



Mississippi River Pool 2 Intensive Study of Perfluorochemicals in Fish and Water: 2009

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Minnesota Pollution Control Agency
520 Lafayette Road North
Saint Paul, MN 55155-4194

<http://www.pca.state.mn.us>

651-296-6300 or 800-657-3864 toll free

TTY 651-282-5332 or 800-657-3864 toll free

Available in alternative formats

Authors and Contributors

Bruce Monson

Laura Solem

Paul Hoff

Marvin Hora

Pat McCann

Mark Briggs

Joel Stiras

Steve DeLain

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Abbreviations Glossary

Groups

PFCs – perfluorochemicals or perfluorinated compounds
PASs – perfluoroalkyl surfactants
PFCAs – perfluorocarboxylic acid
PFSAs – polyfluorinated alkyl substances
FTOH – fluorotelomer alcohols
PFAAs – perfluoroalkyl acids

Individual

PFBA – perfluorobutanoic acid (C4 Acid)
PFBS – perfluorobutane sulfonate (C4 Sulfonate)
PFPeA – perfluoropentanoic acid (C5 Acid)
PFHxA – perfluorohexanoic acid (C6 Acid)
PFHxS – perfluorohexane sulfonate (C6 Sulfonate)
PFHpA – perfluoroheptanoic acid (C7 Acid)
PFOA – perfluorooctanoic acid (C8 Acid)
PFOS – perfluorooctane sulfonate (C8 Sulfonate)
PFOSA – perfluorooctane sulfonamide (C8 Sulfonamide, branched)
PFNA – perfluorononanoic acid (C9 Acid)
PFDA – perfluorodecanoic acid (C10 Acid)
PFUnA – perfluoroundecanoic acid (C11 Acid)
PFDoA – perfluorododecanoic acid (C12 Acid)

Other Abbreviations

AFFF – aqueous fire fighting foam
ECF – electrochemical fluorination
FCA – fish consumption advisory
MDH – Minnesota Department of Health
DNR – Minnesota Department of Natural Resources
WWTP – wastewater treatment plant

Executive Summary

Perfluorochemicals (PFCs) emerged as a global pollutant in 2001 when scientists reported perfluorooctane sulfonate (PFOS) was measured in wildlife throughout the world. Numerous studies have demonstrated that PFOS is the primary form of PFC found in fish and other biota. 3M Company's Cottage Grove facility, in the southeastern Twin Cities Metropolitan Area, was a major manufacturer of PFOS from the 1950's to 2002. The 3M Cottage Grove facility discharges treated process water and cooling water to Pool 2 of the Mississippi River. Although the facility discontinued production of PFOS in 2002, the facility discharge continues to have measurable PFOS concentrations. Pool 2 is a nearly 33 mile reach of the Mississippi River between Lock & Dam 1 and Lock & Dam 2. The Metropolitan Wastewater Treatment Plant (Metro plant), the largest wastewater treatment plant in Minnesota, also discharges to Pool 2, and also has measurable levels of PFOS in its effluent. Wastewater can be a significant source of PFCs because these chemicals have been included in a wide range of consumer and industrial products that can eventually be disposed of in municipal wastewater systems. This report does not examine the loading from possible sources of PFCs to Pool 2, but rather focuses on PFCs in fish and water from Mississippi River Pool 2, based on intensive monitoring completed in the summer of 2009.

Since 2004, the Minnesota Pollution Control Agency (MPCA) and the Department of Natural Resources (MDNR), with participation of the Health Department (MDH), have analyzed fish and river water for PFCs from Pool 2. An intensive study of PFCs in fish and water was completed in the summer of 2009. Of the 367 fish analyzed from 2004 to present, 297 were collected in 2009. In addition, water samples were collected at 12 stations throughout Pool 2 in 2009. To characterize the spatial distribution of PFCs in Pool 2, the reach was divided into four sections, with Section 1 at the most upstream end and Section 4 above the Hastings Dam (Lock & Dam 2). Figure 2 of the main report shows section boundaries and water sample locations.

All fish and water samples were analyzed for PFCs by AXYS Analytical Ltd. For quality assurance, water samples from all 12 stations and 30 randomly-selected fish samples were analyzed by 3M Environmental Laboratory. The high degree of data correlation between the two labs provides confidence in the quality of the results.

The highest water concentrations of PFCs were found in Section 4, in particular, Station 11. Perfluorobutanoic acid (PFBA) was detected at all 12 stations. PFOS, perfluorooctanoic acid (PFOA), and perfluorohexanoic acid (PFHxA) were detected in Sections 2, 3, and 4, with the highest concentrations in Section 4. Three other PFCs—PFPeA, PFBS, and PFHxS—were detected in Section 4.

PFOS was detected in nearly all fish from Pool 2. The highest PFOS concentrations in fish coincided with the highest water concentrations in Section 4. Other PFCs were detected in fish that had higher concentrations of PFOS. Of the five targeted fish species in Pool 2—bluegill sunfish, carp, freshwater drum, smallmouth bass, and white bass—freshwater drum had the highest PFOS concentrations. Drum had not been sampled prior to 2009, because it is not considered a typical sport fish. Based on the

MDNR's observation that the drum is a popular fish harvested in Pool 2 for human consumption, it was included as a target species in 2009.

The MDH has developed a reference dose for PFOS that is used as the basis for fish consumption advice. Mean PFOS concentrations in fish between 40 and 200 parts per billion (ppb) are assigned meal advice of once per week; between 200 and 800 ppb, the advice is one meal per month, and above 800 ppb, do not eat. Fish consumption advisories were modified for Pool 2 based on the 2009 results. Freshwater drum had the highest PFOS concentrations and was the only fish species in Pool 2 assigned a one meal per month advisory based on a mean PFOS concentration of 229 ppb. Smallmouth bass also had a mean PFOS concentration of 209 ppb when data from 2004 to 2009 are combined; however, meal advice is not given for this species in Pool 2 because only catch-and-release fishing is allowed (<http://www.health.state.mn.us/divs/eh/fish/>).

No discernable trends were seen in PFOS over time for species that had been sampled since 2004 or 2005. PFOS concentrations in fish muscle were not correlated with fish age or size, and there was no difference between genders. Bioaccumulation factors (BAFs) were calculated for PFOS using the water and fish data. BAFs for PFOS were in the range of 4000 to 6000 L/Kg, which is at the low end of the range of highly bioaccumulative compounds.

Introduction

Mississippi Pool 2

Mississippi River Pool 2 (Figure 1) extends from Lock & Dam #2 at Hastings, Minnesota, upstream nearly 33 miles to Lock & Dam #1 (Ford Dam). The Mississippi confluence with the Minnesota River is at the upper reach of Pool 2 and the confluence with the St. Croix River is just below Lock & Dam #2. Within Pool 2, average annual flow is about 15,000 cubic feet per second (cfs). Pool 2 is a receiving-water for the largest publically-owned wastewater treatment plant in Minnesota, the Metropolitan WWTP, with an average discharge of 185 million gallons per day (286 cfs), and the Eagles Point WWTP, with an average discharge of 4.2 mgd. The 3M Company Cottage Grove facility is next to, and downstream of, the Eagles Point WWTP. The 3M facility discharges industrial process water and cooling water, with a combined flow of 8 mgd.

What are PFCs and why are they an environmental contaminant?

Perfluorochemicals (PFCs)—also known as perfluorinated compounds—are composed of a carbon chain saturated with fluorine atoms, with a functional group at the end of the chain. The functional groups are typically a sulfonate (-SO₃) or a carboxylic acid group (-COOH). The functional group makes the PFC soluble in water (hydrophilic), whereas the carbon chain makes the PFC molecule soluble in lipids (lipophilic) and resistant to water (hydrophobic). The unique properties of PFCs have been exploited for numerous consumer products, most notably fire-fighting foam, stain protection, and non-stick surfaces.

PFCs “are globally distributed, environmentally persistent, bioaccumulative, and potentially harmful” (Giesy and Kannan, 2002). Although there are naturally occurring fluorinated organic compounds that contain one fluorine atom, all PFCs in the environment are anthropogenic. (Giesy and Kannan, 2002) Various toxic endpoints have been measured in laboratory studies of PFCs. According to a 2007 MDH press release, observed effects of low doses of PFOS include decreased high density lipoprotein cholesterol (HDL) and changes in thyroid hormone levels in some animals. Biological membranes are primarily composed of phospholipids, which are amphiphilic molecules. The amphiphilic property of PFCs might enhance cell membrane permeability of other pollutants, thereby indirectly inducing adverse effects caused by other chemicals (Wang et al., 2009).

Perfluorooctane sulfonate (PFOS) is the predominant PFC found in most fish (Houde et al 2006). Fish from contaminated areas may be a significant source of dietary PFOS exposure (Berger et al., 2009). The first report of PFOS as a global contaminant in wildlife was a study funded by 3M (Giesy and Kannan, 2001). When PFOS concentrations are high in fish tissue, other long carbon-chain PFCs, such as perfluorodecanoic acid (C10), are often detected. Detection limits generally range from 2.5 to 5 nanograms per gram (ng/g), or parts per billion (ppb). Rather than being lipophilic like many other persistent organic pollutants (POPs), several studies have suggested that PFCs are proteinophilic (Conder et al., 2008). PFOS behaves very differently from other POPs, having differences in intrinsic factors, such as surface activity, water solubility, non-measurable octanol/water coefficient values, and relatively low

bioaccumulation potential. Despite these differences, PFOS bioaccumulates in fish tissue and is considered a POP (Wang et al., 2009).

Ambient monitoring of PFCs before 2009

The MPCA summarized ambient monitoring through 2008 in *PFCs in Minnesota's Ambient Environment: 2008 Progress Report* (<http://www.pca.state.mn.us/publications/c-pfc1-02.pdf>). In addition to fish, the report covers PFC monitoring in ground water, surface water, wastewater, and air.

Fish in Pool 2 were first tested for PFCs in August 2004 and fish collection for PFCs has continued every year except 2007. In 2004, PFCs were detected in the fillets of two smallmouth bass (PFOS: 105 ng/g and 950 ng/g) and one composite sample of four white bass fillets (PFOS: 138 ng/g). In 2005, 2006, and 2008, additional tested fish species included walleye, carp, channel catfish, black crappie, smallmouth bass, white bass, smallmouth buffalo, emerald shiner, and gizzard shad. Fillet tissue samples ranged from one to fifteen fish per species. Ancillary measurements included length, weight, age, and sex. In 2005, the highest PFOS concentration was in white bass, with a range of 84 ng/g to 1860 ng/g. In 2006, smallmouth bass had the highest PFOS concentration was in smallmouth bass, with a range of 19 ng/g to 5150 ng/g. Smallmouth bass had the highest concentration again in 2008, but the range was considerably narrower than in 2006 (PFOS: 49 ng/g to 380 ng/g).

In 2006, fish were tested for PFCs in the upper St. Croix River (above the St. Croix Falls dam) and Lake Calhoun in Minneapolis. The PFOS concentrations in fish from the St. Croix, as expected, were below the detection level. In Lake Calhoun, the bluegills had PFOS concentrations of 181 to 373 ng/g; prompting additional lake monitoring in the following year.

In 2007, PFC monitoring in fish focused on 30 Twin Cities metro lakes, lower St. Croix River, and the upper Mississippi River near Brainerd. Five lakes—Elmo, Gervais, Harriet, Johanna, and Tanners—had fish with PFOS concentrations greater than 200 ng/g. Lake Elmo had the highest concentrations of PFOS, ranging from 149 ng/g to 711 ng/g. In the Upper Mississippi River near Brainerd, PFOS concentrations in four fish species ranged from only 6 ng/g to 18 ng/g. In addition to the metro lake samples analyzed by AXYS Analytical Ltd, fish homogenates from 59 lakes from throughout the state and several Mississippi River locations were sent to the USEPA lab in Research Triangle Park, North Carolina (Delinsky et al., 2010). USEPA's analyses looked at bluegill and pumpkinseed sunfish, and black crappie. The samples were mostly composites (only three of the 70 samples were single fillets). Their highest reported PFOS concentrations were in bluegill from Pool 2 (2000 ng/g). Upstream of Pool 2, the highest PFOS concentration was 20 ng/g. Their results for lakes ranged from PFOS less than the limit of quantitation (LOQ = 1 ng/g) to a high of 52 ng/g; 52 of the 59 lakes (88%) had PFOS concentrations less than 3 ng/g.

