dedicated Grundfos Rediflo 2™ pump is installed in well V2 and a portable precleaned Grundfos Rediflo™ pump was used in well J. The tubing in both of these pumps is Teflon lined polyethylene. The MDH reporting limits are <1.0 and <0.5 ug/L respectively but there were no estimates below these levels of PFOS or PFOA in well J. Axys Laboratories analyzed the sample from well J at the ng/mL level and detected only 0.001 of PFNA and 0.002 of PFDoA but not PFOS or PFOA. Samples were collected by the Washington County Landfill sampling contractor using the Battelle protocol for PFCs. Sample containers consisted of polypropylene bottles with screw cap lids. Sample bottles were prepared by the laboratory (methanol rinsed, deionized water, air dried) and were maintained in a sealed condition at all times until use. Fresh nitrile gloves were used for each water sample retrieval and collection. Once filled, sample bottles were sealed individually in a zip lock bag and stored in a cooler at 4 degrees C.

Two surface water samples were collected from ponded water at the site. The ponded water represents water from the groundwater pump-out spray irrigation system. Surface water was collected by direct careful skimming of the ponded water into sample containers. 250 ml sample containers were used due to the smaller diameter bottle opening. The 250 ml sample containers consisted of polypropylene bottles with screw cap lids. Sample bottles were prepared by the laboratory (methanol rinsed, deionized water, air dried) and were maintained in a sealed condition at all times until use.

All samples will be analyzed for the following PFC parameters: PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFBS, PFHxS, and PFOS.

In addition to the above noted specific quality control procedures, all general QA/QC procedures for PFC sample collection were followed for all media sample collections. These include QA/QC procedures such as field personnel wearing only multiple washed clothing, no water resistant clothing or materials, no tyvek materials, use of nitrile or polypropylene gloves worn at all times during collection and handling of samples, replacement of gloves for each sampling, avoidance of any food wrappings, precleaning of all sampling equipment, no post it notes, avoidance of any microwave popcorn, no aluminum foil, and so on. MPCA staff in general followed QAP procedures used by 3M for prior investigations except that Kimwipes or similar lab wipe materials used in prior investigations were not used because of the MPCA contract laboratory (Axys Laboratory) finding that these materials subject samples to PFC contamination. (3M was advised of this finding.)

Soil boring and surface soil and water samples were taken by experienced MPCA staff. Chain of custody procedures were followed and documented.

Equipment: MPCA Geoprobe Model 540B, RS60 sampler, polyethylene core liners, stainless steel spatula and scoop, stainless steel bowl, nitrile gloves, decontamination equipment and solvents, waste bags, coolers, ice, pre-prepared sample bottles and blanks, plastic zip lock bags, field data sheets, chain of custody forms, safety equipment, rinse bottles, groundwater sampling and testing equipment, etc.

Specific Attachments for MPCA Washington County Landfill PFC Sampling: Washington County Landfill PFC Sampling Table, Chain of Custody, Map of Groundwater Monitoring Network around Washington county Landfill

Common Attachments: Axys Laboratory sheet for Collection and Handling of Samples for Analysis of PFOA, PFOS, and Other Fluorinated Compounds, Quality Assurance Project Plan for Empirical Human Exposure Assessment Multi-City Study Sampling Task (Battelle QAP).

MPCA also used portions of the sampling protocol described in the Proposed Quality Assurance Project Plan/Work Plan for the Polybrominated Diphenyl Ethers: Emerging Contaminants in Lake Superior (GL2002-184), where applicable for PFC sampling. See attached document.

MPCA Washington County Landfill PFC Sampling

Sample Location	Sample Type	Date collected	Axys ID	Description	Parameters
surface water	water	11/22/2004	L7419-1	water ponded on surface	12 PFCs
surface water	water	11/22/2004	L7419-2	water ponded on surface	12 PFCs
monitoring well J	water	11/22/2004	L7419-3	groundwater	12 PFCs
monitoring well V2	water	11/22/2004	L7419-4	groundwater	12 PFCs
surface soil #1	soil	11/22/2004	L7422-1	surface soils under ponded water	12 PFCs
surface soil #2	soil	11/22/2004	L7422-2	surface soils under ponded water	12 PFCs
boring 0-1 ft	soil	11/22/2004	L7422-3	soil boring	12 PFCs
boring 1-2 ft	soil	11/22/2004	L7422-4	soil boring	12 PFCs

