

Determination of Perfluorinated Compounds in the Upper Mississippi River Basin

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Abstract

Despite ongoing efforts to develop robust analytical methods for the determination of perfluorinated compounds (PFCs) such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in surface water, comparatively little has been published on method performance, and the environmental distribution of these materials remains poorly described worldwide. In this study, an existing method was improved and applied in a large scale evaluation of the Upper Mississippi River Basin, one of the largest watersheds in the world. Samples were collected in 2008 in an effort that involved multiple sample sites and collection teams, long range transport, and storage of up to 4 weeks before analysis. Ninety four percent of the resulting 177 samples had quantifiable PFC concentrations, with 80% of the individual target compounds below 10 ng/L. The most abundant PFCs were perfluorobutanoic acid (C4; 77% > limit of quantitation, LOQ), perfluorooctanoic acid (C8; 73%), perfluorooctane sulfonate (PFOS; 71%), perfluorohexanoic acid (C6; 70%), and perfluoroheptanoic acid (C7; 69%), with the remaining target compounds occurring above the LOQ in less than 50% of the samples. The highest concentrations recorded include C4 at 458 ng/L, PFOS at 245 ng/L, and C8 at 125 ng/L, suggesting various point source inputs within the Basin.

Keywords

Perfluorinated compounds (PFCs),
Perfluorobutanoic acid (PFBA),
Perfluorooctanoic acid (PFOA),
Perfluorobutane sulfonate (PFBS),
Perfluorooctane sulfonate (PFOS),
Upper Mississippi River

Introduction

In the past decade, a number of studies have been conducted to help characterize the distribution of perfluorinated compounds (PFCs) in surface water resources worldwide. The PFCs are fully fluorinated alkyl compounds which have been used along with their polyfluorinated precursor materials in numerous applications, including stain and moisture repellent surface coatings for carpets, paper, upholstery, and textiles; fire-fighting foams; cosmetics; lubricants; and the synthesis of various polymeric materials (1). Many of these compounds are extremely resistant to degradation, leading to their presence in environmental and biological media worldwide (2-4). While the routes of human exposure remain poorly characterized, many studies have measured PFCs in the serum of individuals in the general population of industrialized countries at concentrations in the ng/mL range (5). At the same time, an increasing number of studies with laboratory animals have documented the toxicity of some of the PFCs (4). Recent studies have suggested that some of the PFCs may be currently declining in human serum (6) as a result of voluntary reductions in production, emissions, and product content by major manufacturers in some parts of the world (7). However, very little is known about sources, fate, and transport of the PFCs in the environment, making it very difficult to prioritize human exposure routes and assess potential risks.

Contaminated water sources have been consistently reported as playing a central role in human exposure. In one of the first investigations of PFCs in surface and drinking water, Saito et al. documented that elevated PFCs in the blood of the residents of a large metropolitan region in Japan was likely due to consumption of contaminated drinking water (8). Emmet et al. subsequently reported on a situation in the US where median PFOA blood levels in residents

living near a major fluorochemical production facility were approximately 100 times higher than controls, with the consumption of contaminated well water being the most important exposure route determined (9). Most recently, a series of studies in Germany has documented that land application of PFC contaminated sludge in the Rhine River drainage basin resulted in elevated PFC concentrations in surface water, drinking water, and the blood of residents who consumed this water (10, 11).

The US Environmental Protection Agency (EPA) has recently issued provisional health advisories for PFOA and PFOS in drinking water (12). While it has been shown that PFCs can be removed from drinking water with activated charcoal, this treatment option is not common and it requires constant monitoring because charcoal becomes saturated relatively quickly (10, 13). Moreover, studies of wastewater treatment plants (WWTP) report that PFCs are not efficiently removed by conventional treatment, with WWTP effluents often having higher concentrations of PFCs than process input water (14, 15). Because it is common for treated wastewater to make up a large proportion of the drinking water source intake for communities downstream, the measurement of surface water for potential contamination becomes essential for the evaluation of potential human exposures.

Despite numerous efforts to develop robust sampling and analytical methods for the PFCs in many matrices, the performance of these methods is often poorly characterized and agreement between laboratories has only recently begun to improve (16). Given the unique chemical properties of the PFCs and the comparatively small number of studies which describe useful assay performance data, it remains important to monitor and report conventional quality control

measures such as accuracy, precision, and recovery. With larger studies that may include complex study designs and multiple field teams, it also becomes important to evaluate the potential loss of analytes during long-term storage and long-range transport; possible contamination during sampling and analytical procedures; and the potential for a wide range of sample matrix contaminants to interfere with sample preparation and LC/MS/MS analysis.

In this study, a method that was previously developed in our laboratory (17) was improved for use in a large scale monitoring effort that required sample collection from a broad geographical area, a number of different sample collection teams, long-range transport, and storage of up to 4 weeks before samples were processed. This method was applied in an evaluation of PFCs in the Upper Mississippi River Basin, thus providing preliminary information about PFC concentrations in a large area of the continental US.

Experimental Section

Standards and reagents. Potassium salts of perfluorobutane sulfonate (PFBS, 98% purity) and perfluorohexane sulfonate (PFHS, 93%) were provided by 3M Company (St. Paul, MN). Perfluorooctane sulfonate (PFOS, 98%) was purchased from Fluka (Sigma-Aldrich, St. Louis, MO). Perfluorobutanoic acid (C4, 98%), perfluoropentanoic acid (C5, 98%) and perfluorodecane sulfonate (PFDS, 98%) were obtained from Wellington Laboratories (Guelph, Ontario, Canada). Perfluorohexanoic acid (C6, 97%), perfluoroheptanoic acid (C7, 99%), perfluorooctanoic acid (C8 or 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). Mass labelled standards including 1,2,3,4-¹³C₄-sodium perfluorooctane sulfonate (MPFOS), ¹⁸O₂-sodium perfluorohexane sulfonate (MPFHS), 1,2-¹³C₂-perfluorohexanoic acid (MC6), and 1,2-¹³C₂-perfluoroundecanoic acid (MC11) were obtained from Wellington Laboratories (Guelph, Ontario, Canada). ¹³C₈-labeled PFOA (MPFOA) was purchased from Cambridge Isotope Laboratories (Andover, MA).

Original method. This laboratory initially developed a sampling and analysis method for surface water which was applied in a study where samples were generally collected and processed within 24 hours (17). In 2007, a series of pilot scale studies was conducted to determine if this method could be used in situations where long-range sample transport and lengthy sample storage times would be necessary. Results (not shown) from this evaluation indicated that: 1) in the time it took to ship the samples from the field site to the analytical laboratory (1 week or longer), approximately 20% of the samples developed so much bacterial and/or algal growth that they could not pass through the initial glass fiber filtration or solid phase extraction (SPE) cleanup steps; 2) the recoveries of the target compounds in the travel spikes ranged from 16% - 48%, suggesting that analytes may have adsorbed onto the interior surface of the sample collection bottle; and 3) trace level LC/MS/MS analysis of many of the samples was affected by varying amounts of matrix interference causing ion suppression or enhancement by as much as 200%, indicating that SPE cleanup was insufficient. A number of small scale experiments lead to the following tentative solutions to these problems: 1) 5 mL of 35% nitric acid was added to all 1L samples immediately after collection to suppress biological activity; 2) at the time of analysis, sample bottles were thoroughly rinsed with 10 mL of methanol to recover adsorbed material, and the rinsate was combined with the filtered sample before further

processing; and 3) to help overcome matrix interferences, a weak anion-exchange (WAX) SPE cartridge was used to provide a better cleanup while also retaining the shortest acids on the target list (\leq C6 acid). In addition, because the PFCs appeared to focus at the head of the cartridge, samples were eluted using a simple back flush technique with a mixture of methanol/MTBE to help minimize co-eluting interferences. With these improvements in place, the modified method was used in the 2008 study as described below.