In 2008, PFC sampling included 22 metro area lakes and 2 lakes near Duluth, in addition to more sampling in Pools 2 and 3 of the Mississippi River. Thirteen of the lakes, not including Calhoun and Elmo (which again showed high PFOS concentrations), had species-mean PFOS concentrations above 40 ng/g. Three lakes—Twin (Brooklyn Center), Harriet, and Lake of the Isles—had species-mean PFOS concentrations above 200 ng/g. In Pools 2 and 3, one to five fish per species were analyzed; bluegills and

smallmouth bass again had maximum PFOS concentrations greater than 200 ng/g, although the species-means in Pool 2 were 173 ng/g for bluegills and 162 ng/g for smallmouth bass.

Why this study?

The MPCA is legally required to list waters as impaired if the fish consumption advisory for a lake or river that is more restrictive than a meal per week (Minn. R. pt. 7050.0150, subp. 7). Pool 2 has been listed as impaired due to PFOS in fish since 2008, based on a once per month advisory for bluegills in 2007. Additional PFC data were warranted given the small sample sizes of fish in years prior to 2009 and because both water and fish PFOS concentrations are needed to establish site-specific water quality criteria. MPCA, MDH, MDNR, and 3M staff met on 13 May 2009 to discuss the intensive monitoring study of Pool 2. 3M solicited a proposal for a study from the consulting firm, Entrix, which was the basis for a discussion. The MDNR offered to collect the fish and MPCA wanted to oversee the study; therefore, it was agreed that MDNR would collect the fish and MPCA would coordinate the laboratory analysis and analyze the results. 3M was provided with split samples of fish and water for analysis in 3M's Environmental Laboratory (more details under Methods).

Methods

Fish Collection

For this study, Pool 2 was divided into four sections (Figure 2), based on the professional judgment of Joel Stiras, MDNR Fisheries; and were agreed to by the representatives from MDH, MPCA, and 3M.

Description of the four Pool 2 Sections:

Section 1: 3.6 river miles from Ford Dam to confluence with Minnesota River.

Section 2: 9.5 river miles from confluence with Minnesota River to lower channel to Hog Lake and Pig's Eye Lake, but not including Hog and Pig's Eye lakes; Metropolitan (Metro) wastewater treatment plant and Holman Field airport are in this section.

Section 3: 13.7 river miles include Hog Lake and Pig's Eye Lake as well as River, Baldwin, Mooers, and Spring lakes and Lower Grey Cloud Slough.

Section 4: 4.7 river miles to Lock & Dam #2 in Hastings; Eagles Point wastewater treatment plant and 3M Cottage Grove facility are in this section.

Five target fish species were agreed upon: bluegill sunfish (BGS), carp (C), freshwater drum (FWD), smallmouth bass (SMB), and white bass (WHB). FWD had not been collected previously; creel surveys and field observations by the MDNR have shown fishers catch and eat FWD.

MDNR collected fish from the 33 mile reach of Pool 2 in late May 2009. Joel Stiras, MDNR Fisheries, and Steve DeLain, MDNR Ecological Resources Long-Term Resource Monitoring Program, collected fish in

three days using electroshocking equipment. The fish collection locations were mapped (Appendix A). Fish were wrapped in aluminum foil and immediately frozen. The frozen fish were labeled with a unique sample ID before shipping overnight to the laboratory.

Water Collection

Water samples were collected at 12 stations—3 stations per section—corresponding to areas where fish were caught. Water samples were collected on July 2, 2009. MPCA collected three samples at each station and 3M collected duplicates plus spike samples at all 12 stations as well. All samples were collected as grab samples just below the water surface using a large polyethylene bottle that was used to split the water samples among 3M and MPCA bottles.

Description of 12 water sample stations (Figure 2):

1. Section 1; main channel at river mile 847
2. Section 1; old Minnesota River channel, near river mile 845.4
3. Section 1; main channel upstream of confluence with Minnesota River at river mile 844
4. Section 2; main channel near boat launch at river mile 842
5. Section 2; main channel adjacent to Holman Field at river mile 837
6. Section 2; bay south of Pigs Eye Lake near river mile 834
7. Section 3; main channel near boat launch and downstream from Ashland Oil refinery at river mile 829.5 (originally intended to be near I494 bridge, at upper end of Section 3, but no fish were collected in that reach)
8. Section 3; main channel upstream of Island 112 at river mile 827.5
9. Section 3; Spring Lake, near river mile 821
10. Section 4; main channel, downstream of Grey Cloud Slough at river mile 819
11. Section 4; near shoreline, downstream of 3M Cottage Grove discharge, near river mile 817.5
12. Section 4; main channel, upstream of Lock & Dam #2 at river mile 816

Laboratory Analysis

AXYS Analytical Services Ltd analyzed all water and fish samples for PFCs. Empty coolers were shipped by AXYS to the MPCA for fish samples and coolers with bottles were shipped for water samples. The whole fish shipped to AXYS were measured for length and weight; also, gender and age were recorded. AXYS homogenized fish fillets with scales off and skin on, which is the protocol used for fish contaminant analysis when results are used for fish consumption advisories.

The USEPA has not yet approved an analytical method for PFCs; however, all laboratories conducting PFC analysis on environmental samples use a method of liquid chromatography-electrospray tandem mass spectrometry (LC/MS/MS). Sample homogenization, extraction, and clean-up steps can vary among laboratories. AXYS describes their method as, *AXYS Method MLA-060: Analytical Procedure for the Analysis of Perfluorinated Organic Compounds in Aqueous Samples by LC-MSIMS*.

The reporting level is the limit of quantitation (LOQ), defined as the lowest non-zero calibration standard having accuracy of 100 ±30%.

Quality Assurance

In addition to the multiple level quality assurance protocol at AXYS, William Scruton, Quality Assurance Coordinator for MPCA's Environmental Analysis and Outcomes Division, reviewed all data packages from AXYS and identified any results needing to be qualified as an estimate if all QA requirements were not met.

Samples were split for fish and water with 3M to verify AXYS laboratory results. Six fish of each of the five fish species were randomly selected before being analyzed for PFCs and homogenates from those fish were shipped back to MPCA and delivered to the 3M Environmental Laboratory. As mentioned above, water samples were collected at the same time by MPCA and 3M at all 12 stations. The results from 3M are given in the 3M Environmental Laboratory Final Analytical Reports No. E09-0365 (surface water) and No. E09-0372 (fish fillet homogenates).

Results and Discussion

Surface Water

Surface water samples were collected on 2 July 2009 from the 12 water sample stations selected for Pool 2 of the Mississippi River. Additional information collected to characterize each site included temperature, dissolved oxygen, depth, and conductivity (Table 1). Temperature was relatively constant, remaining within 24-26 °C range throughout Pool 2. Dissolved oxygen dropped from 9.2 mg/L at Station 1 to 7.3 mg/L at Station 12. Water depths ranged from 1.2 m to 6.7 m. Specific conductivity increased after the Mississippi confluence with the Minnesota River, between Stations 3 and 4 (382 µS/cm to 536 µS/cm), and increased slightly again between Stations 5 and 6 (525 µS/cm to 580 µS/cm), but then remained stable for the rest of Pool 2.

Concentrations for all PFC analytes in each triplicate sample from the 12 water sample stations are given in Table 2. Samples are identified by Section-station-replicate. PFOS concentrations or reporting levels are listed in the second to last column and averages for each station are listed in the final column. When the concentration was below the reporting limit, ½ the reporting level was used to calculate descriptive statistics.

Variability, as indicated by coefficient of variation (CV%) among triplicate water samples was below 10% for PFOS at all stations except station 12, which had a CV% of 26%. The average CV% for PFOS at the five stations where PFOS was detectable was 9.0%. The CV% for PFBA, detectable at all 12 stations, was 13.2%.

A comparison of PFOS concentrations from AXYS and 3M show good agreement (Figure 3). Results of PFOS in water from 3M Environmental Laboratory were generally higher than from AXYS for the same station.

Most of the other PFCs were less than the reporting level, although nine of the 13 analytes were detected in stations 11 and 12. The highest concentrations of all detected analytes were in station 11. PFBA was the only one of the 13 measured PFCs that was measured in detectable concentrations at all water stations. PFOA was detected at stations 6-12 and PFHxA was detected at stations 7-12. PFOS was detectable in stations 6, 7, 8, 11, and 12. The average PFOS concentration at station 11 was 90 ng/L. The next highest PFOS concentration was 15 ng/L at Station 12. The other three stations with detectable PFOS (6, 7, and 8) had PFOS averages of 7.7, 10.3, and 8.5 ng/L, respectively. The high PFOS concentration at station 11 was about equal to the concentration of PFOA (94 ng/L) and one-half the concentration of PFBA at that station (168 ng/L).

The MPCA has established site-specific water quality criteria for PFOS and PFOA in Pool 2 (<http://www.pca.state.mn.us/cleanup/pfc/index.html>) and for PFBA statewide. The PFOS criteria is 7 ng/L. The 2009 water quality station averages exceed this criteria at stations 6, 7, 8, 11, and 12. None of the stations exceeded the PFOA criteria of 2.7 µg/L (2,700 ng/L) or the PFBA criteria of 1 mg/L.

Fish

Quality Assurance

Fish were collected on 28-29 May 2009 and 1 June 2009, throughout the length of Pool 2 (Table 3). The target for each section of 15 individuals per target species was achieved for all sections except for bluegill in Section 1, where 12 individuals were collected. Despite some of the bluegills being extremely small, they were analyzed individually rather than composited.

The inter-lab comparison of PFOS concentrations in the 30 fish homogenates show good agreement (Figure 4). In contrast to the inter-lab comparison for PFOS in water, the results of PFOS in fish from 3M Environmental Laboratory were generally lower than from AXYS for the same fish.

Spatial Distribution of PFOS by Species

The distribution of PFOS concentrations are shown in a series of box-whisker plots. Individual concentrations for each fish are shown as circles. The box is bounded by horizontal sides representing the 25th and 75th percentiles—the boundaries of the interquartile range (IQR)—with the median line (50th percentile) within the box. In other words, the box shows the range of the central 50% of the values. The whiskers show the spread of values that are within 1.5 x IQR above and below the actual

IQR. Values beyond the whiskers are considered outliers. Concentration is given on a log-scale to improve the symmetry on either side of the median (i.e., to better approximate a normal distribution).

A comparison of fish species within each Section and all Sections combined shows the PFOS concentrations were generally below 100 ng/g (ppb) in Sections 1, 2, and 3 (Figure 5). Section 4, in contrast, had higher PFOS concentrations in all species except white bass (WHB). Freshwater drum (FWD) had the highest PFOS concentration in a single fish fillet (3,580 ng/g). The PFOS concentrations in WHB remained about the same in all river sections, in contrast to the other species; when all sections were combined, WHB had the highest species-specific PFOS median (75 ng/g).

Combining the data from all four Sections of Pool 2, carp had the lowest arithmetic mean PFOS concentration, 77 ng/g (Table 4), and FWD had the highest species-mean, 229 ng/g. The other three species had similar averages (approximately 100 ng/g). Fish consumption advice is assigned to each species based on the species-arithmetic mean PFOS concentration from all sections of Pool 2. MDH recommends that consumption of fish fillets with PFOS concentrations in the range 40-200 ng/g be limited to one meal per week. For fish fillets with PFOS concentrations in the range 200-800 ng/g, the advice is one meal per month. MDH advises not to eat fish species that exceed PFOS concentrations of 800 ng/g. MDH calculates meal advice using multiple years of data, depending on the temporal trends in the contaminant. FWD arithmetic mean does not change because they were only collected in 2009. Therefore, FWD will have the more restrictive advice of one meal per month and the other species fall within the one meal per week advisory.