Sample Location	Sample Type	Date collected	Axys ID	Description	Parameters
boring 4.5 ft	soil	11/22/2004	L7422-5	soil boring	12 PFCs
boring 5.5ft	soil	11/22/2004	L7422-6	soil boring	12 PFCs
boring 7.5 ft	soil	11/22/2004	L7422-7	soil boring	12 PFCs
boring 9.5 ft	soil	11/22/2004	L7422-8	soil boring	12 PFCs
boring 12.5 ft	soil	11/22/2004	L7422-9	soil boring	12 PFCs
boring 13.5 ft	soil	12/22/2004	L7422-10	soil boring	12 PFCs
boring 16 ft	soil	12/22/2004	L7422-11	soil boring	12 PFCs
boring 18 ft	soil	12/22/2004	L7422-12	soil boring	12 PFCs
boring 20 ft	soil	12/22/2004	L7422-13	soil boring	12 PFCs
boring 22 ft	soil	12/22/2004	L7422-14	soil boring	12 PFCs
boring 24 ft	soil	11/22/2004	L7422-15	soil boring	12 PFCs
boring 26 ft	soil	11/22/2004	L7422-16	soil boring	12 PFCs
background boring surface	soil	11/22/2004	L7422-17	soil boring	12 PFCs
background boring 4 ft	soil	11/22/2004	L7422-18	soil boring	12 PFCs
background boring 6 ft	soil	11/22/2004	L7422-19	soil boring	12 PFCs
background boring 8 ft	soil	11/22/2004	L7422-20	soil boring	12 PFCs

MPCA MCES Metro Wastewater Treatment Plant PFC Sampling

PFC sampling was conducted at the Metropolitan Council of Environmental Services (MCES) main metro wastewater treatment plant (WWTP) in St. Paul on April 25, 2005. Samples were collected at the following locations: influent wastewater after the primary screens, final treated effluent prior to disinfection chlorination, primary sludge solids, secondary sludge solids, and dewatered sludge prior to incineration. MCES staff assisted MPCA in collection of samples.

Basis for Sampling

The metro WWTP 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 annual 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.

PFC sampling at the metro WWTP was done 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. This study would also help to determine the concentration of PFCs in sludges generated from treatment of these wastewaters, and to determine the levels of PFCs in the discharge.

Sampling and QA/QC

Wastewater samples were obtained from the influent and effluent. A portable sampler, used by MCES for its sample collections, was used to collect both influent and effluent samples. The sampler consisted of a polypropylene sampling beaker of about 1000 ml capacity attached to a 2 meter pole. The sampler was thoroughly flushed/rinsed several times before use. The influent sample was collected from the east channel of the primary clarifier by the sampler. A duplicate influent sample was taken of the influent. The final effluent sample was collected by obtaining one-half of the sample from the west final clarifier (train) and one-half of the sample from the east final clarifier (train). A duplicate sample was taken of the final effluent. Final effluent was collected prior to final disinfection/chlorination. Influent and final effluent water samples were poured into the sample containers. Sample bottles for analyses consisted of 1 liter polypropylene bottles with screw cap lids. Two samples were collected at each location. Sample bottles were prepared by the laboratory (methanol rinsed, deionized water, air dried) and were maintained in a sealed condition at all times until use. New nitrile gloves were used for each water sample collection. Once filled, water sample bottles were sealed individually in a zip lock bag and stored in a cooler at 4 degrees C.

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. Sample bottles for analyses consisted of 1 liter polypropylene bottles with screw cap lids. Two samples were collected at each location. Sample bottles were prepared by the laboratory (methanol rinsed, deionized water, air dried) and were maintained in a sealed condition at all times until use. New nitrile gloves were used for each water sample collection. Once filled, sludge sample bottles were sealed individually in a zip lock bag and stored in a cooler at 4 degrees C.

The biosolids (sludge cake) sample was collected from the incinerator building. The biosolids sample contained about 35% solids. The sample was taken directly from a sampling port off a line feeding sludge cake to the fluidized bed incinerator in operation. A 250 ml sample container was used and 4 samples were collected. Sample bottles were prepared by the laboratory (methanol rinsed, deionized water, air dried) and were maintained in a sealed condition at all times until use. New nitrile gloves were used for each water sample collection. Once filled, sludge sample bottles were sealed individually in a zip lock bag and stored in a cooler at 4 degrees C.

