Geographical Distribution of Perfluorinated Compounds in Fish from Minnesota Lakes and Rivers

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Geographical Distribution of Perfluorinated Compounds in Fish from Minnesota Lakes and Rivers

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Abstract

In response to growing interest in human exposure to perfluorinated compounds (PFCs), the state of Minnesota (MN) measured and reported PFC concentrations in fish collected from the Minneapolis-St. Paul area. To better determine the geographical distribution of PFC contamination throughout MN, fish were collected from 59 lakes throughout the state and several areas along the Mississippi River. Composite fish samples were analyzed for ten PFC analytes using solid phase extraction (SPE) and LC/MS/MS. PFOS (perfluorooctane sulfonate) was the most commonly detected PFC, occurring in 73% of fish from the Mississippi River but only 22% of fish from lakes. Fish from Mississippi River Pool 2 near the Minneapolis-St. Paul area had the highest levels of PFOS, whereas locations upstream had PFOS concentrations below 40 ng/g, the concentration at which MN issues one meal per week fish consumption advice. Fish from most MN lakes tested (88%) had PFOS concentrations below 3 ng/g. Two lakes, McCarrons and Zumbro, contained fish with PFOS levels above 40 ng/g. The results reported here will help researchers to better understand the extent of PFC contamination in MN fish, to evaluate potential sources of contamination, and will provide a basis for comprehensive fish consumption advice.

Keywords: PFCs, PFOS, fish, LC/MS/MS, Minnesota
**Introduction**

Perfluorinated compounds (PFCs) have been used in a wide variety of industrial and consumer products due to their inherently useful chemical properties and resistance to degradation (1). As a result of their widespread use and persistence, PFCs are now found in environmental, biological, and human samples from areas throughout the world (2, 3). Human exposure to the PFCs is of concern because studies have found that perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), the two most commonly studied PFCs, have adverse effects in laboratory animals and their offspring (4, 5). In light of mounting concern over potential adverse effects related to the PFCs, the United States Environmental Protection Agency (USEPA) has recently issued Provisional Health Advisories for PFOS and PFOA in drinking water (6).

Moreover, PFOS has recently been added to the list of restricted use compounds appearing in Annex B of the Stockholm Convention on Persistent Organic Pollutants (POPs) (7).

Although the pathways by which humans are exposed to PFCs are still not well characterized, dietary exposure has been hypothesized to be an important human pathway (8, 9). In particular, studies have suggested that the ingestion of contaminated fish may be an important human exposure route for some PFCs (10, 11). Studies have documented elevated PFC concentrations (particularly PFOS) in the fillets of fish species commonly consumed by humans; however, limited information is available regarding the mechanisms by which fish become contaminated and the geographical distributions of contaminated fish (12 -16). There are many proven health benefits associated with eating fish, but because they may also contain relatively high levels of environmental pollutants (primarily metals and POPs), an evaluation of these potential exposures is helpful in selecting food items.
The state of Minnesota (MN) may be in a unique position of both having PFCs present in the environment from known local sources and having a large number of lakes and rivers from which many recreational anglers catch and eat fish (17). In response to the growing concerns over potential human exposure to PFCs, MN state agencies collected both water and fish samples for PFC analysis (17). Fish fillets from 53 St. Paul - Minneapolis metropolitan area lakes and two Duluth, MN area lakes have been analyzed for PFCs (18, 19). Fillet samples from several lakes in the Minneapolis-St. Paul area, the two Duluth lakes, and some areas of the Mississippi River contained PFOS at concentrations that were high enough to prompt state officials to issue fish consumption advisories for PFOS (17, 20). Specifically, MN fish consumption advisories recommend eating no more than one meal of fish per week when PFOS levels in fish are above 40 ng/g and eating no more than one meal per month when PFOS levels are above 200 ng/g (20).

Minnesota state agencies then collected additional fish samples from a variety of lakes throughout the state and several locations on the Mississippi River in MN in an effort to establish a more complete determination of the extent of PFC contamination.