Going from Section 1 to Section 4, cumulative distributions of PFOS by species show a clear shift from lower to higher concentrations in four of the five species, whereas in white bass (WHB) PFOS distributions remain relatively constant (Figure 6). Also, the ranges of PFOS concentrations are narrow in WHB compared to the other species. The movement of PFCs through food webs is not understood. One possible explanation consistent with these results is that all the fish species, except WHB have limited home ranges. White bass have been documented to travel long distances: 40 miles in the Missouri River and throughout the entire Lake Erie basin (Morgan and Harrel, 2006). Home ranges in bluegill sunfish have been reported at only 30 square meters (Parr, 2002), although a study in Minnesota lakes found some bluegill and black crappies move among connected lakes (Parsons and Reed, 2005). There is some evidence indicating the majority of common carp remain within 100 meters of their nesting area although some may travel long distances (Jones and Stuart, 2008).

Temporal Distribution of PFOS Concentrations

Fish were collected for PFCs in 2004, 2005, 2006, 2008, and 2009. Only three fish were collected in 2004 (Table 5). More fish were collected in subsequent years, although the total per species remained low until the sample collection in 2009. Because of the low numbers within most years, assessing temporal trends is difficult. A plot of the concentration distributions by species for each year suggests a downward trend in PFOS concentrations, especially in smallmouth bass (Figure 7). However, prior to 2009 the fish were collected only in Section 4; re-plotting the annual distributions by species with only Section 4 from 2009 does not show a noticeable downward trend in the PFOS concentrations (Figure 8).

It appears additional years are needed to make a proper assessment of temporal trends of PFOS in fish from Pool 2.

Relationship of PFOS levels to fish gender, age, and size

PFOS concentrations among females, males, and juveniles did not show a noticeable difference (Figure 9), except bluegill juveniles were lower than adults. There was also not much difference among age classes within each species (Figure 10). The two highest PFOS concentrations in the freshwater drum were in a 3 year old and 8 year old fish. These results indicate PFOS does not bioaccumulate with age as it does in most bioaccumulative compounds, such as mercury and PCBs. Another observation from these concentration distributions by age class is the wide range within age classes in most species, especially the freshwater drum, whereas the white bass shows very little range in concentrations among and within age classes.

Also, there was no relationship between PFOS concentrations and fish length or percent lipids (Figures 11 and 12).

Bioaccumulation Factors and Water Quality Criteria

Bioaccumulation factors (BAFs) for PFOS were calculated for each species, in each section. Water concentrations from the three stations within each section were averaged. Individual fish fillet PFOS concentrations were divided by the average PFOS concentration. The individual BAFs were then combined as a geometric mean (geomean) for each species. (A geometric mean is the antilog of the average of log-transformed values.) The final BAF is a geomean of all species geomeans. This calculation had been done in previous years, using a much smaller dataset (STS Consultants, 2007). The resulting water quality criteria based on fish consumption (referred to as fish consumption criteria, fCC, were 6 ng/L for Pool 3 and 4 ng/L for Pool 2. The 2009 study has allowed for a robust recalculation of the BAFs and water quality criterion.

PFOS water concentrations in the upper 3 Sections of Pool 2 were predominately less than the reporting level (i.e., Level of Quantitation, LOQ). For water concentrations below the reporting level, one-half the reporting level was used. A BAF was calculated for only Section 4, where PFOS water concentrations were all above the reporting level, to avoid having to use non-detectable concentrations. The species-specific BAFs ranged from 2,519 L/Kg for carp to 7,010 L/Kg for freshwater drum. The geometric mean of all species in Section 4 is 3,877 L/Kg. The geometric mean of all species from all Sections is 7,554.

These BAFs can be applied to the equation for calculating a fish consumption criterion (fCC). The equation is

$$fCC = \frac{RfD + BW + K}{IW + CR \times BAF}$$

where,

RfD = reference dose, 0.00008 mg/kg/d

BW = body weight, 70 kg

K = exposure fraction attributed to water and fish consumption, 0.2

IW = incidental ingestion of water, 0.01 L/d

CR = fish consumption rate, 0.030 Kg/d

Applying the BAF from 2009, the resulting fCC is 7 ng/L using all Pool 2 fish.

Comparison to Other Locations

Where point sources have not discharged PFCs, one might reasonably assume that concentrations are zero because PFOS is strictly an anthropogenic compound; however, PFOS has been found in wildlife, including fish, throughout the world (Giesy and Kannan 2001; Houde et al 2006). PFCs are globally distributed and the levels increase with proximity to urban area (Houde et al., 2006).

A comparison of whole fish composites (one small fish and one large fish composite per site) from 30 sites within the Missouri, Ohio, and Mississippi Rivers found median PFOS concentrations of 24.2 ng/g, 31.8 ng/g, and 53.8 ng/g, respectively (Ye et al., 2008a). Although the Mississippi has the higher PFOS level, the ten fish samples above 200 ng/g PFOS were distributed throughout the three rivers, indicating the PFOS contamination is widespread.

An EPA study of PFCs in carp collected in 2006 from the Upper Mississippi River, reported median concentrations of PFOS ranging from 8 ng/g upstream of St. Cloud to 26 ng/g and 40 ng/g at Pig's Eye Lake and downstream at Spring Lake (Ye et al., 2008b) (Table 6). The latter two sites are in Section 2 and Section 3 of Pool 2, respectively. No carp were collected by the MDNR or MPCA in 2006 from the Mississippi River. Median concentrations of PFOS in carp from our 2009 study were 28 ng/g for all of Pool 2, 13 ng/g for Section 2 and 87 ng/g for Section 4.

PFOS levels in whole, four year-old lake trout collected from the Great Lakes in 2001 (Furdui et al., 2007) were lowest in Lake Superior (4.8 ng/g) and highest in Lake Erie (121 ng/g). In a separate study of PFCs in the Lake Ontario food web, mean PFOS concentration in slimy sculpin was 450 ng/g, while whole lake trout were 170 ng/g (Martin et al., 2004). Lake trout eat alewife (90%) and smelt (7-8%); sculpin eat mysis and Diporeia. Because the sculpin diet is benthic-based rather than pelagic, the authors suggested the sediment was the primary source of PFOS. The results of the 2009 Pool 2 support the sediment-source hypothesis, because the highest PFOS concentrations were in freshwater drum, which is a bottom feeder. They move rocks and substrate to flush their prey, which are primarily aquatic insects, small fish, and mollusks. They are known for eating zebra mussels (Sluss and Harrel, 2006).

Reported BAFs for PFOS have varied greatly from study to study and among species within studies. In the Lake Ontario food web BAFs ranged from 9,800 L/Kg for alewife to 95,000 for sculpin; lake trout BAF was 16,000 (Houde et al., 2008). In a comparison of 4-year old lake trout among the Great Lakes, the BAF ranged from 5,000 to 20,000 L/Kg (Furdui et al, 2007); this study reported a lake trout BAF of 5000 L/Kg. In Pool 2, species geometric mean values ranged from 2500 to 7000 L/Kg for Section 4 and 4,400 to 11,500 for all sections combined. On an order-of-magnitude scale (i.e., log-scale) these BAFs look more

similar; that is, the logBAF is about 4, which can be compared to PCBs and mercury logBAFs around 6 or 7 (1-10 million L/Kg).

PFCs with seven or less fluorinated carbons are not considered bioaccumulative according to regulatory definitions (Conder et al., 2008). The evidence supports that claim because PFCs less than C8 (PFOA and PFOS) are often not detected in fish (Powley et al., 2008). On the other side, C8-C12 PFCs have been detected at in fish, although the non-PFOS PFCs occur at much lower concentrations than PFOS. A previous study reported that there is a significant correlation between PFOS and the PFCAs greater than C8 (Powley et al., 2008). This was reported for fish in Lake Calhoun and Mississippi River Pools 2-5a collected in 2006 (Delinsky et al., 2009), and it is true for the 2009 results for Pool 2. In the 2009 Pool 2 results, when PFOS concentration was very high, the longer carbon-chain PFCs were also detectable (Figure 14). PFDA (C10) was highly correlated with the PFOS concentrations. The Pearson correlation coefficients between PFOS and the C9 (PFNA), C10 (PFDA), and C11 (PFUnA), and C12 (PFDoA) were 0.010, 0.943, 0.732, and 0.280. The correlation with PFOSA was 0.717.

Delinsky et al. (2009) noted that the C10-C12 concentrations in the Haw and Deep rivers in North Carolina—with no documented source of PFCs—were some of the highest in the literature; Lake Calhoun was also high and higher than fish from Pools 2-5a (from 2006 collection); the only study reported higher C10 and C11 levels was from a creek in Canada where aqueous fire-fighting foam had been released (Moody et al., 2002). Maximum concentrations of C10 and C12 in Pool 2 from 2009 were 32.1 and 29.8 ng/g and exceeded the maxima reported for the two North Carolina rivers. C11 maxima from the two rivers were much higher than in Pool 2 (42.2 and 50.5 ng/g, compared to 11.8 ng/g in Pool 2). In the 2009, Pool 2 results, all PFCs other than PFOS had median concentrations at or below the LOQ, but nearly all of them had a detectable concentration at some point.

One final point to address is the biomagnification of PFOS and the apparent discrepancy between literature results and this study. Numerous studies have reported PFOS levels increase with trophic level in freshwater and marine food webs (Kannan et al., 2005), sometimes by as much as a factor of three between trophic levels. This was not seen for PFOS concentrations in fish from Mississippi River Pool 2. The wide and overlapping ranges of PFOS concentrations within and among species in Pool 2 may hide the possible differences among trophic levels. Comparison of PFOS concentrations in largemouth bass and bluegill sunfish from the same lakes in Minnesota suggest there may be trophic magnification of PFOS (data not presented in this report). The fish from Pool 2 cannot be paired by location. Furthermore, they are all carnivores, albeit at somewhat different levels.

Conclusions

All fish and water samples were analyzed for PFCs by AXYS Analytical Ltd. All water samples and 30 fish samples were also analyzed by 3M Environmental Laboratory for quality assurance. The match between results of split samples from the two labs was very good for both water and fish, which reinforced confidence in the quality of the results.

Water concentrations of PFCs were highest in Section 4 and in particular, Station 11. Perfluorobutanoic acid (PFBA) was detected at all stations. PFOS, perfluorooctanoic acid (PFOA), and perfluorohexanoic acid (PFHxA) were detected in Sections 2, 3, and 4, with the highest concentrations in Section 4. Three others—PFPeA, PFBS, and PFHxS—were detected in Section 4.

PFOS was detectable in nearly all fish from Pool 2, with the highest concentrations in fish and water in Section 4, the most downstream section of Pool 2. Most other PFCs were near or below the reporting level, although longer carbon-chain PFCs were detectable when PFOS concentrations were high. Of the five targeted fish species in Pool 2—bluegill sunfish, carp, freshwater drum, smallmouth bass, and white bass—freshwater drum had the highest PFOS concentrations. Drum had not been sampled prior to 2009 because it is not considered a typical sport fish, but it was included as a targeted species because of the DNR's observation that it is a popular fish kept for human consumption and has been harvested by commercial fishing operations.

No discernable trends were seen in PFOS over time for species that had been sampled since 2004 or 2005. PFOS concentrations in fish muscle were not correlated with fish age or size, and there was no difference between genders. Bioaccumulation factors (BAFs) were calculated for PFOS using the water and fish data. BAFs for PFOS were in the range of 4000 to 6000 L/Kg, which is at the low end of the range of highly bioaccumulative compounds.