In addition to the above noted specific procedures, all general QA/QC procedures for PFC sample collection were followed for wastewater, sludge, and sludge cake sample collection. These include QA/QC procedures such as field personnel wearing only multiple washed clothing, no water resistant clothing or materials, no tyvek materials, use of nitrile or polypropylene gloves worn at all times during collection and handling of samples, replacement of gloves for each sampling, avoidance of any food wrappings, precleaning of all sampling equipment, and so on. MPCA staff in general followed QAP procedures used by 3M for prior investigations except that Kimwipes or similar lab wipe materials used in prior investigations were not used because of the MPCA contract laboratory (Axys Laboratory) finding that these materials subject samples to PFC contamination. (3M was advised of this finding.)

Analysis will be completed on all samples for the following PFC compounds: PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFBS, PFHxS, and PFOS.

See the attached MPCA MCES Metro WWTO PFC Sampling Table for sample location, type, date, laboratory ID number, and parameters analyzed.

Equipment: Nitrile gloves, a trash receptacle, coolers, ice, pre-prepared sample bottles and blanks, plastic zip lock bags, field data sheets, chain of custody forms, safety equipment, rinse bottles, etc

Specific Attachments for MPCA MCES Metro wastewater Treatment Plant PFC Sampling: MPCA MCES Metro WWTP PFC Sampling table**,** Chain of Custody form

Common Attachments: Axys Laboratory sheet for Collection and Handling of Samples for Analysis of PFOA, PFOS, and Other Fluorinated Compounds, Quality Assurance Project Plan for Empirical Human Exposure Assessment Multi-City Study Sampling Task (Battelle QAP).

MPCA also used portions of the sampling protocol described in the Proposed Quality Assurance Project Plan/Work Plan for the Polybrominated Diphenyl Ethers: Emerging Contaminants in Lake Superior (GL2002-184), where applicable for PFC sampling. See attached document.

MPCA MCES Metro Wastewater Treatment Plant PFC Sampling

Sample Location	Matrix	Date	Axys ID	description	parameters
Metro WWTP effluent	raw influent wastewater	4/25/2005	L7789-8	final effluent wastewater	12 PFCs
Metro WWTP influent	effluent wastewater	4/25/2005	L7789-9	raw influent wastewater to plant	12 PFCs
Metro primary sludge	sludge	4/25/2005	L7789-12	sludge from primary clarifiers	12 PFCs
Metro secondary sludge	sludge	4/25/2005	L7789-13	sludge off secondary system, DAF	12 PFCs
Metro biosolids (cake)	biosolids	4/25/2005	L7789-14	biosolids to incinerator	12 PFCs

MPCA Pine Bend Landfill PFC Sampling

PFC sampling was conducted at the Pine Bend Landfill on April 27, 2005. The Pine Bend Landfill receives wastewater sludges from the 3M Cottage Grove plant, beginning about 1975. 3M wastewater sludges contain PFCs. The extent of PFC concentrations in the 3M sludges deposited at the Pine Bend Landfill is unknown since 3M does not monitor PFCs in its sludges.

The Pine Bend Landfill site is located in Inver Grove Heights, Dakota County, Minnesota. The Pine Bend Landfill 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. Pine Bend Landfill, Inc., a wholly owned subsidiary of Browning-Ferris Industries (BFI), who is the owner and permittee. The landfill has both unlined and lined portions. Unlined portions of the landfill received final cover during 1995-1996.

Lined areas of the landfill use a liner consisting of 2 ft compacted clay and a 60 mil synthetic liner. The liner system is overlaid with a 1 ft sand drainage layer. 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. Leachate is collected from 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 for treatment at MCES wastewater treatment system.

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. The gas to energy facility has 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. The site also includes 4 stormwater retention ponds.

Basis for Sampling

Because of the active disposal of 3M sludges at the landfill containing PFCs this study was done to begin determination of the extent of PFC concentrations in leachate generated at the landfill, 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. Samples were taken from the leachate storage tanks since they represent the total collected leachate from the landfill leachate collection system. This study will provide an initial assessment of the extent of PFC levels in the leachate, with a goal of eventually assessing the levels of PFC within the landfill contents and the loading of PFCs produced in the leachate. The study may also provide information to begin assessment if any additional treatment of landfill leachate is needed to remove PFCs prior to disposal at MCES wastewater treatment.