Ten PFCs were analyzed in the fillets of fish from the Mississippi River and 59 lakes throughout MN using LC/MS/MS analysis with a method that has been thoroughly evaluated and was determined to have good performance characteristics (precision, accuracy, recovery) for PFC analysis (15). Prior to the work reported here, fish from lakes outside urban areas in MN had not been tested for PFCs. The results of this study provide a better understanding of where contamination may occur, the potential sources of contamination, and the extent to which consumption of fish may be a pathway by which MN residents are exposed to PFCs.

Materials and Methods
**Chemicals and Reagents.** Potassium salts of perfluorobutane sulfonate (PFBS, 98% purity) and perfluorohexane sulfonate (PFHS, 93%) were provided by 3M Company (St. Paul, MN). The potassium salt of perfluoroctane sulfonate (PFOS, 98%) was purchased from Fluka (Buchs, Switzerland). Perfluorohexanoic acid (C6, 97%), perfluoroheptanoic acid (C7, 99%), perfluorooctanoic acid (PFOA, 96%), perfluorononanoic acid (C9, 97%), and perfluorodecanoic acid (C10, 98%) were purchased from Sigma-Aldrich (St. Louis, MO). Perfluoroundecanoic acid (C11, 96%) and perfluorododecanoic acid (C12, 96%) were purchased from Oakwood Products (West Columbia, SC). Four isotopically labeled internal standards were used for the quantitation of PFCs. Oxygen labeled ammonium perfluoroctane sulfonate ([18O]2-PFOS) was purchased from RTI International (Research Triangle Park, NC). Isotopically labeled PFOA ([13C2]-PFOA) was purchased from Perkin-Elmer Life and Analytical Sciences, Inc. (Waltham, MA). Labeled sodium perfluorohexane sulfonate ([18O]2-PFHS) and labeled perfluoroundecanoic acid ([13C2]-PFUnA) were purchased from Wellington Laboratories (Ontario, Canada). HPLC-grade methanol (MeOH) was purchased from Burdick-Jackson (Muskegon, MI) and contained no measurable PFCs. Deionized (DI) water was obtained from a Barnstead EASYpure ultraviolet/ultrafiltration (UV/UF) compact reagent grade water system (Dubuque, IA) and had no detectable amounts of PFCs. Sodium hydroxide (NaOH), sodium acetate, glacial acetic acid, ammonium acetate and ammonium hydroxide (NH4OH) were purchased from Sigma-Aldrich (St. Louis, MO).

**Fish collection.** Fish were collected by electroshocking and netting from areas of the Upper Mississippi River in MN and from lakes throughout MN by the Minnesota Department of Natural Resources (MDNR) and the Minnesota Pollution Control Agency (MPCA) in 2007 as part of routine collections of fish for contaminant monitoring by the Minnesota Interagency Fish
Contaminants Monitoring Program (Figure 1, Figure S1). Fish included for PFC analysis were a convenience sample based on availability of fish tissue and lakes selected for scheduled fisheries assessments or other monitoring purposes. Fish from a range of lake sizes, locations, and major watersheds were included in this study (Figure 1, Table S1). Lake size ranged from 10 to over 130,000 acres. This screening study included at least one lake from 29 of the 81 major watersheds in MN. Land use in these watersheds ranged from <1 to 86 percent forested, <1 to 47 percent developed and <1 to 87 percent cultivated crops/hay/pasture lands. Some lakes had no public access while others had multiple public access sites. Lakes within 500 meters of a fire station and those associated with a National Pollutant Discharge Elimination System (NPDES) permit are noted (Table S1). PFCs are not regulated under NPDES in MN; however a permit indicates a point source discharge into the waterbody.

Species of fish that were included in the current study were bluegill (*Lepomis macrochirus*), black crappie (*Pomoxis nigromaculatus*), and pumpkinseed (*Lepomis gibbosus*). Sunfish and crappie were selected for analysis to allow comparisons to data from previously sampled Minneapolis-St. Paul metro area lakes. Most existing data from these metro lakes are for sunfish, crappie and bass. Mississippi River Pool 2 fish were collected to serve as a reference because fish from this area have historically had elevated PFC concentrations (14, 17).