References

- Berger U., Glynn A., Holmstrom K.E., Berglund M., Ankarberg E.H., Tornkvist A. (2009) Fish consumption as a source of human exposure to perfluorinated alkyl substances in Sweden - Analysis of edible fish from Lake Vattern and the Baltic Sea. *Chemosphere* 76:799-804. DOI: 10.1016/j.chemosphere.2009.04.044.
- Conder J.M., Hoke R.A., De Wolf W., Russell M.H., Buck R.C. (2008) Are PFCA's bioaccumulative? A critical review and comparison with regulatory lipophilic compounds. *Environmental Science & Technology* 42:995-1003. DOI: 10.1021/es070895g.
- Delinsky A.D., Strynar M.J., Nakayama S.F., Varns J.L., Ye X.B., McCann P.J., Lindstrom A.B. (2009) Determination of ten perfluorinated compounds in bluegill sunfish (*Lepomis macrochirus*) filets. *Environmental Research* 109:975-984. DOI: 10.1016/j.envres.2009.08.013.
- Delinsky A.D., Strynar M.J., McCann P.J., Varns J.L., McMillan L., Nakayama S.F., Lindstrom A.B. (2010) Geographical Distribution of Perfluorinated Compounds in Fish from Minnesota Lakes and Rivers. *Environmental Science & Technology ASAP* 17FEB2010. DOI: 10.1021/es903777s.
- Furdui V.I., Stock N.L., Ellis D.A., Butt C.M., Whittle D.M., Crozier P.W., Reiner E.J., Muir D.C.G., Mabury S.A. (2007) Spatial distribution of perfluoroalkyl contaminants in lake trout from the Great Lakes. *Environmental Science & Technology* 41:1554-1559. DOI: 10.1021/es0620484.
- Giesy J.P., Kannan K. (2001) Global distribution of perfluorooctane sulfonate in wildlife. *Environmental Science & Technology* 35:1339-1342. DOI: 10.1021/es001834k.
- Giesy J.P., Kannan K. (2002) Perfluorochemical surfactants in the environment. *Environmental Science & Technology* 36:146A-152A.
- Houde M., Martin J.W., Letcher R.J., Solomon K.R., Muir D.C.G. (2006) Biological monitoring of polyfluoroalkyl substances: A review. *Environmental Science & Technology* 40:3463-3473. DOI: 10.1021/es052580b.
- Jones M.J., Stuart I.G. (2008) Lateral movement of common carp (*Cyprinus carpio* L.) in a large lowland river and floodplain. *Ecology of Freshwater Fish* 18:17-82.
- Kannan K., Tao L., Sinclair E., Pastva S.D., Jude D.J., Giesy J.P. (2005) Perfluorinated compounds in aquatic organisms at various trophic levels in a Great Lakes food chain. *Archives of Environmental Contamination and Toxicology* 48:559-566. DOI: 10.1007/s00244-004-0133-x.
- Martin J.W., Whittle D.M., Muir D.C.G., Mabury S.A. (2004) Perfluoroalkyl contaminants in a food web from lake Ontario. *Environmental Science & Technology* 38:5379-5385. DOI: 10.1021/es019331a.
- Moody C.A., Martin J.W., Kwan W.C., Muir D.C.G., Mabury S.A. (2002) Monitoring Perfluorinated Surfactants in Biota and Surface Water Samples Following an Accidental Release of Fire-Fighting Foam into Etobicoke Creek. *Environmental Science & Technology* 36:545-551. DOI: 10.1021/es011001+.
- Morgan T., Harrel S. (2006) Morone chrysops, Animal Diversity Web.
- Parr C. (2002) *Lepomis macrochirus*, Animal Diversity Web.
- Parsons B.G., Reed J.R. (2005) Movement of Black Crappies and Bluegills among Interconnected Lakes in Minnesota. *North American Journal of Fisheries Management* 25:689-695. DOI: 10.1577/M04-021.1.
- Powley C.R., George S.W., Russell M.H., Hoke R.A., Buck R.C. (2008) Polyfluorinated chemicals in a spatially and temporally integrated food web in the Western Arctic. *Chemosphere* 70:664-672. DOI: 10.1016/j.chemosphere.2007.06.067.

- STS Consultants. (2007) Surface Water Quality Criterion for Perfluorooctane Sulfonic Acid Minnesota Pollution Control Agency.
- Wang T., Wang Y.W., Liao C.Y., Cai Y.Q., Jiang G.B. (2009) Perspectives on the Inclusion of Perfluorooctane Sulfonate into the Stockholm Convention on Persistent Organic Pollutants. *Environmental Science & Technology* 43:5171-5175. DOI: 10.1021/es900464a.
- Ye X.B., Strynar M.J., Nakayama S.F., Varns J., Helfant L., Lazorchak J., Lindstrom A.B. (2008a) Perfluorinated compounds in whole fish homogenates from the Ohio, Missouri, and Upper Mississippi Rivers, USA. *Environmental Pollution* 156:1227-1232. DOI: 10.1016/j.envpol.2008.03.014.
- Ye X.B., Schoenfuss H.L., Jahns N.D., Delinsky A.D., Strynar M.J., Varns J., Nakayama S.F., Helfant L., Lindstrom A.B. (2008b) Perfluorinated compounds in common carp (*Cyprinus carpio*) fillets from the Upper Mississippi River. *Environment International* 34:932-938. DOI: 10.1016/j.envint.2008.02.003.

Tables

Table 1 Ancillary information about water sampling stations (2 July 2009)

Station ID	UTM Coordinates		Time (HH:MM)	Water Depth (m)	Temp (°C)	Sp. Cond. (µS/cm)	D.O. (mg/L)
1	0484143	4973007	14:08	4.0	25.74	378	9.24
2	0486067	4971149	13:51	3.0	25.21	380	9.28
3	0487624	4971560	13:30	3.7	24.93	382	8.93
4	0489737	4973910	13:17	6.7	24.21	536	8.67
5	0496075	4975366	12:47	4.0	25.52	525	9.46
6	0497900	4971442	12:30	1.2	25.03	580	8.72
7	0499081	4965125	8:43	3.4	24.71	587	7.96
8	0499272	4963280	9:06	3.7	24.73	576	7.82
9	0503642	4956878	9:40	2.7	24.38	579	7.85
10	0505348	4958622	9:58	3.7	23.87	579	7.41
11	0508546	4958789	10:24	1.2	23.86	566	7.92
12	0510018	4956960	10:47	5.2	24.28	574	7.26

Table 2 PFC concentrations in water at 12 stations in Mississippi Pool 2

Sample ID ^a	UNITS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDaA	PFBS	PFHxS	PFOSA	PFOS	Mean PFOS ^b
1-01-1	ng/L	3.76	< 2.56	< 2.56	< 2.56	< 2.56	< 2.56	< 2.56	< 2.56	< 2.56	< 5.12	< 5.12	< 2.56	< 5.12	2.56
1-01-2	ng/L	4.33	< 2.57	< 2.57	< 2.57	< 2.57	< 2.57	< 2.57	< 2.57	< 2.57	< 5.14	< 5.14	< 2.57	< 5.14	
1-01-3	ng/L	5.16	< 2.54	< 2.54	< 2.54	< 2.54	< 2.54	< 2.54	< 2.54	< 2.54	< 5.08	< 5.08	< 2.54	< 5.08	
1-02-1	ng/L	4.4	< 2.54	< 2.54	< 2.54	< 2.54	< 2.54	< 2.54	< 2.54	< 2.54	< 5.08	< 5.08	< 2.54	< 5.08	2.53
1-02-2	ng/L	4.16	< 2.55	< 2.55	< 2.55	< 2.55	< 2.55	< 2.55	< 2.55	< 2.55	< 5.10	< 5.10	< 2.55	< 5.10	
1-02-3	ng/L	5.38	< 2.51	< 2.51	< 2.51	< 2.51	< 2.51	< 2.51	< 2.51	< 2.51	< 5.02	< 5.02	< 2.51	< 5.02	
1-03-1	ng/L	6.79	< 2.58	< 2.58	< 2.58	< 2.58	< 2.58	< 2.58	< 2.58	< 2.58	< 5.15	< 5.15	< 2.58	< 5.15	2.53
1-03-2	ng/L	5.01	< 2.52	< 2.52	< 2.52	< 2.52	< 2.52	< 2.52	< 2.52	< 2.52	< 5.03	< 5.03	< 2.52	< 5.03	
1-03-3	ng/L	5.08	< 2.49	< 2.49	< 2.49	< 2.49	< 2.49	< 2.49	< 2.49	< 2.49	< 4.97	< 4.97	< 2.49	< 4.97	

Table 2 (continued) PFC concentrations in water at 12 stations in Mississippi Pool 2

Sample ID ^a	UNITS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFBS	PFHxS	PFOSA	PFOS	Mean PFOS ^b
2-04-1	ng/L	3.96	< 2.51	< 2.51	< 2.51	< 2.51	< 2.51	< 2.51	< 2.51	< 2.51	< 5.03	< 5.03	< 2.51	< 5.03	2.53
2-04-2	ng/L	4.81	< 2.55	< 2.55	< 2.55	< 2.55	< 2.55	< 2.55	< 2.55	< 2.55	< 5.09	< 5.09	< 2.55	< 5.09	
2-04-3	ng/L	4.45	< 2.52	< 2.52	< 2.52	< 2.52	< 2.52	< 2.52	< 2.52	< 2.52	< 5.04	< 5.04	< 2.52	< 5.04	
2-05-1	ng/L	4.87	< 2.54	< 2.54	< 2.54	< 2.54	< 2.54	< 2.54	< 2.54	< 2.54	< 5.07	< 5.07	< 2.54	< 5.07	2.52
2-05-2	ng/L	5.25	< 2.56	< 2.56	< 2.56	< 2.56	< 2.56	< 2.56	< 2.56	< 2.56	< 5.11	< 5.11	< 2.56	< 5.11	
2-05-3	ng/L	5.23	< 2.46	< 2.46	< 2.46	2.51	< 2.46	< 2.46	< 2.46	< 2.46	< 4.93	< 4.93	< 2.46	< 4.93	
2-06-1	ng/L	8.95	< 2.50	< 2.50	< 2.50	3.74	< 2.50	< 2.50	< 2.50	< 2.50	< 5.01	< 5.01	< 2.50	7.1	7.71
2-06-2	ng/L	8.61	< 2.52	2.63	< 2.52	3.94	< 2.52	< 2.52	< 2.52	< 2.52	< 5.05	< 5.05	< 2.52	7.8	
2-06-3	ng/L	5.79	< 2.55	< 2.55	< 2.55	3.2	< 2.55	< 2.55	< 2.55	< 2.55	< 5.09	< 5.09	< 2.55	8.24	
3-07-1	ng/L	10.6	< 2.53	3.00	< 2.53	4.48	< 2.53	< 2.53	< 2.53	< 2.53	< 5.06	< 5.06	< 2.53	10.5	10.30
3-07-2	ng/L	10.7	< 2.49	3.58	< 2.49	5.01	< 2.49	< 2.49	< 2.49	< 2.49	< 4.98	< 4.98	< 2.49	10.5	
3-07-3	ng/L	9.82	< 2.53	2.57	< 2.53	4.75	< 2.53	< 2.53	< 2.53	< 2.53	< 5.07	< 5.07	< 2.53	9.91	
3-08-1	ng/L	11	< 2.55	3.14	< 2.55	5.42	< 2.55	< 2.55	< 2.55	< 2.55	< 5.10	< 5.10	< 2.55	8.74	8.51
3-08-2	ng/L	9.63	< 2.55	< 2.55	< 2.55	3.91	< 2.55	< 2.55	< 2.55	< 2.55	< 5.09	< 5.09	< 2.55	8.4	
3-08-3	ng/L	9.44	< 2.56	2.77	< 2.56	4.5	< 2.56	< 2.56	< 2.56	< 2.56	< 5.11	< 5.11	< 2.56	8.4	
3-09-1	ng/L	13.2	< 2.52	3.06	< 2.52	4.22	< 2.52	< 2.52	< 2.52	< 2.52	< 5.05	< 5.05	< 2.52	< 5.05	2.54
3-09-2	ng/L	13.3	< 2.52	2.76	< 2.52	4.63	< 2.52	< 2.52	< 2.52	< 2.52	< 5.04	< 5.04	< 2.52	< 5.04	
3-09-3	ng/L	11.9	< 2.59	3.12	< 2.59	5.03	< 2.59	< 2.59	< 2.59	< 2.59	< 5.17	< 5.17	< 2.59	< 5.17	
4-10-1	ng/L	14.8	< 2.54	2.91	< 2.54	3.91	< 2.54	< 2.54	< 2.54	< 2.54	< 5.07	< 5.07	< 2.54	< 5.07	2.52
4-10-2	ng/L	12.9	< 2.53	2.93	< 2.53	4.21	< 2.53	< 2.53	< 2.53	< 2.53	< 5.05	< 5.05	< 2.53	< 5.05	
4-10-3	ng/L	9.81	< 2.48	< 2.48	< 2.48	4.07	< 2.48	< 2.48	< 2.48	< 2.48	< 4.97	< 4.97	< 2.48	< 4.97	
4-11-1	ng/L	161	14.7	16.7	5.77	88.1	< 2.54	< 2.54	< 2.54	< 2.54	40.2	28.8	< 2.54	84.4	90.07
4-11-2	ng/L	155	15.3	17.9	5.83	95.8	< 2.59	< 2.59	< 2.59	< 2.59	41.7	27.7	< 2.59	91.3	
4-11-3	ng/L	189	16.9	18	6.05	98.4	< 2.48	< 2.48	< 2.48	< 2.48	41.9	27.9	< 2.48	94.5	
4-12-1	ng/L	48.6	5.78	5.23	< 2.54	17.5	< 2.54	< 2.54	< 2.54	< 2.54	12.9	11.8	< 2.54	15.1	15.17
4-12-2	ng/L	51.6	6.15	6.85	2.91	21.3	< 2.55	< 2.55	< 2.55	< 2.55	16.1	13.1	< 2.55	19.2	
4-12-3	ng/L	31.4	3.18	4.6	< 2.53	11.3	< 2.53	< 2.53	< 2.53	< 2.53	7.69	5.64	< 2.53	11.2	