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.

Groundwater from these well will be analyzed for PFCs to determine the extent of PFC contamination, if any, in groundwater at the site.

Sampling and QA/QC

Leachate was collected from east and west leachate storage tanks. Pine Bend Landfill staff assisted in collection of these samples. Leachate was collected from the storage tanks by direct collection from the storage tank sampling ports. No intermediate sampling device was required. Sample bottles for analyses consisted of 1 liter polypropylene bottles with screw cap lids. Two samples were collected at each location. Sample bottles were prepared by the laboratory (methanol rinsed, deionized water, air dried) and were maintained in a sealed condition at all times until use. New nitrile gloves were used for each water sample collection. Once filled, water sample bottles were sealed individually in a zip lock bag and stored in a cooler at 4 degrees C.

Leachate was also collected from the duel landfill gas and leachate extraction wells. Samples were taken from the #15 unlined and #219 lined areas. Samples were collected by shutting off extraction pumps, disconnection of the gas line from the gas header, and pumping after extraction of the leachate discharge line from the gas header. Pine Bend

Landfill staff assisted in collection of these samples. The sampler contacted the discharge line and sampling bottle only, minimizing any cross contamination. Sample bottles for analyses consisted of 1 liter polypropylene bottles with screw cap lids. Two samples were collected at each location. Sample bottles were prepared by the laboratory (methanol rinsed, deionized water, air dried) and were maintained in a sealed condition at all times until use. New nitrile gloves were used for each water sample collection. Once filled, water sample bottles were sealed individually in a zip lock bag and stored in a cooler at 4 degrees C.

The gas condensate sample was collected from the landfill gas collection system. The gas condensate sample was collected by GSA staff under supervision of MPCA staff. The gas condensate sample was collected directly from a sampling port. Two samples were collected. Sample bottles were prepared by the laboratory (methanol rinsed, deionized water, air dried) and were maintained in a sealed condition at all times until use. New nitrile gloves were used for each water sample collection. Once filled, water sample bottles were sealed individually in a zip lock bag and stored in a cooler at 4 degrees C.

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. These groundwater samples were collected following the protocol outlined in Minnesota Pollution Control Agency Closed Landfill Program Sampling Protocol for Monitoring Wells, updated April 22, 2005, normally used at the landfill. Sample bottles for analyses consisted of 1 liter polypropylene bottles with screw cap lids. Two samples were collected at each well. Sample bottles were prepared by the laboratory (methanol rinsed, deionized water, air dried) and were maintained in a sealed condition at all times until use. New nitrile gloves were used for each water sample collection. Once filled, water sample bottles were sealed individually in a zip lock bag and stored in a cooler at 4 degrees C.

All samples will be analyzed for the following PFC parameters: PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFBS, PFHxS, and PFOS.

In addition to the above noted specific quality control procedures, all general QA/QC procedures for PFC sample collection were followed for all media sample collections. These include QA/QC procedures such as field personnel wearing only multiple washed clothing, no water resistant clothing or materials, no tyvek materials, use of nitrile or polypropylene gloves worn at all times during collection and handling of samples, replacement of gloves for each sampling, avoidance of any food wrappings, precleaning of all sampling equipment, no post it notes, avoidance of any microwave popcorn, no aluminum foil, and so on. MPCA staff in general followed QAP procedures used by 3M for prior investigations except that Kimwipes or similar lab wipe materials used in prior investigations were not used because of the MPCA contract laboratory (Axys Laboratory) finding that these materials subject samples to PFC contamination. (3M was advised of this finding.)

Equipment: nitrile gloves, decontamination equipment and solvents, waste bags, coolers, ice, pre-prepared sample bottles and blanks, plastic zip lock bags, field data sheets, chain of custody forms, safety equipment, rinse bottles, groundwater sampling and testing equipment, etc.

Specific Attachments for MPCA Pine Bend Landfill PFC Sampling: Pine Bend County Landfill PFC Sampling Table, Chain of Custody

Common Attachments: Axys Laboratory sheet for Collection and Handling of Samples for Analysis of PFOA, PFOS, and Other Fluorinated Compounds, Quality Assurance Project Plan for Empirical Human Exposure Assessment Multi-City Study Sampling Task (Battelle QAP)

MPCA also used portions of the sampling protocol described in the Proposed Quality Assurance Project Plan/Work Plan for the Polybrominated Diphenyl Ethers: Emerging Contaminants in Lake Superior (GL2002-184), where applicable for PFC sampling. See attached document.