Water collection. Samples ($n = 177$) were collected from 88 sampling sites between March and August of 2008 from the Upper Mississippi River Basin and a portion of the Missouri River Basin (Figure 1) by member agencies of the Upper Mississippi River Basin Association (UMRBA). Seventy-two samples were collected by the Minnesota Pollution Control Agency, 33 by the Wisconsin Department of Natural Resources, 49 by the Illinois Environmental Protection Agency, and 23 by the US EPA Region 7 Water Quality Monitoring Team in consultation with the Iowa and Missouri Departments of Natural Resources. The Upper Mississippi River Basin is one of the largest river basins in the United States, including large parts of the states of Illinois, Iowa, Minnesota, Missouri, and Wisconsin (18). This river basin consists of the upper half of the Mississippi River (~2,000 km), 12 major tributaries including the Minnesota, Wisconsin, Iowa, Illinois, and Missouri Rivers, and many other streams, which sum up to approximately 50,000 km. Approximately 30 million residents depend on surface and ground water resources from the Mississippi River Basin to supply their drinking water. Sampling locations were chosen by each of the participating agencies with the primary intention of providing preliminary PFC data in these individual regions. Sample sites were coded as follows: river abbreviation/state abbreviation-sample number (smaller numbers are closer to the headwaters). In some cases, sites

were re-sampled on multiple occasions. For each sampling event, a shipping container holding approximately 6 empty pre-cleaned (methanol rinsed) one-liter high density polyethylene (HDPE) bottles (Thermo Fisher Scientific, Rochester, NY) and one travel spike sample was sent from the analytical laboratory to the field crew for collection. Surface water was collected by hand approximately 15 to 30 cm beneath the surface of the water, and were preserved by adding 5 mL of 35% nitric acid (EP Scientific Products, Miami, OK). Samples were then shipped at ambient temperature using a commercial freight carrier to the analytical laboratory where they were stored at room temperature and analyzed within 4 weeks.

Quality assurance samples. For each sampling event, a one-liter sample containing deionized water that was spiked with a PFC mixture (final concentration being = 50 ng/L for all target analytes) and nitric acid preservative and was shipped to the field as a travel spike (F-QC) along with the empty pre-cleaned sample collection bottles. The F-QCs were shipped back to the laboratory with the field samples and analyzed at the same time to evaluate analyte loss or contamination during sample transport and storage. Field personnel were asked to collect at least 10% of the samples in duplicate. In-house laboratory spikes (L-QCs) were also prepared at the time of analysis to assess the performance of the assay. At least two solvent blanks and matrix blanks (deionized water with internal standards that went through whole extraction process) were analyzed with every analytical batch.

Sample preparation and solid phase extraction (SPE). Water samples were filtered with GF/A glass fiber filter cups (Whatman Inc., Piscataway, NJ) into a polypropylene vacuum flask (Thermo Fisher Scientific, Rochester, NY). Filter cups were determined to be PFC free and did

182 not retain target analytes. Filtered solids were also tested and found to contain only negligible
183 amounts of PFCs (< 0.5 ng/L). The original emptied sample container was then thoroughly
184 rinsed with 10 mL of methanol and the filtered water was poured back into the original container,
185 thus combining the filtered sample and the methanol rinse. The samples were then spiked with
186 100 μ L of a 0.10 ng/ μ L solution (10 ng) of the internal standards (MPFHS, MPFOS, MC6, MC8,
187 and MC11) and divided into two 500-mL aliquots. Oasis® WAX Plus (225 mg) cartridges
188 (Waters Corporation, Milford, MA) were conditioned with 10 mL of methanol followed by 10
189 mL of deionized water, each at a flow rate of 10 mL/min. A 500-mL aliquot of each water
190 sample was loaded onto the pre-conditioned cartridges at a flow rate of 10 mL/min with a
191 positive pressure pump system (Sep-Pak Concentrator, Waters Corporation). The remaining
192 500-mL sample aliquot was stored at room temperature in case additional analysis was required.
193 The cartridges were washed with 10 mL of 25 mM sodium acetate buffer (pH 4) followed by 10
194 mL of methanol and were dried completely by purging with high purity nitrogen gas for 10 min.
195 For sample elution, the cartridges were set up in the vacuum manifold in an inverted direction
196 (back flush technique) and the target analytes were eluted from the cartridge with 2 mL of
197 ammonium hydroxide (NH_4OH , 28% in water)/methanol/methyl-tert-butyl ether (MTBE)
198 solution (v:v:v, 1:2:27) at a flow rate of 1 mL/min. The eluate was reduced in volume to 500 μ L
199 with TurboVap® II nitrogen evaporator at 35°C (Caliper Life Sciences, Hopkinton, MA). A 100
200 μ L aliquot of the concentrated eluate was mixed with 100 μ L of 2 mM ammonium acetate buffer
201 (pH 6.5) to approximate the initial mobile phase conditions.

202

203 **Instrumental Analysis.** Samples were analyzed using a Waters Acquity ultra-performance
204 liquid chromatography system coupled with a Waters Quattro Premier XE triple quadrupole mass

spectrometer (UPLC-MS/MS; Waters Corporation). In order to reduce PFC background in the instrument, the polytetrafluoroethylene (PTFE) tubing was replaced with polyetheretherketone (PEEK) material. To further reduce instrumental contamination, a C18 hold-up column (prototype provided by Waters and now available as a PFC Kit from Waters) was installed on the aqueous solvent line just before the mixing chamber. A 20 μ L aliquot of each sample was injected onto an Acquity UPLC BEH C18 Column (1.7 μ m, 1.0 \times 50 mm; Waters Corporation) that was maintained at 50°C. Separation was achieved using a gradient mobile phase of 2 mM ammonium acetate buffer and methanol at a flow rate of 500 μ L/min (Table S1, Supporting Information).

Electro-spray negative ionization (ESI) was used with the mass spectrometer operating in the multiple-reaction-monitoring (MRM) mode (Table S1). Ionization and collision cell parameters were optimized for each individual analyte. One MRM transition was used for quantitation and another transition was used for confirmation for each analyte (Table S2).

Quantitation. The instrumental quantitation limit (IQL), based on methanolic standards and a 10:1 signal to noise ratio, was approximately 0.5 pg on column for all target compounds. Using the same criteria and a series of fortified deionized water samples, the limit of detection (LOD) was determined to be 0.02 ng/L. Six point calibration curves were prepared for each analytical batch in the range of 0.2–500 ng/L, but consistent measurements for all compounds giving precision of $\pm 15\%$ and accuracy of $100\% \pm 20\%$ were obtained between 1.0 and 500 ng/L, making this the reporting range. The lower limit of quantitation (LOQ) was set to be 1.0 ng/L. Quantitation was performed with the MassLynx 4.1 (Waters Corporation) using a linear “1/x”

weighted regression fit with a coefficient of correlation greater than 0.99. Data were considered reportable if the ion ratio (quantifier/confirmatory) for samples was within 70% to 130% of the average ion ratio for calibration standards. Additionally, data from an analytical batch were only considered acceptable if blanks were below the IQL and the QC samples were within $\pm 25\%$ of their theoretical concentrations.

Statistical Analyses. All statistical analyses were performed using R-2.9.0 software (19). When duplicate samples were collected, mean values were reported and used in all analyses. Summary statistics used (LOQ/2) for samples listed as < LOQ.

Results and Discussion

Quality control. The performance characteristics of the improved method for remote sampling and long range transport are presented in Table S3. All 16 of the travel spike samples prepared at the 50 ng/L level had mean recoveries of between 91.7%–108% for all compounds, with relative standard deviations (RSD) $\leq 15\%$. The laboratory spike samples prepared at the 5 ng/L and 50 ng/L levels had similar accuracy and precision, with mean recoveries ranging from 89.3%–105%, and all RSDs being $\leq 14\%$. Recoveries of internal standards ranged from 75 – 125%. None of the blanks (n = 16) had quantifiable PFCs. Overall, the average percent relative difference for duplicate field samples (n = 31) was 12% (range 0.1%–134%), with most of this variation occurring in cases where one sample was below the LOQ. The average relative percent difference for duplicate PFOS and PFOA measurements above 10 ng/L was 13.3% and 3.7 %, respectively.