- a. sample ID: Section-Station-Replicate
- b. 1/2 detection limit used for calculating mean

Table 3 Fish collection in Mississippi Pool 2 by MDNR

Section	River Mile	County	Date Collected	Time Collected	Species	Species Count
1	847-847.5	Ramsey	5/28/09	0900-1400	Smallmouth Bass (SMB)	15
1	846.5-847.5	Ramsey	5/28/09	0900-1400	Freshwater Drum (FWD)	15
1	845.4-847.5	Ramsey	5/28/09	0900-1400	Carp (C)	15
1	844.3-847.5	Ramsey	5/28/09	0900-1400	White Bass (WB)	15
1	844.1-847	Ramsey	5/28/09	0900-1400	Bluegill Sunfish (BGS)	12
2	840.5-841.0	Ramsey	5/29/09	0830-1330	White Bass (WB)	15
2	840.5-842.6	Ramsey	5/29/09	0830-1330	Carp (C)	15
2	836.4-842.6	Ramsey	5/29/09	0830-1330	Freshwater Drum (FWD)	15
2	840.5-842.6	Ramsey	5/29/09	0830-1330	Smallmouth Bass (SMB)	15
2	840.5-842.6	Ramsey	5/29/09	0830-1330	Bluegill Sunfish (BGS)	15
3	834-833.5 and Hog Lake	Ramsey	5/29/09	1400-1700	White Bass (WB)	15
3	834-833.5 and Hog Lake	Ramsey	5/29/09	1400-1700	Bluegill Sunfish (BGS)	15
3	834-833.5 and Hog Lake	Ramsey	5/29/09	1400-1700	Carp (C)	15
3	834-833.5 and Hog Lake	Ramsey	5/29/09	1400-1700	Freshwater Drum (FWD)	1
3	829.7-827.2	Dakota	6/1/09	0830-1030	Freshwater Drum (FWD)	14
3	829.7-827.2	Dakota	6/1/09	0830-1030	Smallmouth Bass (SMB)	15
4	819.8-815.2	Dakota	6/1/09	1130-1700	Freshwater Drum (FWD)	15
4	819.8-815.2	Dakota	6/1/09	1130-1700	Bluegill Sunfish (BGS)	15
4	819.8-815.2	Dakota	6/1/09	1130-1700	Smallmouth Bass (SMB)	15
4	819.8-815.2	Dakota	6/1/09	1130-1700	Carp (C)	15
4	819.8-815.2	Dakota	6/1/09	1130-1700	White Bass (WB)	15

Table 4 Summary statistics for PFOS concentrations by species in Pool 2

Statistic	Species				
	Bluegill (BGS)	Carp (C)	Freshwater Drum (FWD)	Smallmouth Bass (SMB)	White Bass (WHB)
Arithmetic Mean	110	77	229	94	97
N of Cases	57	60	60	60	60
Maximum	1350	1340	3580	612	764
Minimum	8	5	5	13	38
Median	45	28	63	41	75
Geometric Mean	51	31	70	50	83
Standard Deviation	219	203	602	141	95

Table 5 Number of fish collected each year by species

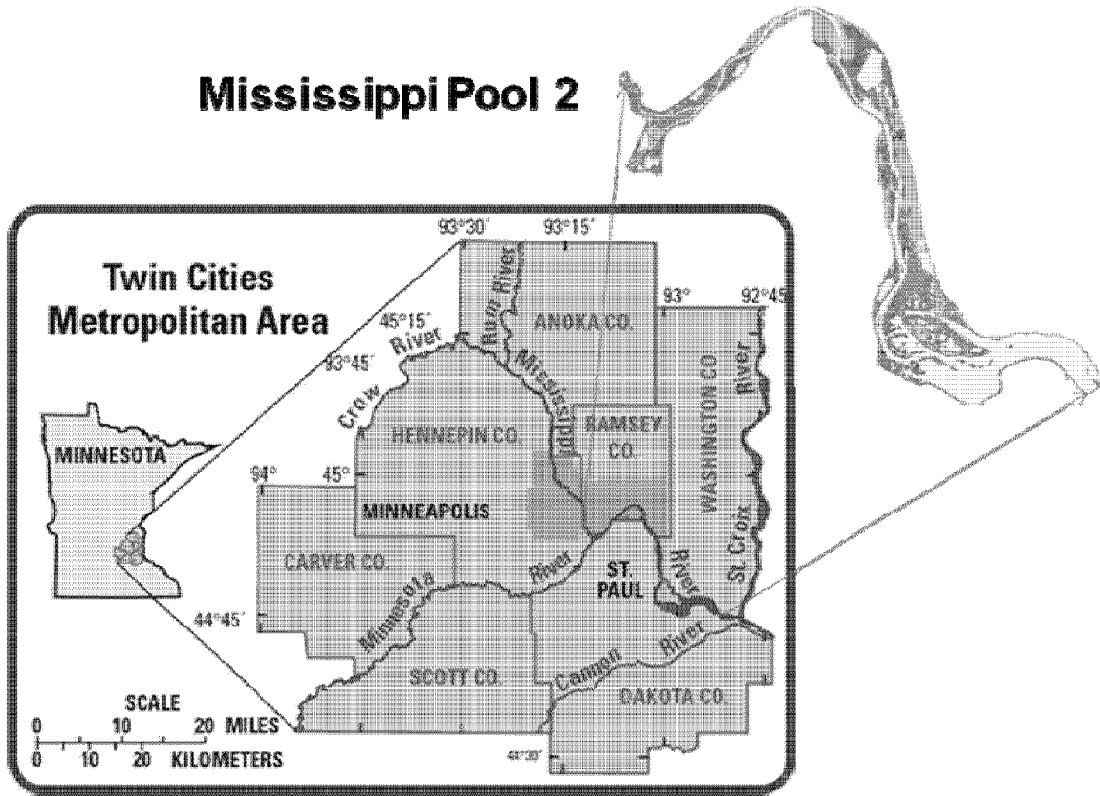
Year	Species									
	SMB	WHB	C	WE	BGS	CHC	BKS	SAG	FWD	Total
2004	2	1								3
2005	7	5	5	4						21
2006	11				6	15				32
2008	5			4	5		1	2		17
2009	60	60	60		57				60	297
Grand Total										370

Table 6 Published PFOS concentrations in fish

Species	Location	N	PFOS		Reference
			(ng/g)		
Common Carp (fillet)	Mississippi R. - St. Cloud (R.M. 938)	9	8.1		Ye et al 2008b (collection 2006)
	Miss. R. - Pig's Eye Lake vicinity (R.M. 833)	10	26		
	Miss. R. - Spring Lake (R.M.816)	11	40		
	Saginaw Bay, Lake Michigan	10	124		Kannan et al 2005
Lake Trout (whole)	Lake Ontario	7	170		Martin et al. 2004 (collection 2001)
Sculpin		15	450		
Rainbow Trout		30	110		
Alewife		12	46		
Mysis		NA	13		
Diporeia		NA	280		
Lake Trout (4 yr old; whole)	Lake Superior	10	4.8		Furdui et al. 2007 (collection 2001)
	Lake Michigan	10	16		
	Lake Huron	10	39		
	Lake Erie	6	131		
	Lake Ontario	10	46		

Figures

Mississippi Pool 2



Graphics from uga.gov (mn_water and unsec)