MPCA Pine Bend Landfill PFC Sampling

Sample Location	Matrix	Sampling Date	Sampling Time	AXYS ID	Description	Parameters
Pine Bend-East	Leachate	4/27/2005	1:30 PM	L7789-7	East channel will be later combined with the west channel leachate making the total leachates before combine with condensated gas and discharge to Metro WWTP	12 PFCs
Pine Bend-West	Leachate	4/27/2005	1:30 PM	L7789-3	West channel will be combined with the east channel leachates giving the total leachate before combined with the condensated gas and discharge to the Metro WWTP	12 PFCs
Pine Bend-15 Unlined	Leachate	4/27/2005	1:45 PM	L7789-4	Extraction well #15 from unlined leachate site	12 PFCs
Pine Bend-219 Lined	Leachate	4/27/2005	2:00 PM	L7789-6	Extraction well #219 from lined leachate site	12 PFCs
Pine Bend-gas condensate	Condensated gas	4/27/2005	2:45 PM	L7789-5	Condensated gas will be combined with the total leachates and will be discharged as part of the Metro WWTP influent	12 PFCs

Sample Location	Matrix	Sampling Date	Sampling Time	AXYS ID	Description	Parameters
Pine Bend-Well 11A	Groundwater	4/28/2005	3:00 PM	L7789-15	Pine Bend landfill monitoring well (upgradient, clean)	12 PFCs
Pine Bend-Well 26	Groundwater	4/28/2005	3:00 PM	L7789-16	Pine Bend landfill monitoring well - contaminated	12 PFCs

MPCA PFC Fish Sampling in Mississippi River

Basis for Sampling

The objective of fish sampling was to provide high quality data of concentrations of PFC residues in fish from Mississippi River and to determine the concentrations of 12 PFC contaminants in different fish species from two distinct ecological groups (benthivorous and piscivorous) from the study area.

The fish data will be used to associate any trends from other sampling media (water and sediment), and will help us to construct a model of PFC bioaccumulation. This model will serve to assess potential human and wildlife exposures from consuming PFC contaminated fish.

Fish sampling was performed along the Mississippi River miles 818-828, upstream of the 3M Cottage Grove Plant (Figure 1.) Future fish sampling may concentrate in other areas of the Mississippi River proximate to the 3M Cottage Grove discharge to further assess the impacts of current and past PFC discharges from the 3M plant. The fish samples were collected by the experienced MNDNR fisheries biologists according to the EPA Sample Collection Activities QAPP. Mr. Mark Briggs from MN DNR was responsible for managing the Mississippi fish procurement process which used boat-mounted electrofishing methodology.

Sampling and QA/QC

Fish species, length, and weight were recorded in the field. All fish samples were supplied as individual frozen whole fish, wrapped in the Al-foil, and stored at -20 degree C and were shipped immediately to Fardin O. at MPCA.

Target species for the fish sampling effort were included Common carp (*Cyprinus carpio*), Walleye (*Stizostedion vitreum*), White bass (*Morone chrysops*), and Smallmouth bass (*Micropterus dolomieui*). These four target species were selected in accordance with EPA's Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, Volume 1: Fish Sampling and Analyses (US EPA, 1995).

The primary criteria for selecting the above four target species are:

1. The species were commonly consumed in the area and are of commercial and recreational fishing value.

2. The species have the potential to bioaccumulate PFC contaminants.

3. The species have a wide geographic distribution and are easy to identify taxonomically.

4. The species represent two distinct ecological groups of benthivorous (bottom feeders) and piscivorous (predators). This allows monitoring variety of habitats, feeding strategies, and physiological factors that might results in differences in bioaccumulation of different PFC contaminants. Benthivors (i.e. Common carp) 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) are good indicator of PFC contamination that may be biomagnified through several trophic levels of the food web.

Upon receipt of samples from MNDNR, Fardin O checked that each shipping container was arrived undamaged and samples were still frozen and in good condition, verified that all individual fish listed on the paperwork were included in the shipment and were properly wrapped in aluminum foil and labeled. Fardin O documented information about each fish in a lab notebook. The selected frozen samples were sent to AXYS to determine their age and to be analyzed accordingly for PFC contamination. The lipid content (wet weight) will be done by Axys on every sample. A total of 11 fish liver samples were selected for analyzes of PFCs.