Fish were wrapped in aluminum foil, kept on ice during transport, and then stored in a -10°C laboratory freezer. Each fish was thawed and filleted (skin-on), and composite samples from each sampling location were made in a MN state lab by combining fillets of one to seventeen fish of the same species. Only three of the seventy samples were from a single fillet. Combined fillets were homogenized in a MN state lab using a meat grinder, with aliquots of the ground composites stored in polypropylene Falcon Tubes (Becton Dickinson, Franklin Lakes,
NJ) at -20°C until they were shipped to the analytical laboratory at EPA. At the EPA analytical laboratory, samples were stored at -80°C prior to further processing.

**Sample homogenization and preparation.** Samples were prepared and analyzed at the EPA analytical laboratory following a method previously described by Delinsky et al. (15). Briefly, water was added to the ground composite samples at a ratio of three mL DI water for every gram of fish fillet tissue. Samples were homogenized using a Polytron PT 10/35 homogenizer (Brinkmann Instruments, Westbury, NY) or a Waring blender (Waring Laboratory Science, Torrington, CT). Fish fillet homogenate was stored at -20°C in 50 mL polypropylene Falcon tubes prior to sample preparation and analysis.

Fillets of tilapia (*Tilapia aurea*) containing no PFCs above the assay limit of detection (LOD) were purchased from a local market (Grand Asia Market, Cary, NC), processed identically as samples, and used as a blank matrix for blank samples and the construction of calibration curves. Quality control (QC) samples were prepared from unspiked bluegill samples that were previously determined to contain naturally occurring high and low PFC levels. All fish homogenates (used in blanks, calibration curves, samples, and QCs) that were frozen after homogenization were thawed and re-homogenized immediately before sample preparation.

The SPE-LC/MS/MS method used in the current analysis has been thoroughly evaluated for method performance and is shown to have good precision, accuracy, and recovery (15). A 2 mL aliquot of either DI water, tilapia blank homogenate, or unknown sample homogenate was placed in a pre-weighed 15 mL Falcon tube. Aliquots of QC samples (2 mL) had been previously placed into pre-weighed Falcon tubes. Each tube containing DI water or fish fillet homogenate was reweighed to determine the weight of the homogenate. An appropriate amount of the 10 PFC analytes were spiked into each of eight tilapia blank samples to generate a
calibration curve. Eight mL of 0.01 N NaOH in MeOH containing 15 ng each of the four isotopically labeled internal standards was added to each 2 mL sample and vortexed. Each sample was then sonicated in an ultrasonic water bath for 30 minutes, centrifuged at 16800g for 5 minutes, and 3 mL of the supernatant were placed into a 50 mL Falcon tube. DI water (27 mL) was added to the supernatant (3 mL) of each sample and vortex mixed. Solid phase extraction (SPE) was performed on the diluted supernatant using Waters Oasis WAX cartridges (60 mg sorbent, 60 µm particle size). SPE cartridges were conditioned with 4 mL of 0.03% NH₄OH in MeOH, followed by 4 mL of MeOH, and equilibrated with 4 mL of DI water. The entire 30 mL sample was then loaded onto the SPE cartridge. Each cartridge was then washed with 4 mL of 25 mM acetate buffer (pH = 4) followed by 4 mL of MeOH. PFCs were eluted from the cartridge with 4 mL of 0.03% NH₄OH in MeOH. The eluates were evaporated to approximately 0.5 mL in a TurboVap sample concentrator (Caliper Life Sciences, Mountain View, CA) at 35°C and 10-15 psi. An aliquot of each concentrated sample (280 µL) was added to individual autosampler vials containing 120 µL of 2 mM ammonium acetate buffer for sample analysis.