Distribution of PFCs in the basin. Table 1 shows summary statistics for all measurements made in this study. At least one target compound was above the LOQ in 94% of the samples collected, with 80% of all of the individual compound measurements being below 10 ng/L. The most frequently measured compounds and the percentage above the LOQ were C4 (77%), C8 (73%), PFOS (71%), C6 (70%), and C7 (69%). The remaining target compounds occurred above the LOQ in less than 50% of the samples. Median concentrations ranged from no detection at all for PFDS, to a high of 3.01 ng/L for PFOS. While compound measurements in most samples were comparable to low level “background” concentrations reported in previous studies (< 10 ng/L) (8, 17, 20), samples occasionally had elevated levels. The highest individual concentrations recorded include C4 at 458 ng/L, PFOS at 245 ng/L, and C8 at 125 ng/L, suggesting the influence of point source inputs at some specific sampling locations. Table 2 summarizes the ten highest C8, C4, and PFOS concentrations recorded during this investigation.

WWTPs and PFCs. In the spring of 2007, the Minnesota Pollution Control Agency (MPCA) conducted systematic measurements of PFCs in influent, effluent, and sludge at wastewater treatment plants (WWTPs) across the state of Minnesota (21). The MPCA reported that multiple PFCs were measured in WWTP effluents from plants located in larger urban areas, with these compounds being attributed to local sources such as refineries, airports, and PFC production sites, which discharged waste to these WWTPs (21). The current study confirms these earlier findings, as, for example, the samples collected below the Metropolitan WWTP (MS/MN-19; Figure S1) and adjacent to a major chemical manufacturer showed higher PFC concentrations than samples collected upstream of this area (MS/MN-18). Specifically, in August at MS/MN-19, C8 was 23.2 ± 0.9 ng/L (mean \pm SD), C4 30.9 ± 4.7 ng/L, PFOS 24.0 ± 7.1 ng/L, PFHS 13.1 ± 0.4 ng/L, and

274 PFBS 11.9 ± 4.4 ng/L. Upstream at MS/MN-18, C8 was 8.69 ± 1.03 ng/L, C4 11.9 ± 1.2 ng/L,
275 PFOS 13.2 ± 0.6 ng/L, PFHS 5.65 ± 0.47 ng/L, and PFBS 3.14 ± 0.57 ng/L.

276 Also, samples collected on the Mississippi River at the outfall of the Brainerd WWTP (MS/MN-
277 8 (August); Figure S1), had PFOS and PFBS at 226 ± 28 and 65.5 ± 26.4 ng/L, respectively (Table
278 S4). During the same sample period, several samples collected upstream of this point (MS/MN-
279, 5–7) indicated typically low concentrations of all compounds (< 10 ng/L), suggesting that the
280 WWTP was a point source of these PFCs in this area. An earlier study by the Minnesota
281 Department of Health (MDH) found that until September 2007, a local chrome plating plant used
282 a mist suppressant reagent containing 1%–7% “organic fluorosulfonate” (21). The results of the
283 current study indicate that PFC material was still present in this area, perhaps as a residual from
284 the plating plant or possibly from other industries. It should also be noted that a sample collected
285 on the same day just 200 m downstream of the WWTP outflow site (MS/MN-9) did not have
286 elevated concentrations of the target compounds ($< \text{LOQ}$ for most measurements), suggesting
287 that the volume of flow at this point in the river water diluted upstream inputs to “background”
288 levels. Moreover, this also suggests that identification of point source inputs may require
289 intensive sampling to pinpoint their specific origins.

290

291 Additional evidence of the potential impact of WWTPs came from Wisconsin samples collected
292 at the outfalls of the La Cross and Prairie du Chien WWTPs (MS/WI-7 and 12, Figure S2). Both
293 sites had elevated PFCs with the Prairie du Chien site (MS/WI-12) having PFOS at 61.7ng/L and
294 PFHS at 101 ng/L (Table S5). Evaluation of the operations of the various sources that make
295 discharges to these plants would be helpful for determining why these samples were elevated.

296

297 *Historical fire-fighting activity.*

298 Samples were collected from a waterway near Duluth International Airport (TR/MN-1, Figure
299 S1), despite the fact that it was not part of the Mississippi River Basin, because of suspected
300 contamination related to the historic use of fire fighting foams. Initial samples from this site
301 collected in April exhibited notably elevated levels of some of the PFCs with C8 at 50.5 ng/L;
302 C6 53.4 ng/L; PFOS 124 ng/L; PFHS 169 ng/L; and PFBS 19.2 ng/L (Table S4). To confirm the
303 initial test results, this location was re-sampled in triplicate in July. Results again indicated
304 elevated levels of the same PFCs, with concentrations of C8 at 92.1 ± 3.1 ng/L; C6 131 ± 8 ng/L;
305 PFOS 287 ± 15 ng/L; PFHS 367 ± 3 ng/L; and PFBS 41.7 ± 0.6 ng/L (Table S4). The possible link
306 to the use of fire fighting foams is anecdotal but consistent with previous reports implicating fire
307 fighting activities at airports (17, 22).

308

309 *Differing results from samples collected in nearby locations.* Samples were collected from the
310 same pool (MS/MN-19 and MS/WI-1; below Lock and Dam 2; Figures S2 and S3) in the
311 Mississippi River but they were separated by 1.3 km distance. MS/MN-19 and MS/WI-1 were
312 sampled on August 20 and 13 in 2008, respectively, on which days the flow rates were 72 and
313 $130 \text{ m}^3/\text{s}$, respectively. At low flow, C8 was 23.8 ng/L (MS/MN-19), but when the flow was
314 almost two times higher the concentration increased by a factor of more than five to 125 ng/L
315 (MS/WI-1). In contrast, PFOS concentrations were very similar to each other despite the
316 increased flow: 29 ng/L for MS/MN-19 and 27 ng/L for MS/WI-1. The increased amount of
317 PFOA in the Wisconsin sample may be due to vertical mixing or turbulent resuspension of
318 previously deposited materials in sediments since the sample was collected at the immediate
319 outflow of the Lock and Dam 2. All of the carboxylic acids from C6 to 11 exhibited similar

several fold increases during high flow conditions, but PFOS and the other sulfonates remained at roughly the same concentrations. This may indicate an important difference in how these two classes of PFCs are transported in the environment.

C4 elevation. The highest PFC concentrations measured in this survey are the C4 (also known as PFBA) levels in samples from the Mississippi River in the vicinity of Cordova, IL. Upstream of this area, C4 was found in the <LOQ to < 10 ng/L concentration range, except for samples from below Mississippi River Lock and Dam 2 in Minnesota (MS/MN-18 and MS/MN-19) collected in August (11.0–34.2 ng/L) in an area where a historical C4 input source has been identified (21). In IL however, C4 clearly becomes the most prominent compound measured in the Basin. For instance, at MS/IL-3 (Figure S3), C4 was measured at 325 ng/L in March, 420 ng/L in April, and 458 ng/L in May, 2008 (Table S6). It is interesting to note that the water concentrations here remain fairly consistent, despite increasing total flow estimates (> 5). This may suggest that the samples were collected at a point within the plume of a discharge and were not well mixed, or it may imply a larger scale area source. Some 30 km downstream near Rock Island, IL (MS/IL-4) concentrations of C4 were about 2 to 4 times lower, but still substantially elevated in comparison to other areas in this survey, confirming the presence of a major source in this region.