The sample collection methods for fish sampling are detailed in the Quality Assurance Project Plan for Sample Collection Activities for a National Study of Chemical Residues in Lake Fish Tissue (US EPA, Office of Water/Office of Science and Technology, 2000); Quality Assurance for Field Sampling Plan for the National Study of Chemical Residues in Lake Fish Tissue, (US EPA, Office of Water/Office of Science and Technology, 2000) and Quality Assurance Report for the National Study of Chemical Residues in Lake Fish Tissue: Year 1 Analytical Data, January 2002 (Attachment A).

The custody procedures applied until fish sample delivery to Axys Analytical at which time handling and QC procedures as specified in the Axys QC Manual apply. A copy of the Axys QC Manual is on file at MPCA. The fish samples will be analyzed for 12 PFCs.

The fish sampling method used for this study are well documented, thus no validation study information for non-standard situations is being presented here. No non-standard situations during sampling were anticipated.

Equipment: See MDNR procedures for equipment used

Specific Attachments: Mississippi River Fish PFC Sampling table, chain of custody

Common Attachments: Axys Laboratory sheet for Collection and Handling of Samples for Analysis of PFOA, PFOS, and Other Fluorinated Compounds, Quality Assurance Project Plan for Empirical Human Exposure Assessment Multi-City Study Sampling Task (Battelle QAP)

MPCA PFC Fish Sampling in Mississippi River

Mississippi River Fish	Matrix	Date Collected	AXYS ID	Sex	Age (year)	Length (inches)	Description	Parameters
Smallmouth bass #1	Liver tissue	8/31/2004	L7474-18	F	8	15.5	Analyze the liver as one sample	12 PFCs
Smallmouth bass #2a	Liver tissue	8/31/2004	L7474-19	M	2	10.5	Composite the livers of Smallmouth bass # 2a, 2b, 2c, and 2d and analyze as one sample	12 PFCs
Smallmouth bass #2b	Liver tissue	8/31/2004	L7474-19B	M	2	10.5		
Smallmouth bass #2c	Liver tissue	8/31/2004	L7474-19C	F	2	9		
Smallmouth bass #2d	Liver tissue	8/31/2004	L7474-19D	M	2	10.5		
Smallmouth bass #3a	Liver tissue	8/31/2004	L7474-20	F	3	11.5	composite the livers of smallmouth bass # 3a and 3b and analyze as one sample	12 PFCs
Smallmouth bass #3b	Liver tissue	8/31/2004	L7474-21	F	3	11.5		
Smallmouth bass #4	Liver tissue	8/31/2004	L7474-22	F	4	12.5	Analyze the liver as one sample	12 PFCs
White bass #1	Liver tissue	8/31/2004	L7474-23	F	7	16	Analyze the liver as one sample	12 PFCs
White bass #2a	Liver tissue	8/31/2004	L7474-24	F	6	14.5	Composite the livers of white bass # 2a, 2b, 2c, and 2d and analyze as one sample	12 PFCs
White bass #2b	Liver tissue	8/31/2004	L7474-25	F	6	15		
White bass #2c	Liver tissue	8/31/2004	L7474-26	F	6	14		
White bass #2d	Liver tissue	8/31/2004	L7474-27	M	6	14.5		
Common Carp #1	Liver tissue	8/31/2004	L7474-28	F	8	25	Analyze the liver as one sample	12 PFCs

Mississippi River Fish	Matrix	Date Collected	AXYS ID	Sex	Age (year)	Length (inches)	Description	Parameters
Common Carp #2a	Liver tissue	8/31/2004	L7474-29	M	6	19.5	composite livers of carp # 2a, 2b, and 2c and analyze as one sample	12 PFCs
Common Carp #2b	Liver tissue	8/31/2004	L7474-31	F	6	19		
Common Carp #2c	Liver tissue	8/31/2004	L7474-32	F	6	20		
Common Carp #3	Liver tissue	8/31/2004	L7474-30	F	7	20.5	Analyze the liver as one sample	12 PFCs
Walleye #1	Liver tissue	8/31/2004	L7474-33	F	9	25	Analyze the liver as one sample	12 PFCs
Walleye #2	Liver tissue	8/31/2004	L7474-34	F	4	15.5	Analyze the liver as one sample	12 PFCs