**Instrumental analysis.** Each analytical batch consisted of approximately 20 to 30 unknown fish composite samples, eight double blanks (consisting of methanol and buffer, 3 prior to the run and 5 throughout the run) one method blank (DI water), two matrix blanks (tilapia homogenate), eight calibration curve standards (spiked in tilapia homogenate), and four QC samples (unspiked bluegill homogenate, two low and two high for each analyte). Samples were analyzed using an Agilent 1100 HPLC (Agilent Technologies, Palo Alto, CA) interfaced with a Sciex 3000 triple quadrupole mass spectrometer (Applied Biosystems/MDS Sciex, Foster City, CA). A 10 minute isocratic HPLC run was used with a mobile phase consisting of 25% 2 mM ammonium acetate buffer (component A) and 75% MeOH (component B) at a flow rate of 200 µL/min. The HPLC
column was a Phenomenex Luna C18 (2) column (3.0 x 50 mm, 5.0 µm) with an injection volume of 10 µL. Electrospray ionization was used in the mass spectrometer source, which was maintained at 400 ºC. Analyte-specific mass spectrometer parameters were optimized for each individual compound and mass transitions for each analyte and internal standard were monitored using multiple reaction monitoring (MRM, Table S2). Because the potential for incorrect identification of PFOS and PFHS in biological matrices has been reported (21), a subset of samples was reanalyzed using quantitation and confirmation ion mass transitions for each analyte in order to ensure correct analyte identification and quantification.

Quantitation. A new eight point calibration curve was prepared for all 10 analytes with each analytical batch. The calibration curve was run at the beginning and the end of each analytical batch and the replicate injections were used to construct the calibration curve for sample quantitation. The calibration range was 1 ng/g to 600 ng/g for PFOS and 0.4 to 50 ng/g for the remaining PFCs. Analyst software (version 1.4.2, Applied Biosystems/MDS Sciex, Foster City, CA) was used for the quantitation of all compounds. Linear calibration curves with 1/x weighting were required to have a correlation coefficient (r) of greater than 0.99, with all points except the lowest point being within ± 20% of the theoretical concentration (± 30% for the lowest calibration curve point). Isotopically labeled PFOS ([18O2]-PFOS) was the internal standard used for PFOS quantitation, [18O2]-PFHS was used for the quantitation of PFHS and PFBS, [13C2]-PFOA ([13C2]-C8) was used for quantitation of the C6 to C9 acids, and [13C2]-PFUnA ([13C2]-C11) was used for the quantitation of C10 to C12 acids. The ratio of the analyte/internal standard area counts was used for quantification. Linear and branched isomers were present in chromatograms for unlabeled PFOS, and all isomers were integrated for quantitation. Chromatograms of [18O2]-PFOS had a peak for the linear isomer only, and this
isomer was integrated for quantitation. Samples with calculated concentrations outside of the calibration range were diluted with tilapia blank matrix, re-prepared, and reanalyzed in a separate analytical batch.

**Quality control.** Quality control samples were prepared from two pools of unspiked bluegill homogenate that each contained naturally occurring levels of the target PFCs at two distinct levels. Samples from each QC pool were run at the analytical laboratory on multiple days in order to characterize the average concentration for each PFC in each QC pool (Table 1). Two samples from each QC pool (A and B) were run with each sample set, with one replicate run immediately after the calibration curve at the beginning of the run and the other replicate run immediately before the calibration curve at the end of the run. In order for an analytical batch to be considered acceptable for an analyte, the average of the duplicate QC samples had to be within two standard deviations of the characterized average for that analyte.

Previously determined performance characteristics of the current method showed that at three concentration levels 1) LOQs were 0.52 ng/g for PFOS; 5.21 ng/g for C7; and a range from 0.01 to 1.89 ng/g for the remaining 8 analytes, 2) inter-day and intra-day precision values were less than 20% RSD, 3) inter-day and intra-day accuracy values were less than 20% different from theoretical values for all analytes except C6 and C7, 4) recovery of the 10 target PFCs from blank tilapia fillet matrix were 76.2 to 133%, and 5) bluegill samples spiked with 20 ng/g PFOS and 4 ng/g of the remaining nine PFC analytes had accuracies ranging from 74.9 to 136% (15).