Near Chicago. Some of the samples collected in the upper reaches of the Illinois River watershed near Chicago had relatively high PFC concentrations (i.e., C6, C8, and PFOS; Table S6). Samples from where the Cal Sag Channel meets the Chicago Ship and Sanitary Canal (IL/IL-1, Figure S3) had the highest PFOS levels in this region, with concentrations ranging from 17.6 ng/L to 50.8 ng/L. Both of these waterways are extensively polluted with a substantial

portion of their flows derived from WWTP effluent. Further evaluation of this area would be helpful in determining specific sources in this complex urban environment.

Missouri and Iowa Samples. Samples collected in Missouri and Iowa consistently had some of the lowest PFC measurements recorded in this survey. For most of the target analytes, more than 90% of the sites showed concentrations below LOQ. PFOS was found to be above the LOQ at 78% of the sample sites, but the only notable concentrations were 11.0 ng/L and 15.2 ng/L from sites MO/MO-3 and TR/MO-1, respectively (Figure S4) in the vicinity of Kansas City.

Mass flux estimation. As indicated in Figure 2, there were many sampling points with localized increases in PFC concentrations in the Basin. The overall trend was for these increases to be dissipated shortly down stream, suggesting small point source inputs relative to the ever increasing volume of the River. Figure 2 also indicates that the concentrations of C8, PFOS, and PFBS are generally flat after the mid portion of the Upper Mississippi River despite the continuous increase in flow. Since two-dimensional sampling was not performed across the River, a true mass flux cannot be calculated. However, it is still useful to calculate provisional total mass flow estimates in order to help describe large scale trends in transport. Figure S5 shows the estimated mass flux of C4, C8, PFBS, and PFOS in the main stream of the Upper Mississippi River in May, 2008. At the MS/IL-3 site near Cordova, IL the largest local increase occurred for C4, with large increases in C8, PFBS, and PFOS also being apparent. Calculations of the C4 flux stabilize as the input from the Cordova area becomes more homogenous downstream, and it is interesting to note that a total loading of approximately 20 kg per day is maintained even after the confluence of the Ohio and Missouri Rivers. This suggests that there

are no additional sources of C4 of similar magnitude in the lower reaches of the basin, and that this single source dominates C4 in this section of the Mississippi River. The overall increase in all of the PFCs from the Minneapolis Metropolitan area in Minnesota to the southern boundary of the Basin clearly suggests an increasing number of sources proceeding downstream. Several possible explanations of this observation can be considered: 1) multiple PFC discharges from private or public WWTP along the River and tributaries, 2) surface water run-off from cities and farm fields reflecting area source inputs, 3) ground water input from agricultural areas. The importance of any of these potential sources is unknown and would be a good subject of further research.

The modified method for 13 PFCs in surface water used in this study showed acceptable performance characteristics, making it useful for large scale monitoring surveys that require long range transport and relatively long term storage without appreciable loss of target compounds. The results indicate multiple input sources and a continuous increase in PFC loading as the River proceeds through the Basin. Many localized areas with elevated PFC levels have been identified, indicating that PFC inputs are common and widespread. The relatively high concentration of the C4 acid in some of these samples likely reflects a shift toward lower molecular weight PFCs made by US industries. These data also support the hypothesis that WWTPs can be sources of PFCs.

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Supporting Information Available

Additional method description, tables showing UPLC-MS/MS conditions, mass transitions of each analyte, method performance, raw data for all samples, and figures showing sampling sites and estimated mass flux are available in Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- 474

Table 1. Statistical summary of measurements

	N	%>LOQ ^a	%ND ^b	Median ^c	95% CI ^d for median	p90 ^e	p95 ^f	p99 ^g	Max
C12	173	9.8	9.8	0.71	0.71 – 0.71	0.71	2.33	10.9	24.7
C11	173	6.4	21	0.71	0.71 – 0.71	0.71	1.14	23.6	29.1
C10	173	14	12	0.71	0.71 – 0.71	1.30	2.54	14.3	42.0
C9	173	29	13	0.71	0.71 – 0.71	3.33	4.51	8.84	72.9
C8	173	73	2.9	2.07	1.46 – 2.54	11.9	19.8	36.5	125
C7	173	69	5.8	2.16	1.56 – 2.46	6.91	8.89	11.5	90.2
C6	173	70	1.2	1.59	1.34 – 1.83	7.07	12.9	28.4	53.4
C5	167	41	34	0.71	0.71 – 0.71	6.03	9.27	12.4	31.5
C4	167	77	16	2.73	2.18 – 3.42	27.9	47.9	357	458
PFDS	158	0	61						
PFOS	173	71	2.9	3.01	2.03 – 3.78	17.0	27.2	147	245
PFHS	173	40	11	0.71	0.71 – 0.71	5.11	6.79	38.7	169
PFBS	173	43	23	0.71	0.71 – 1.00	4.21	10.4	31.2	84.1

a: Percentage of samples above limit of quantitation (LOQ). LOQ = 1.0 ng/L

b: Percentage of samples not detected (below limit of detection, LOD). LOD = 0.02 ng/L

c: For calculation of median, values of LOQ/sqrt(2) = 0.707 and LOD/sqrt(2) = 0.014 were assigned for LOQ and ND, respectively.

d: 95% confidence interval

e: 90th percentile

f: 95th percentile

g: 99th percentile

Table 2. Sites with the 10 highest concentrations for C8, C4, and PFOS (ng/L)

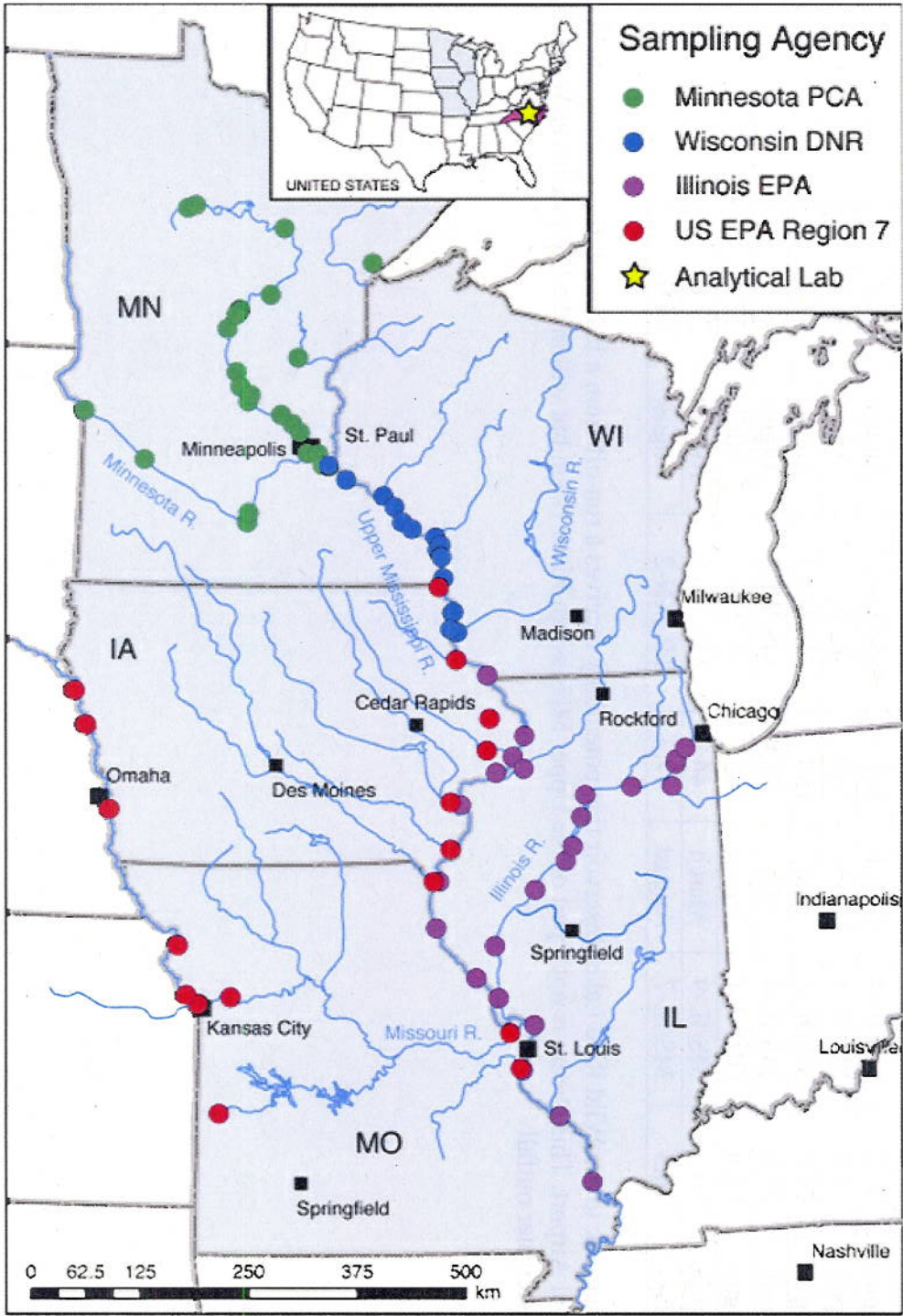
Site	Month	C8	Site	Month	C4	Site	Month	PFOS
MS/WI-1	August	125	MS/IL-3	May	458	TR/MN-1 ^a	July	287
TR/MN-1 ^a	April	50.5	MS/IL-3	April	420	MS/MN-8	August	226
MS/WI-12 ^b	August	31.0	MS/IL-3	March	325	TR/MN-1 ^a	April	124
MS/WI-7 ^b	August	30.7	MS/IL-4	March	161	MS/WI-12 ^b	August	61.7
IL/IL-1	April	26.9	MS/IL-4	April	160	IL/IL-1	May	50.8
TR/MN-2	August	23.2	MS/IL-5	May	158	MS/WI-4	August	37.1
IL/IL-2	April	23.0	MS/IL-4	May	73.9	MS/WI-2	August	27.9
TR/WI-4	August	18.0	TR/WI-4 ^c	August	48.7	IL/IL-1	April	27.4
IL/IL-3	April	16.5	MS/IL-9	March	46.7	MS/WI-1	August	27.0
IL/IL-2	May	16.3	MS/IL-7	August	47.6	TR/MN-2	August	24.0