Figure 1 Location of Mississippi Pool 2

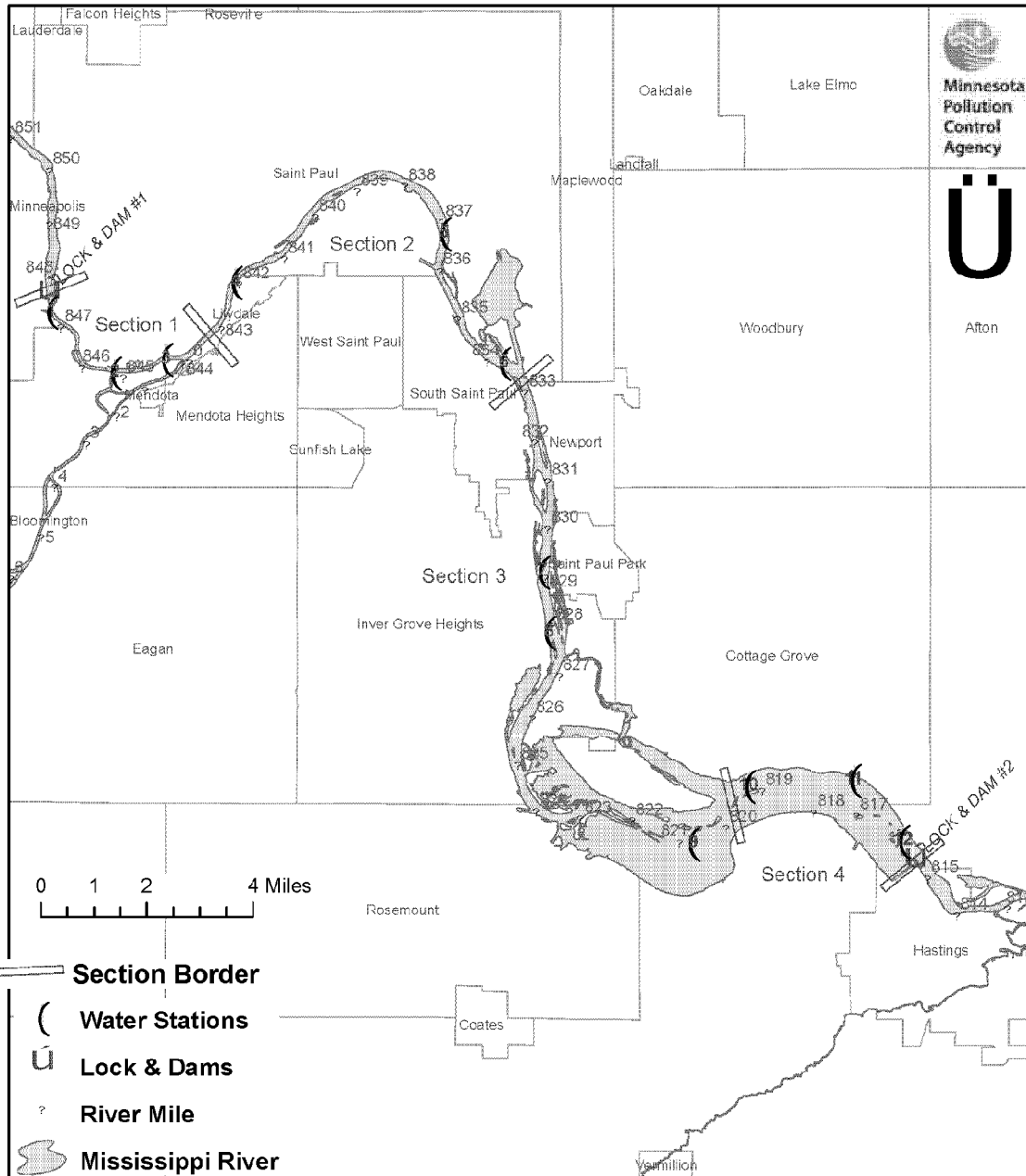


Figure 2 Mississippi Pool 2 sections and water sample stations

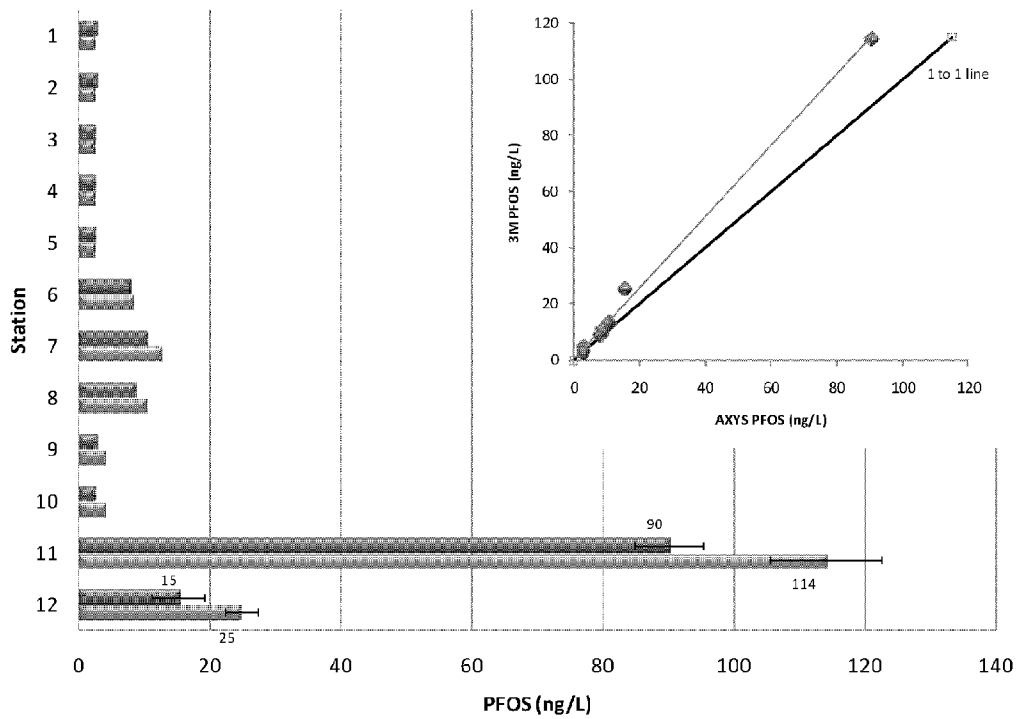


Figure 3 Comparison of AXYS (red, top bar) and 3M (blue) results for PFOS concentrations in water from 12 stations in Pool 2; embedded figure shows AXYS versus 3M PFOS with 1:1 line

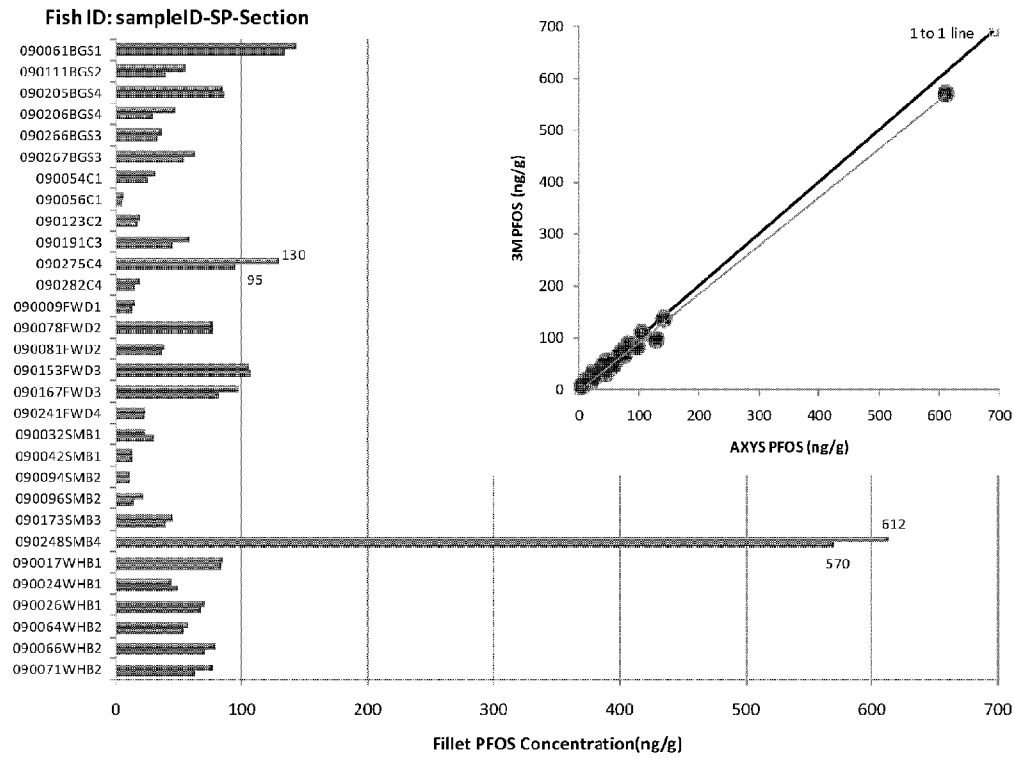


Figure 4 Comparison of AXYS (red, top bar) and 3M (blue) results for PFOS concentrations from same fish homogenates; embedded figure shows AXYS versus 3M PFOS with 1:1 line

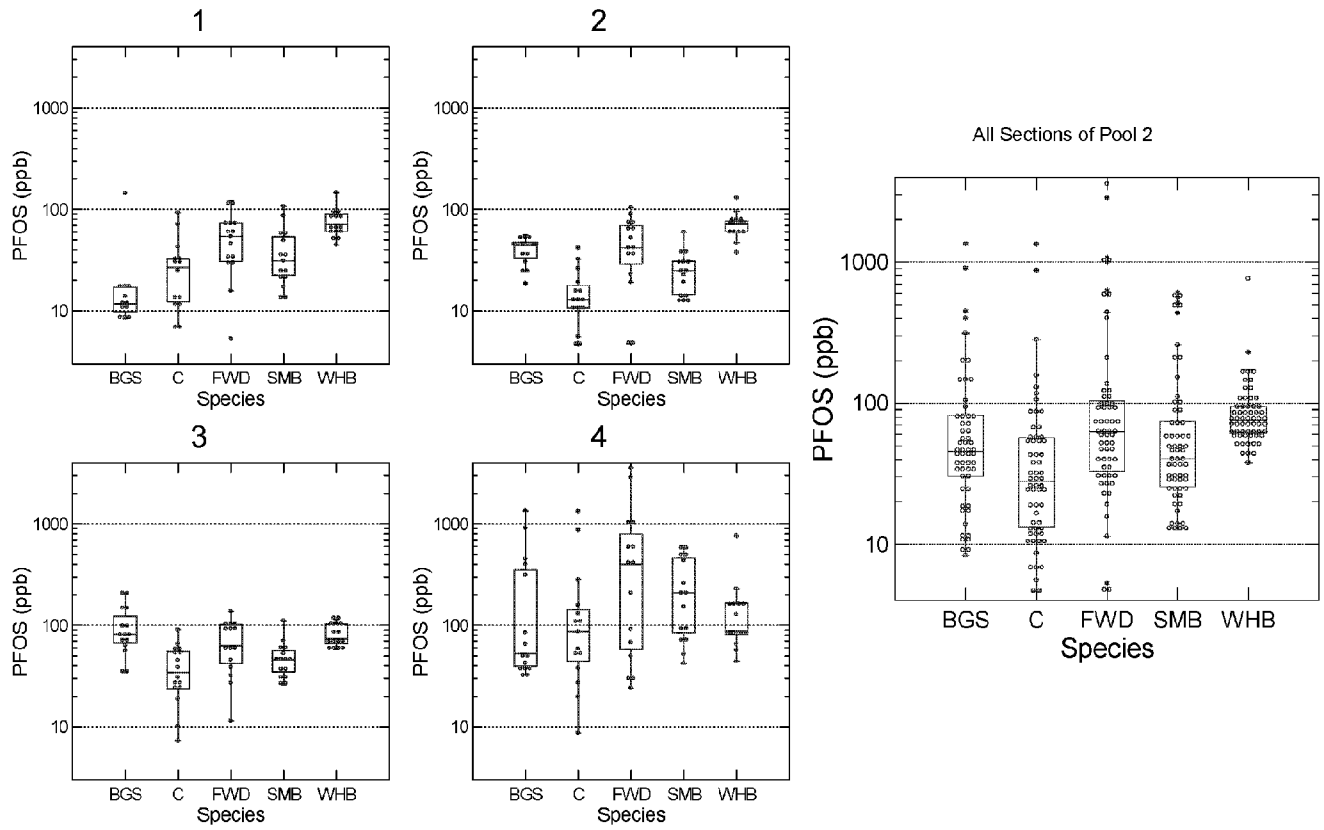


Figure 5 Distributions of PFOS by species within each Section (1-4) and all sections combined