Repeated analyses of fish samples with this method has shown that 1) PFOS and $[^{18}O_2]$-PFOS have retention times within 2% of each other and 2) taurodeoxycholic acid (TDCA), a bile acid found to potentially interfere with PFOS analysis (21), has a retention time that is 6% or more different (later retention time) than PFOS and $[^{18}O_2]$-PFOS. Therefore, unknown samples
containing detectable amounts of PFC analytes for which corresponding labeled internal standards were available (such as PFOS and corresponding internal standard $[^{18}O_2]$-PFOS) were required to have analyte and internal standard retention times within 2% of each other in order to ensure proper analyte identification. Unknown samples containing detectable levels of analytes with no corresponding labeled internal standard (such as C10 and $[^{13}C_2]$-C11 internal standard) were required to have an analyte/internal standard retention time ratio within 2% of the average retention time ratio in standards. Comparisons of calculated analyte concentrations using quantitation and confirmation ions were also used as an indicator of proper analyte identification, with concentrations less than 25% different indicating proper analyte identification.

Results

Quality control. In the current study, none of the blank tilapia samples had any quantifiable PFCs above the assay limit of detection (LOD, n = 6). QC samples for PFOS, C10, C11, and C12 showed good method performance and met the acceptance criteria for analytical batches containing samples with detectable levels of the PFC analytes (Table 1). Black crappie samples spiked with 20 ng/g PFOS and 4 ng/g of the remaining 9 PFCs exhibited accuracies of 88 to 107% (Table S3). All calibration curves had r values of greater than 0.99 for all analytes. Calculated concentrations of PFOS, C10, C11, and C12 determined using both quantitation and confirmation ions were within 25% of each other for all samples containing detectable levels of PFCs, indicating that all analytes were properly identified and quantitated. For the detectable PFC analytes, the percent difference for duplicate samples (n = 8) ranged from 1 to 20%, with much of the variation occurring at the lowest levels of the calibration curve. Percent differences for replicate PFOS analyses ranged from 1 to 5%.
Overview. A summary of all of the analytical data generated in this investigation can be found in Table S4. PFOS was the most commonly detected PFC, occurring above the limit of quantitation (LOQ = 1 ng/g, the lowest calibration curve point) in 30% of all fish taken from MN lakes and the Mississippi River. C10 was found above the limit of quantitation (LOQ = 1.11 ng/g) in 7% of samples and C11 and C12 were each present above the LOQ (1.05 ng/g for C11, 0.72 ng/g for C12) in 3% of samples. PFHS was found above the LOQ (0.40 ng/g = lowest calibration curve point) in one sample. None of the remaining PFC analytes were found above the LOQ.

Mississippi River Samples. Sampling sites along the Mississippi River can be found in Figure 1 and Figure S1. PFOS was found above the LOQ of 1 ng/g in 73% of fish collected from the Mississippi River and was the most commonly detected PFC (Table 2). The highest concentrations of PFOS (144 ng/g in pumpkinseed and 2000 ng/g in bluegill fillet) were found in two composite samples from Pool 2, an area of the Mississippi River with historically high PFC concentrations (14, 17). Both composite fish samples from Pool 2 contained C10 to C12 at concentrations of 2.13 to 15.0 ng/g fish. The bluegill from Pool 2 with a PFOS concentration of 2000 ng/g also contained 0.47 ng/g PFHS. Six separate composite samples from fish collected 110 to 150 miles upstream of Pool 2 all had PFOS concentrations above the LOQ, ranging from 3.06 to 20 ng/g fillet. The lowest PFOS concentrations (<LOQ) were found in three different composite samples from fish collected approximately 400 miles upstream of Pool 2.