a: Collected from a creek to the Wild Rice Lake Reservoir that potentially receives a run-off from a historical fire-training site at the Duluth International Airport. This stream is not a part of the Upper Mississippi River Basin but within the Cloquet River Watershed.

b: Collected at wastewater outfall

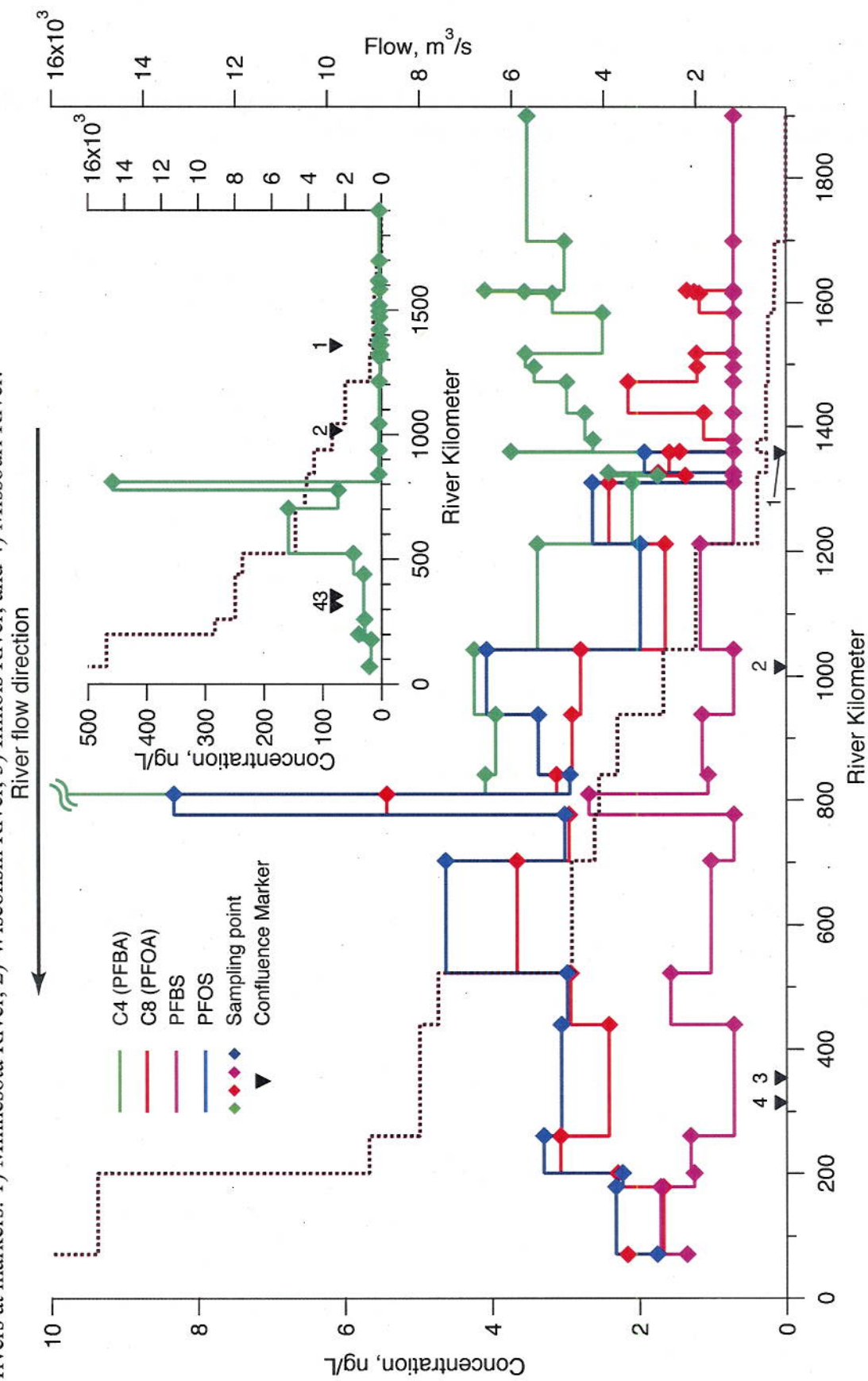
c: Well water

494 Figure 1. Sampling locations coloured by sampling agencies
495



496
497

Figure 2. Concentrations for perfluorobutanoic acid (C4 or PFBA), perfluorooctanoic acid (C8 or PFOA), perfluorobutane sulfonate (PFBS), and perfluorooctane sulfonate (PFOS) in the Upper Mississippi River (0 kilometer point at the confluence of the Mississippi and Ohio Rivers). Three-day averaged flow is depicted as the dotted line, with flow measured in $\text{m}^3/\text{s} \times 10^3$. Confluence of other rivers at markers: 1) Minnesota River, 2) Wisconsin River, 3) Illinois River, and 4) Missouri River.



503	
504	The Table of Contents Brief:
505	
506	Perfluorinated compounds are measured in the Upper Mississippi River Basin, providing the first
507	large scale evaluation of surface water in North America.
508	
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512	

Supporting Information

Title:

Cross Sectional Determination of Perfluorinated Compounds in the Upper Mississippi River Basin

Authors:

Shoji F. Nakayama, Mark J. Strynar, Jessica L. Reiner, Amy D. Delinsky, and Andrew B. Lindstrom

Number of pages: 25

Number of tables: 7

Number of figures: 5

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38 Method and materials

39 Water sampling

40 Total of 177 samples were collected from 88 sites in the Upper Mississippi Basin and a
41 part of Missouri River Basin (Figure 1 and Figure S1–S4). Samples were collected by
42 researchers from three state and one federal agencies under the collaboration with the
43 Upper Mississippi River Basin Association.