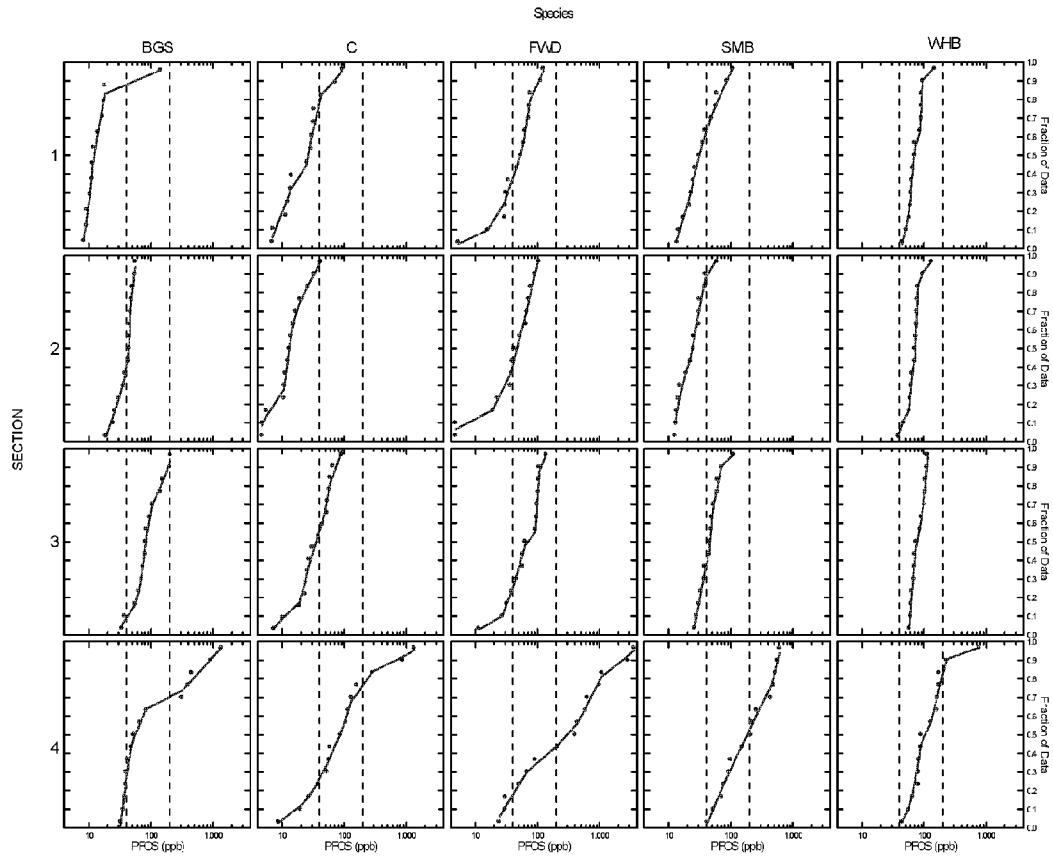


Figure 6 PFOS in Species-Section Matrix; vertical bars are 40 ppb and 200 ppb

All Sections of Pool 2

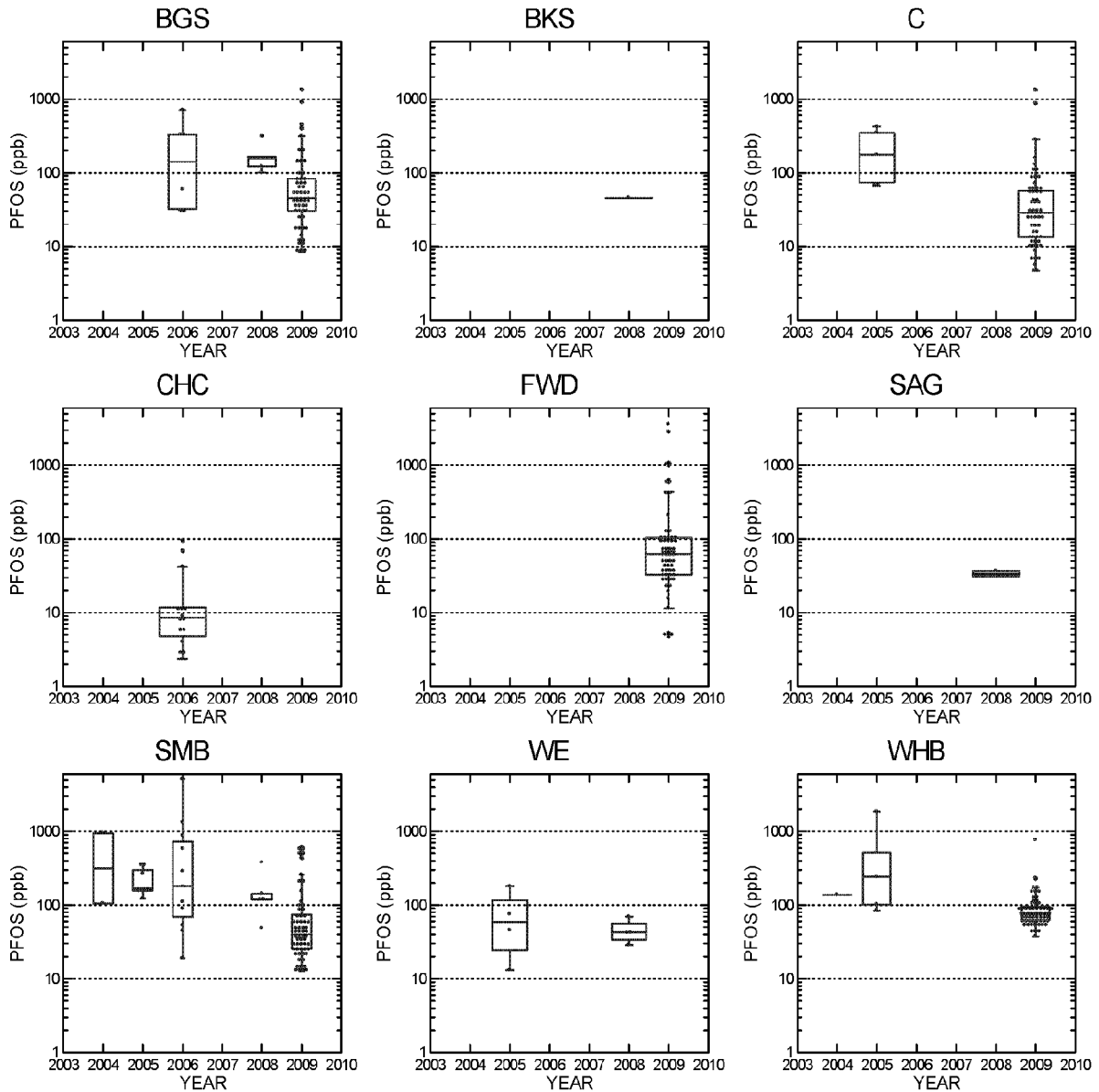


Figure 7 Distributions of PFOS by year for each species (all sections)