Minnesota Lakes. PFOS was the most commonly detected PFC in fish collected from 59 lakes throughout the state, occurring above the LOQ at 22% of the sites, with quantifiable concentrations ranging from 1.08 ng/g (Fall Lake) to 52.4 ng/g in fish from Zumbro Lake (Table 2). Fish collected from 52 of 59 lakes (88% of lakes sampled) had PFOS levels below 3 ng/g.
PFOS concentrations in fish from only two lakes (McCarrons and Zumbro) were above 40 ng/g. Fish from the four Minneapolis-St. Paul area lakes included in the study (McCarrons, Nokomis, Pickerel, Simley) had PFOS concentrations ranging from 4.39 to 47.3 ng/g. C10 was the only other PFC found in fish from MN lakes (1.23 to 3.24 ng/g), and occurred only in lakes where PFOS concentrations in fish were 10 ng/g or greater (Pickerel, McCarrons, Zumbro).

**Comparison with Previous Studies of MN Fish.** Previous studies regarding PFC concentrations in Minnesota fish fillet samples agree with the current study in that: 1) PFOS is the predominate PFC present, 2) C10, C11, and C12 acids are found above the LOQ in some samples, and 3) PFHS, PFBS, and the C6 to C9 carboxylic acids are found either in very low concentrations or are below the LOQ (14-18). PFOS concentrations in fish taken from Pool 2 of the Mississippi River have historically been high compared to fish taken from other stretches of the Mississippi River in MN (14, 17). In two previous studies involving the analysis of fillets from Pool 2 fish, PFOS concentrations in carp ranged from 15 to 90 ng/g, and ranged from 25 to 5150 ng/g in the fillets of seven species of fish (14, 16). The MPCA reported concentrations of PFOS ranging from 13.1 to 1860 ng/g in the fillets of seven species of fish collected from Mississippi River Pool 2 (17). The PFOS levels measured in Mississippi River Pool 2 fish in the present study were lower in pumpkinseed (144 ng/g) compared to bluegill (2000 ng/g), a finding that is consistent with the MPCA study that measured these two species in a MN Lake (17). This suggests that species-specific concentration factors may be very different for fish living in the same water and that there is considerable value in determining these relationships. The highest measured value of 2000 ng/g PFOS in Pool 2 bluegill in the current study is eight times higher than the average bluegill PFOS concentration previously reported (approximately 250 ng/g), but is within the range of Pool 2 PFOS concentrations previously reported in fish fillets (14).
finding indicates that there is considerable variation in PFC concentrations within a single species living in one section of the river. Further investigation of the factors that influence this variation would be useful.

Concentrations of PFOS in composite samples from Mississippi River fish taken 110 to 150 miles upstream of Pool 2 in the current study (3.06 to 20 ng/g) agree well with previously reported PFOS concentrations in fillets of fish taken from similar stretches of the Mississippi River at the following locations: 1) between Brainerd and St. Cloud, 120 miles upstream of Pool 2 (4.3 to 19 ng/g in carp) and 2) Brainerd area, approximately 200 miles upstream of Pool 2 (7.38 to 18 ng/g in four fish species) (16, 17). The concentrations of PFOS in Mississippi River fish in the current study taken 110 to 150 miles upstream of Pool 2 are also lower than previously determined concentrations of PFCs in bluegill from Pools 3 to 5a (approximately 23.5 to 200 ng/g), which are located downstream of Pool 2 and the Minneapolis/St. Paul area (14, 16, 17). In the current study, PFOS concentrations in samples taken approximately 400 miles upstream of the Minneapolis-St. Paul area (<LOQ) are comparable to previously reported values in the St. Croix River (<LOQ), which is an area with minimal known industrial inputs (14, 17).

Concentrations of C10 to C12 acids in Pool 2 of the Mississippi River in the current study (2.13 to 15.0 ng/g fish) compared well with previously reported Pool 2 C10 to C12 concentrations in the fillets from seven fish species (<LOQ to 17.5 ng/g) (16, 17).