44

45 Recovery and matrix effect

46 Recoveries were calculated based on a matrix matched spike extraction. Local pond
47 water was spiked with known amounts of perfluorinated compounds (PFCs) and then
48 extracted using a solid phase extraction (SPE) cartridge. After elution of the PFCs from
49 the cartridge, the internal standards were added to the eluate. The same volume of
50 unspiked pond water was extracted using a second SPE cartridge. After elution, the
51 same amount of PFCs and internal standards were added to the eluate. The area ratio of
52 the first sample (pre-addition to cartridge) was divided by that of the second eluate
53 (post-addition) to give a recovery determination. The equation used for the calculation
54 is shown below. Each level had five replicates.

55

$$Rc = \frac{SB - Blk}{SA - Blk}, \text{ where:}$$

57

58 Rc is the recovery

59 *SB* is the response for the extract of matrix spiked before SPE

60 *SA* is the response for the extract of matrix spiked after SPE

61 *Blk* is the response for the extract of matrix without spike

62

63 Matrix effects were calculated comparing a blank matrix extract spiked with PFCs to a
64 blank methanol solution spiked with the same amount of PFCs. Unspiked pond water
65 was extracted using the SPE method described above. After elution, PFCs and internal
66 standards were added to the eluate. The same volume of methanol was spiked with the
67 same amount of PFCs and internal standards. The area ratio of the first sample (post-
68 spike) was divided by that of the methanol solution (solvent) to give a matrix effect
69 determination. The equation used for the calculation is shown below. Each level had five
70 replicates.

71

72 $ME = \frac{SA - Blk}{Sstd}$ where:

73

74 *ME* is the matrix effect

75 *SA* is the response for the extract of matrix spiked after SPE

76 *Sstd* is the response for elution solvent spiked (no matrix)

77 *Blk* is the response for the extract of matrix without spike

78 Tables

79

80 Table S1. UPLC gradient program (A) and Quatro Premier MS parameters (B)

81 (A)

Time	A	B	Curve
0.00	60	40	initial
0.50	60	40	6
3.50	10	90	6
3.60	0	100	6
4.50	0	100	6
4.60	60	40	6
6.00	60	40	6

82 A: 2 mM ammonium acetate in deionized water with 5% methanol, B: 2 mM ammonium acetate in 100% methanol

83

84 (B)

Instrument Parameters	
Capillary (kV)	-0.40
Source temperature	150°C
Desolvation temperature	350°C
Cone gas flow	2 L/hr
Desolvation gas flow	1200 L/hr
Cone voltage	Optimized for
Collision energy	each compound

85

86

87 Table S2. MS transition monitored for target compounds

88

Analyte	Acronym	MS/MS Transition		IS used
		Quantifier	Qualifier	
Perfluorobutanoic acid	C4	212.80 > 168.75	NA ^a	MC6
Perfluoropentanoic acid	C5	262.85 > 218.75	NA ^a	MC6
Perfluorohexanoic acid	C6	312.70 > 268.70		MC6
Perfluoroheptanoic acid	C7	362.65 > 318.70	312.70 > 118.70	MC8
Perfluorooctanoic acid	C8 or PFOA	412.60 > 368.65	362.65 > 168.65	MC8
Perfluorononanoic acid	C9	462.60 > 418.60	412.60 > 168.70	MC8
Perfluorodecanoic acid	C10	512.60 > 468.55	462.60 > 218.75	MC8
Perfluoroundecanoic acid	C11	562.60 > 518.60	512.60 > 218.75	MC11
Perfluorododecanoic acid	C12	612.60 > 568.55	562.60 > 268.65	MC11
Perfluorobutane sulfonate	PFBS	298.70 > 98.80	612.60 > 168.75	MC11
Perfluorohexane sulfonate	PFHS	398.65 > 98.80	298.70 > 79.90	MPFHS
Perfluorooctane sulfonate	PFOS	498.65 > 98.80	398.65 > 79.90	MPFHS
Perfluorodecane sulfonate	PFDS	598.60 > 98.80	498.65 > 79.90	MPFOS
1,2- ¹³ C ₂ -Perfluorohexanoic acid	MC6	314.75 > 269.75	598.60 > 79.90	MPFOS
1,2,3,4,5,6,7,8- ¹³ C ₂ -Perfluorooctanoic acid	MC8	402.65 > 83.90	-	Internal Standards (IS)
1,2- ¹³ C ₂ -Perfluoroundecanoic acid	MC11	429.65 > 375.75	-	
¹⁸ O ₂ -Perfluorohexane sulfonate	MPFHS	502.60 > 83.90	-	
¹⁸ O ₂ -Perfluorooctane sulfonate	MPFOS	564.60 > 519.65	-	

89 a: No secondary MS/MS transition was found for C4 and C5 that could be used as qualifier ions.

Table S3. Method performance characteristics: Mean, minimum, and maximum recoveries and relative standard deviation (RSD)

Compounds	L-QC ^a , 5.0 ng/L					L-QC ^a , 50 ng/L					F-QC ^b , 50 ng/L				
	N	Mean	RSD	Min	Max	N	Mean	RSD	Min	Max	N	Mean	RSD	Min	Max
C12	16	91.6	11	79.8	116	16	93.0	5.5	85.7	110	16	93.5	12	77.0	108
C11	16	93.2	9.5	81.3	118	16	92.8	11	82.2	108	16	102	14	79.4	124
C10	16	89.3	7.5	81.1	108	16	91.9	12	77.1	115	16	100	14	76.1	123
C9	16	94.6	11	79.0	111	16	98.5	11	86.3	116	16	101	15	75.9	119
C8	16	94.4	5.4	85.8	105	16	93.2	12	82.6	111	16	103	15	79.7	125
C7	16	104	14	80.2	117	16	96.5	5.9	87.9	105	16	96.6	14	75.9	122
C6	16	100	3.8	90.5	108	16	90.2	5.2	84.4	97.7	16	95.5	15	75.8	119
C5	14	104	8.5	90.2	118	14	105	5.2	92.4	109	12	108	6.5	94.5	119
C4	14	101	7.5	87.7	112	14	99.1	9.7	83.3	116	12	99.5	10	85.8	123
PFDS	15	99.4	10	80.0	111	15	92.6	11	78.2	110	15	91.7	12	75.0	105
PFOS	16	96.2	6.9	82.7	107	16	95.1	4.5	87.2	104	16	97.9	12	75.2	123
PFHS	16	99.0	4.9	90.4	106	16	100	5.8	89.6	111	16	105	10	86.9	125
PFBS	16	95.9	7.8	84.4	111	16	89.7	6.1	76.7	100	16	95.4	10	79.8	113

a: Spike samples prepared at the same time as calibration curves in the laboratory

b: Spike sample prepared and carried to field

Table S4. Perfluorinated compounds in samples collected by Minnesota State personnel

