H. PFC Contamination in Mississippi River Fish

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

Persistent - 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 bio-concentration 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).

<u>Toxicity</u> - 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 in Fish from Mississippi River

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 existing PFCs that accumulated over the 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.

<u>Criteria for Fish Species Collection</u> - 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 Result

<u>PFC Contmination of Fish Liver Samples</u> - 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. In concentrations in the 2 white bass liver composites were 305 and 1120 ppb. PFOS in the two walleye livers the levels of PFOS were 184 and 371 ppb. PFOSA was found at 481 ppb in the smallmouth bass 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	**6600.214**	**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
WE = walleye

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	4 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, the PFOS concentrations found in 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 (perfluoroctane 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.

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.

Table 15 - PFC Contamination Lvels 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

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.

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 human and wildlife consumption of 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.

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

Fish 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 fluorchemical 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.

Summary Report for PFC Contamination in Mississippi River Fish

- Analysis of fish in the Mississippi River, collected in August 2004 and October 2005, demonstrate that these fish are heavily contaminated with variety of 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 likely pose a significant risk to humans and wildlife consuming these fish, and require immediate assessment.

Immediate Needs for Rigorous 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.