The current study contains the first measurements of PFOS concentrations in fish from rural MN lakes. PFOS concentrations in fish fillets (<LOQ to 52.3 ng/g) were generally lower than those previously found in Minneapolis-St. Paul metropolitan area lakes (<LOQ to 345 ng/g in bluegill and <LOQ to 574 ng/g in black crappie) (14, 17). Fish from only two out of 59 lakes had PFOS concentrations above the MN fish consumption advisory level of 40 ng/g. One of the
two lakes (McCarrons, 47.3 ng/g) is located in the Minneapolis-St. Paul metropolitan area, while the other (Zumbro, 52.4 ng/g) is downstream of the effluent from the Pine Island Waste Water Treatment Plant (WWTP), which had elevated PFOS concentrations and may be a contributing factor to the higher levels of PFOS in the fish (17). Fish from 52 out of 59 sampling sites in the current study had PFOS concentrations that were below 3 ng/g, which is generally much lower than PFOS concentrations in urban lakes (17). Previously, the release of aqueous fire fighting foams (AFFF) to a body of water was shown to result in high concentrations of PFOS in the water to which the AFFF were applied, the livers of fish living in the waters where AFFF were applied, and in local groundwater (22, 23). In the current study, the presence of a fire station within 500 meters of the lakes sampled was not an indicator of higher PFC concentrations in fish. There have been no known previous reports of C10 concentrations in fish from Pickerel, McCarrons, and Zumbro Lakes. However, concentrations of C10 found in fish from these lakes (1.23 to 3.24 ng/g) compare well with levels of C10 reported in other Minneapolis-St. Paul metropolitan area lakes (<LOQ to 8.02 ng/g) (17).

In summary, concentrations of 10 PFCs were measured in composite fish fillet samples from the Mississippi River and 59 MN lakes using a previously described LC/MS/MS method in order to provide preliminary information on the geographic distribution of PFCs in MN fish. Results indicate that PFOS contamination in fish collected in Minnesota occurs primarily in watersheds that are in close proximity to the Minneapolis/St. Paul metropolitan area and other waterbodies with potential PFC sources. The results also suggest that fish from rural lakes throughout MN and areas of the Mississippi River located 110 to 450 miles upstream Pool 2 have PFOS concentrations below the concentration (40 ng/g) at which MN recommends limiting fish consumption. These findings should help researchers better understand the extent of PFOS
contamination in MN fish, provide information for fish advisories, and determine areas of focus for future fish collection efforts. Additional studies will be useful in order to better understand the geographical distributions of PFCs in MN fish.

Acknowledgements

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Supporting Information Available

Table S1. Land use information for Minnesota lakes and fish species collected from each lake.

Table S2. Mass transitions monitored for labeled and non-labeled PFC analytes. Table S3. Accuracy determination in black crappie. Table S4. All PFC concentrations in all 70 samples.

Figure S1. Identifications of Minnesota lakes and river sampling locations. This information is available free of charge via the internet at [http://pubs.acs.org](http://pubs.acs.org).
References


(18) 2008 Minnesota Pollution Control Agency fish PFC data summary table. Available at http://www.pca.state.mn.us/cleanup/pfc/index.html#sedimentfish.

(19) Perfluorochemicals. Available at http://www.pca.state.mn.us/cleanup/pfc/index.html#.

(20) Minnesota Department of Health Fish Consumption Advisory Program meal advice categories summary table. Available at http://www.health.state.mn.us/divs/eh/fish/eating/mealadvicetables.pdf.


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\(^a\)Number of replicates, with each replicate representing the average of duplicate samples

\(^b\)Quality control

\(^c\)Percent relative standard deviation of QC samples run in sample batches in the current study
Table 2. Concentrations of PFCs (ng/g) in samples containing PFOS above the LOQ

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<th>Sampling Location</th>
<th>PFOS</th>
<th>C10</th>
<th>C11</th>
<th>C12</th>
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</table>
A designation of — indicates that no determination of the sample concentration was made because the calculated concentration was below the limit of quantitation (<LOQ).

Sample locations beginning with MR are Mississippi River samples collected from 1 of 11 locations along the river; exact locations of these sampling locations can be found in Figure S1. The remaining samples in this table were collected from lakes whose locations can also be found in Figure S1.
Figure 1

Figure 1. Sampling locations in Minnesota
Table of Contents Brief

Concentrations of ten perfluorinated compounds are measured in the fillets of fish from lakes throughout Minnesota and the Mississippi River.