April

QC, % accuracy	C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFHS	PFBS
L-QC, 5.0 ng/L	94.3	96.6	86.5	86.2	91.6	114	99.6	97.6	102	104	102	106	95.6
L-QC, 50 ng/L	92.3	82.2	82.9	91.3	83.9	96.4	86.9	107	102	84.1	92.6	96.1	90.0
F-QC, 50 ng/L	107	105	103	110	117	97.4	101	103	98.7	85.0	92.3	93.5	85.9
Samples, ng/L	Flow ^a	C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFHS
MS/MN-1	—	<1	<1	<1	<1	<1	2.41	<1	ND	2.28	<1	<1	<1
MS/MN-2	—	<1	<1	<1	<1	<1	2.46	1.04	ND	2.77	<1	<1	<1
MS/MN-3	39	<1	<1	<1	<1	<1	2.63	1.14	<1	3.52	<1	<1	<1
MS/MN-3D	39	<1	<1	<1	<1	<1	<1	1.18	<1	2.18	ND	<1	ND
MS/MN-4	280	<1	<1	<1	<1	<1	2.61	1.25	ND	3.01	<1	<1	<1
MS/MN-5	290	<1	<1	<1	<1	1.34	4.62	1.49	ND	4.09	<1	<1	<1
MS/MN-6	290	ND	<1	<1	<1	1.24	4.36	1.60	<1	3.55	<1	<1	<1
MS/MN-7	290	<1	<1	<1	<1	1.17	2.31	3.25	ND	3.17	<1	<1	<1
MS/MN-10	420	<1	ND	<1	<1	<1	<1	<1	ND	2.49	<1	<1	<1
MS/MN-11	420	<1	<1	<1	<1	1.21	4.58	1.74	<1	3.54	<1	<1	<1
MS/MN-12	420	<1	<1	<1	<1	1.20	2.36	<1	<1	3.42	<1	<1	<1
MS/MN-13	470	<1	<1	<1	1.14	2.14	6.62	2.39	<1	2.74	<1	<1	<1
MS/MN-13D	470	<1	<1	<1	<1	<1	1.30	<1	<1	2.98	<1	<1	ND
TR/MN-1 ^b	—	<1	<1	<1	2.73	50.5	10.5	53.4	7.60	2.60	<1	124	169
TR/MN-2	150	<1	ND	<1	<1	1.10	2.66	1.39	ND	1.26	ND	1.35	<1
TR/MN-3	21	<1	<1	<1	<1	<1	<1	1.09	<1	3.49	<1	<1	ND

May

QCs, % accuracy	C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFHS	PFBS	
L-QC, 5.0 ng/L	104	91.5	92.2	92.9	89.4	117	97.9	106	94.0	91.4	89.5	98.8	95.3	
L-QC, 50 ng/L	90.2	83.4	85.9	89.5	82.6	90.6	87.3	109	102	85.7	91.8	95.2	90.4	
F-QC, 50 ng/L	82.4	105	99.0	76.1	86.7	99.6	102	103	99.1	76.2	92.7	96.1	87.3	
Samples, ng/L	Flow ^a	C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFHS	PFBS
MS/MN-14	470	<1	<1	<1	<1	1.11	<1	<1	ND	2.73	<1	<1	<1	ND
MS/MN-15	660	<1	ND	<1	<1	<1	1.45	<1	ND	2.62	ND	<1	<1	ND
MS/MN-16	660	<1	<1	<1	<1	1.44	1.06	1.96	<1	3.74	<1	<1	<1	ND
MS/MN-17	660	<1	<1	<1	<1	<1	<1	<1	ND	<1	<1	<1	<1	ND
MS/MN-17D	660	<1	<1	<1	<1	1.73	<1	<1	ND	2.41	ND	<1	<1	ND
MS/MN-18	660	<1	<1	<1	<1	1.36	<1	<1	ND	1.74	ND	<1	<1	<1
MS/MN-18D	660	<1	<1	<1	<1	1.28	<1	<1	ND	1.26	<1	1.78	<1	<1
MS/MN-19	660	<1	<1	<1	<1	1.81	<1	<1	<1	1.60	<1	1.74	<1	<1
MS/MN-19D	660	<1	<1	<1	<1	2.40	<1	<1	<1	2.09	ND	2.63	<1	<1
MN/MN-1	17	<1	<1	<1	<1	1.15	<1	<1	ND	1.17	ND	ND	<1	ND
MN/MN-2	110	<1	<1	<1	<1	<1	<1	<1	ND	1.41	ND	2.41	ND	ND
MN/MN-3	690	<1	<1	<1	<1	1.33	1.80	<1	ND	1.13	ND	<1	<1	ND
MN/MN-3D	690	<1	<1	<1	<1	1.10	1.00	<1	ND	<1	ND	1.14	<1	<1
MN/MN-4	690	<1	<1	<1	<1	<1	<1	<1	ND	1.81	<1	<1	<1	ND
MN/MN-5	690	<1	<1	<1	<1	1.26	<1	<1	ND	1.82	<1	<1	<1	ND
MN/MN-6	460	<1	<1	<1	<1	1.58	<1	<1	ND	<1	ND	1.92	<1	ND
MN/MN-6D	460	<1	<1	<1	<1	1.00	<1	<1	<1	<1	ND	<1	<1	ND
TR/MN-4	79	<1	<1	<1	<1	1.37	1.41	<1	ND	4.87	ND	<1	ND	ND

July

QCs, % accuracy	C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFHS	PFBS	
L-QC, 5.0 ng/L	89.5	81.9	84.8	90.4	95.8	91.3	90.5	109	103	111	102	99.2	88.2	
L-QC, 50 ng/L	95.6	84.1	77.1	86.3	83.8	87.9	86.2	106	93.8	106	95.9	104	76.7	
F-QC, 50 ng/L	93.0	86.4	89.7	106	111	115	115	108	95.2	105	82.6	101	87.3	
Samples, ng/L	Flow ^a	C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFHS	PFBS
TR/MN-1 ^b	–	<1	<1	<1	6.36	95.6	28.6	128	44.9	12.5	<1	296	365	42.3
TR/MN-1D	–	<1	<1	<1	6.25	89.5	32.0	140	44.6	14.7	ND	270	371	41.1
TR/MN-1DD	–	<1	<1	<1	6.59	91.3	28.4	126	45.0	12.0	ND	296	365	41.7

QC, % accuracy	C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFHS	PFBS
L-QC, 5.0 ng/L	82.0	99.8	98.0	103	102	114	108	102	112	80.0	107	101	111
L-QC, 50 ng/L	93.3	95.5	92.7	97.1	93.5	97.4	93.1	92.4	83.3	98.4	104	108	87.6
F-QC, 50 ng/L	106	99.4	94.7	99.3	105	104	107	101	85.8	104	107	115	96.7
Samples, ng/L	Flow ^a	C12	C11	C10	C9	C8	C7	C6	C5	PFDS	PFOS	PFHS	PFBS
MS/MN-1	—	ND	ND	ND	ND	ND	8.24	1.45	<1	1.83	ND	ND	<1
MS/MN-2	—	1.28	<1	<1	<1	3.49	13.2	3.29	1.39	<1	ND	ND	<1
MS/MN-3	11	ND	ND	ND	<1	<1	4.88	1.09	<1	1.79	ND	ND	<1
MS/MN-3D	11	ND	ND	ND	<1	<1	5.36	1.31	<1	ND	1.30	ND	<1
MS/MN-4	21	3.07	ND	ND	<1	1.14	2.75	<1	1.11	<1	ND	3.48	<1
MS/MN-5	25	<1	<1	<1	<1	<1	2.41	<1	ND	2.38	ND	ND	<1
MS/MN-6	25	<1	<1	<1	1.98	3.63	5.65	2.29	<1	2.44	ND	<1	1.39
MS/MN-7	25	<1	<1	ND	<1	1.48	3.95	1.41	<1	2.00	ND	<1	ND
MS/MN-8	25	<1	1.97	2.46	8.52	8.18	6.07	5.81	1.96	2.27	ND	245	3.02
MS/MN-8D	25	4.36	<1	ND	5.66	5.48	7.06	5.19	2.42	2.43	ND	206	1.09
MS/MN-9	25	ND	ND	ND	<1	<1	3.15	<1	<1	1.74	ND	<1	<1
MS/MN-9D	25	ND	ND	ND	<1	1.34	4.47	1.10	<1	2.14	ND	<1	<1
MS/MN-10	47	<1	<1	ND	ND	2.01	5.72	1.68	<1	1.72	ND	<1	<1
MS/MN-11	47	<1	ND	ND	<1	1.35	3.35	1.00	<1	2.95	ND	<1	<1
MS/MN-12	47	ND	<1	ND	<1	1.23	4.15	1.55	ND	2.10	ND	1.86	<1
MS/MN-13	50	ND	ND	ND	<1	1.27	<1	1.17	<1	2.37	ND	1.00	<1
MS/MN-13D	50	ND	ND	ND	<1	1.20	2.21	1.18	<1	2.46	ND	1.62	<1
MS/MN-14	6.6	ND	<1	ND	ND	2.20	3.26	1.83	<1	4.21	ND	<1	<1
MS/MN-15	72	3.83	ND	ND	1.20	2.65	4.02	2.30	1.95	<1	ND	20.3	<1
MS/MN-16	72	ND	ND	<1	<1	5.13	4.34	3.48	1.51	4.11	ND	4.05	3.57
MS/MN-17	72	ND	<1	1.16	2.01	8.01	4.71	5.76	2.14	6.26	ND	10.2	1.14
MS/MN-17D	72	<1	ND	<1	1.35	9.29	3.69	6.20	3.22	5.70	ND	4.68	<1
MS/MN-18	72	1.76	<1	<1	1.38	7.96	4.16	5.67	3.92	12.7	ND	13.6	2.74
MS/MN-18D	72	2.52	<1	<1	2.53	9.42	4.41	6.40	3.07	11.0	ND	12.8	3.54
MS/MN-19	72	<1	<1	1.35	2.54	23.8	4.19	9.23	6.15	34.2	ND	29.0	15.0
MS/MN-19D	72	<1	ND	<1	1.90	22.5	3.50	9.35	5.54	27.5	ND	18.9	8.84