Section 4 of Pool 2

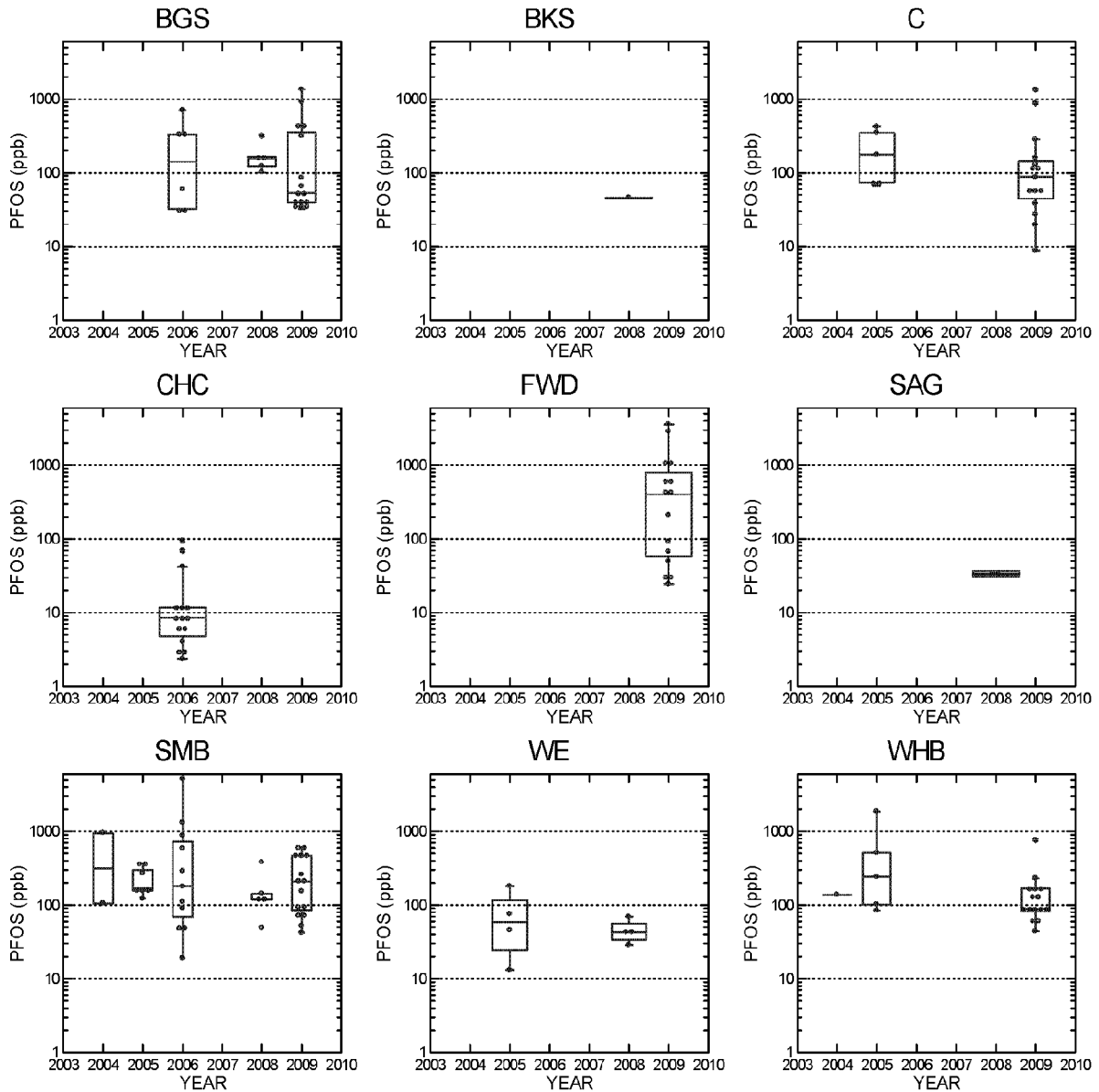


Figure 8 Distributions of PFOS by year for each species limited to Section 4

Pool 2 2009

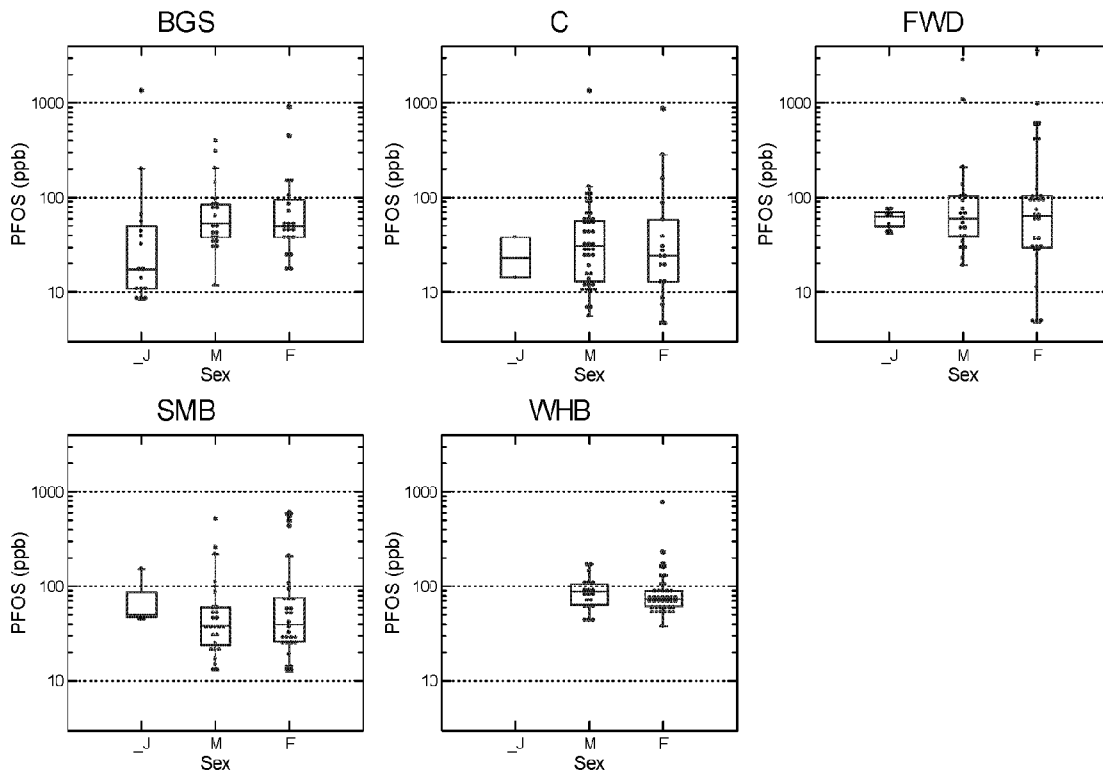


Figure 9 PFOS concentrations by gender of each species

Pool 2 2009

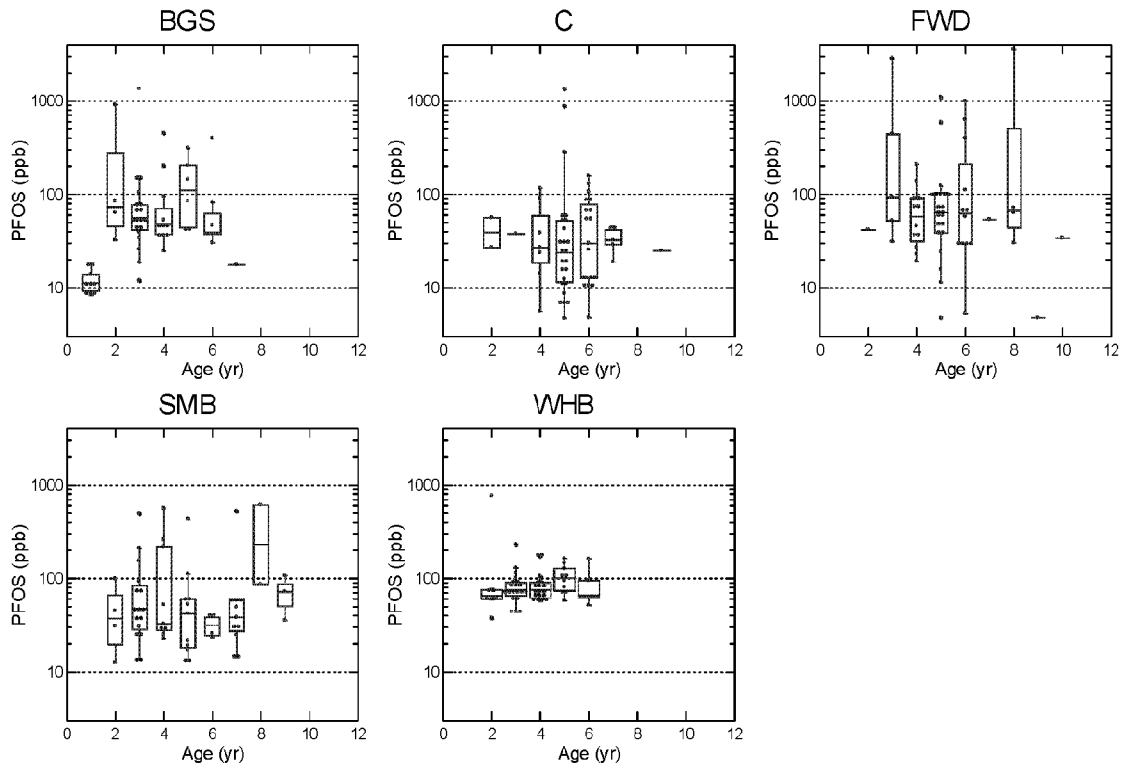


Figure 10 PFOS concentration by age for each species

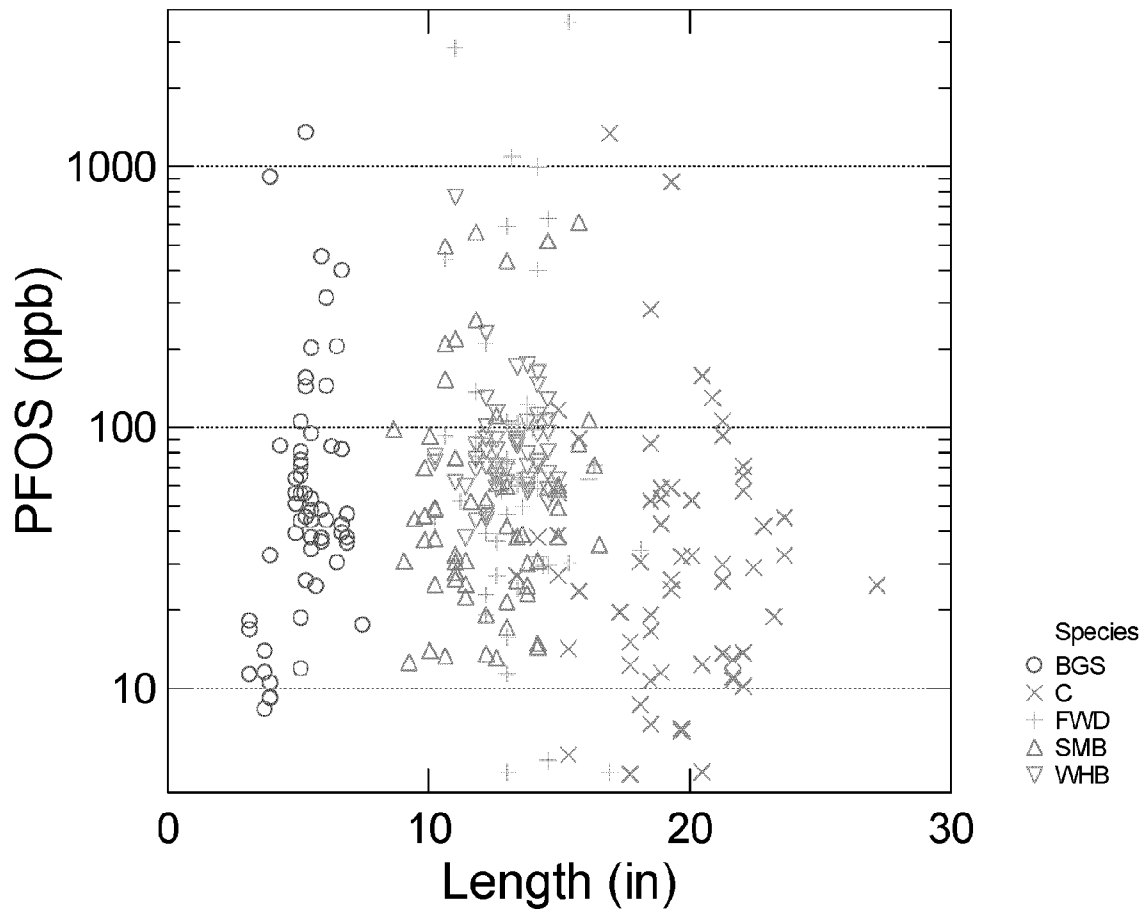


Figure 11 PFOS concentrations by length for each species

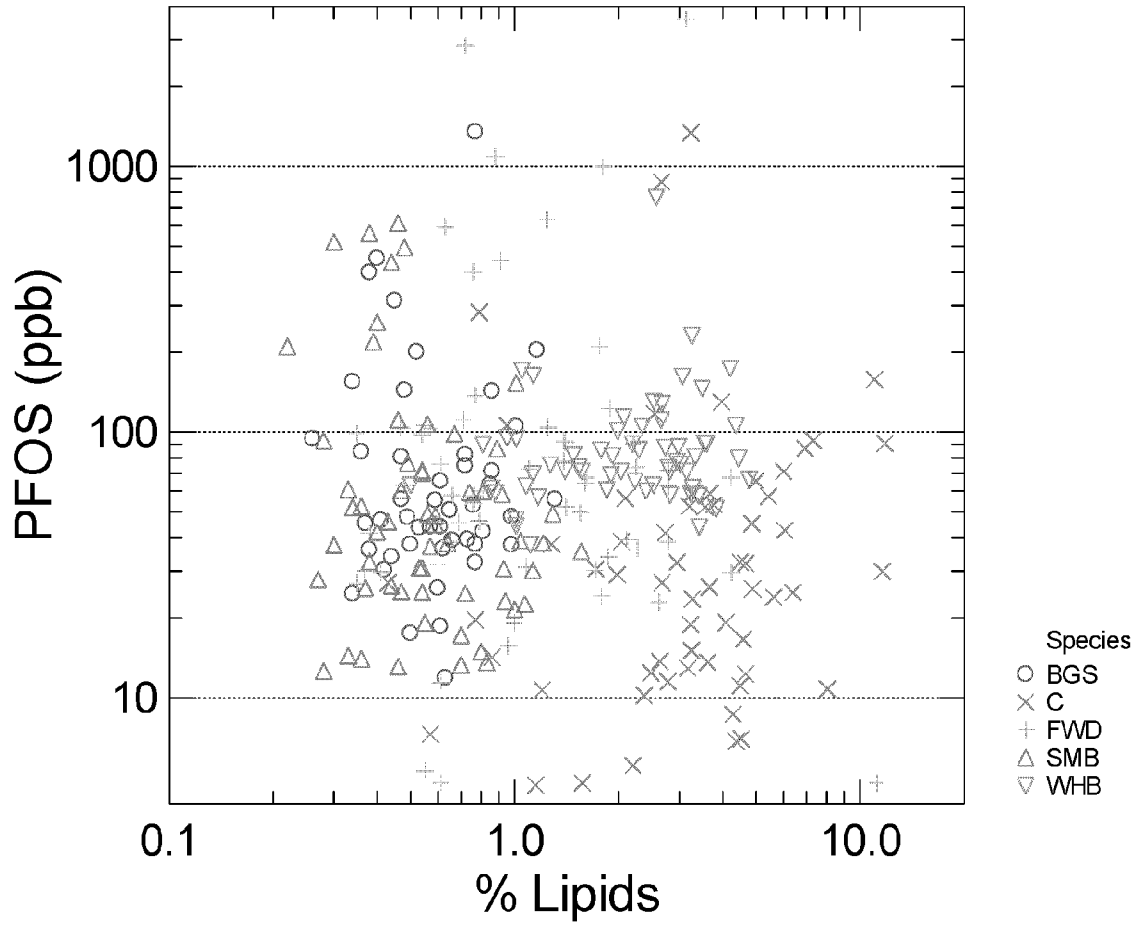


Figure 12 PFOS concentration by percent lipids for each species

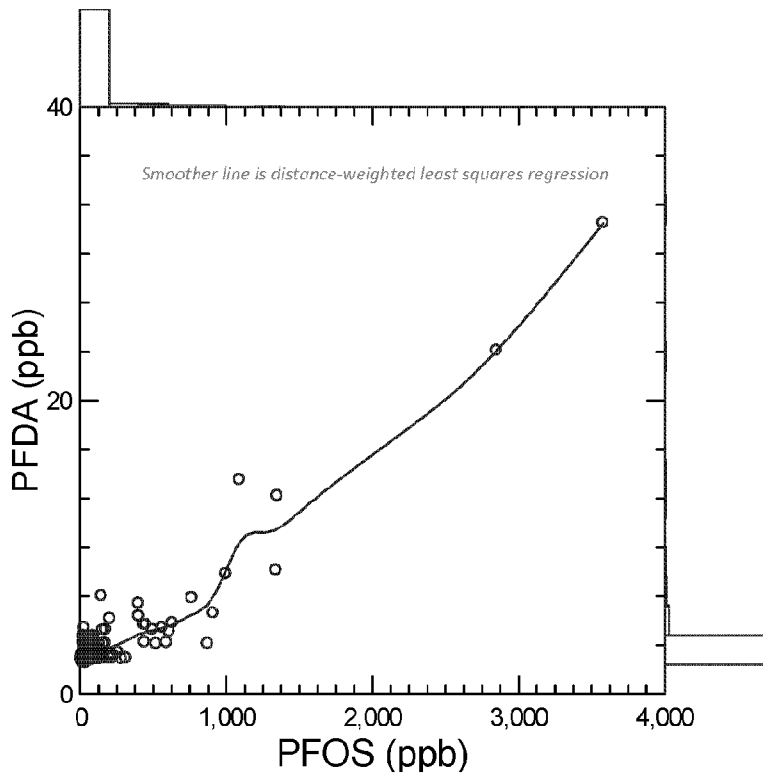


Figure 13 Relationship between PFDA (C10) and PFOS from Pool 2 (all species and sections)

Resources

Cover Photo: Upper Midwest Environmental Sciences Center.

http://www.umesc.usgs.gov/aerial_photos/s/s31g1_1997ob.html

For more information on this report contact:

Bruce Monson
Research Scientist
Minnesota Pollution Control Agency
520 Lafayette Road N
St. Paul, MN 55155
Phone: (651) 757-2579

Minnesota Pollution Control Agency PFCs

<http://www.pca.state.mn.us/cleanup/pfc/index.html>

Minnesota Department of Health PFCs

<http://www.health.state.mn.us/divs/eh/hazardous/topics/pfcs/index.html>

Minnesota Department of Health Fish Consumption Guidelines

<http://www.health.state.mn.us/divs/eh/fish/index.html>

Appendix A

Map of fish collections in Pool 2

Appendix B

Results of PFCs analysis of fish collected in Mississippi Pool 2 in 2009