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August—continued

Samples, ng/L	Flow ^a	C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFHS	PFBS
MN/MN-1	—	< 1	ND	ND	ND	< 1	2.81	1.07	< 1	ND	ND	5.19	ND	< 1
MN/MN-2	—	< 1	< 1	ND	ND	1.13	4.10	1.10	ND	1.82	ND	< 1	ND	< 1
MN/MN-3	—	ND	< 1	ND	< 1	1.46	1.67	< 1	ND	1.69	ND	1.97	< 1	< 1
MN/MN-3D	—	1.32	ND	< 1	< 1	2.14	3.73	1.80	< 1	1.25	ND	9.20	< 1	< 1
MN/MN-4	—	1.88	ND	ND	ND	< 1	3.98	2.26	1.26	< 1	ND	6.47	2.00	ND
MN/MN-5	—	< 1	ND	ND	ND	1.46	1.80	1.40	< 1	1.52	ND	6.02	< 1	< 1
MN/MN-6	44	2.21	ND	< 1	1.14	3.95	5.14	3.60	3.00	1.47	ND	8.76	5.87	1.15
MN/MN-6D	44	ND	ND	< 1	< 1	4.06	3.74	2.92	2.07	1.57	ND	4.42	2.87	< 1
TR/MN-4	50	ND	ND	ND	ND	2.00	4.32	1.61	1.27	2.77	ND	2.10	< 1	< 1

a: Three days average sandwiching each sampling day at the nearest gauging station in m³/s

b: Collected from a creek to the Wild Rice Lake Reservoir that potentially receives a run-off from a historical fire-training site at the Duluth International Airport. This stream is not a part of the Upper Mississippi River Basin but within the Cloquet River Watershed.

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Table S5. Perfluorinated compounds in samples collected by Wisconsin State personnel

March (all sites were covered by ice)

QC, % accuracy	C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFHS	PFBS
L-QC, 5.0 ng/L	89.8	89.3	95.1	108	105	107	97.0	NA	NA	85.1	101	100	108
L-QC, 50 ng/L	85.7	108	111	111	109	105	97.7	NA	NA	78.2	104	105	88.5
F-QC, 50 ng/L	88.0	79.4	85.4	83.3	79.7	85.7	75.8	NA	NA	97.4	123	125	108
Samples, ng/L	Flow ^a	C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFBS
MS/WI-3	340	ND	ND	<1	6.69	<1	2.65	NA	NA	NA	ND	14.2	3.76
MS/WI-3D	340	<1	ND	<1	2.20	9.47	1.79	2.68	NA	NA	ND	15.6	3.42
MS/WI-11	630	<1	<1	<1	5.01	<1	1.54	NA	NA	NA	ND	9.44	2.85
TR/WI-1	-	<1	ND	<1	ND	<1	2.01	NA	NA	NA	ND	4.69	1.90
TR/WI-2	-	<1	<1	<1	<1	1.44	1.94	NA	NA	NA	ND	2.07	<1
WI/WI-1	-	<1	ND	<1	2.86	1.50	3.38	NA	NA	NA	ND	7.03	<1

April

QC, % accuracy	C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFHS	PFBS
L-QC, 5.0 ng/L	84.5	92.3	84.7	111	93.6	81.4	101	118	109	99.3	90.5	96.8	84.4
L-QC, 50 ng/L	91.7	103	97.2	116	109	103	96.5	104	92.6	110	96.2	104	84.8
F-QC, 50 ng/L	108	87.9	87.2	88.9	85.2	87.3	79.0	107	123	95.1	120	124	102
Samples, ng/L	Flow ^a	C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFBS
MS/WI-3	2000	<1	ND	<1	ND	<1	<1	<1	ND	ND	ND	1.71	<1
MS/WI-11	2700	<1	ND	<1	<1	2.31	ND	<1	ND	ND	ND	3.54	<1
MS/WI-11D	2700	<1	ND	<1	<1	2.54	<1	<1	ND	ND	ND	4.16	1.00
TR/WI-1	650	ND	<1	<1	ND	<1	ND	<1	ND	ND	ND	<1	<1
TR/WI-2	370	<1	ND	<1	ND	<1	ND	<1	ND	ND	ND	<1	ND
WI/WI-1	970	<1	<1	<1	<1	2.12	<1	1.58	ND	ND	<1	2.88	<1

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May

QCs, % accuracy	C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFHS	PFBS	
L-QC, 5.0 ng/L	79.8	84.5	85.6	95.9	96.2	117	103	97.4	91.9	110	95.7	95.5	96.9	
L-QC, 50 ng/L	90.7	90.7	85.6	93.7	86.9	90.1	84.4	109	116	91.0	95.4	99.3	100	
F-QC, 50 ng/L	83.9	119	76.1	75.9	82.4	97.7	103	119	97.4	75.0	88.0	96.7	84.5	
Samples, ng/L	Flow ^a	C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFBS	
MS/WI-3	2000	<1	<1	<1	<1	1.64	<1	1.18	<1	3.38	<1	1.98	<1	1.16
MS/WI-3D	2000	<1	<1	<1	<1	2.07	<1	<1	<1	3.94	ND	3.07	<1	<1
MS/WI-11	2700	<1	<1	<1	<1	2.79	1.17	1.44	<1	4.24	ND	4.07	<1	<1
TR/WI-1	650	<1	<1	<1	<1	<1	<1	1.40	<1	<1	<1	1.56	<1	<1
TR/WI-2	370	<1	<1	<1	<1	<1	<1	<1	ND	<1	<1	<1	<1	<1
WI/WI-1	970	<1	<1	<1	<1	2.54	1.39	1.88	<1	1.91	ND	4.32	<1	<1

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August

QCs, % accuracy	C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFHS	PFBS	
L-QC, 5.0 ng/L	116	118	108	83.2	99.4	97.0	98.4	90.2	87.7	N/A	92.6	90.4	96.5	
L-QC, 50 ng/L	110	107	115	91.2	96.0	93.9	93.1	93.9	89.8	N/A	87.2	89.6	88.5	
F-QC, 50 ng/L	98.2	103	115	114	108	105	108	NA	NA	N/A	94.7	104	98.1	
Samples, ng/L	Flow ^a	C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFHS	PFBS
MS/WI-1	130	9.75	29.1	42.0	72.9	125	90.2	46.3	7.39	37.1	N/A	27.0	14.5	12.8
MS/WI-2	200	24.7	21.7	13.2	4.45	15.9	5.30	6.76	5.14	26.4	N/A	27.9	7.85	16.5
MS/WI-2D	200	7.29	14.9	8.42	3.13	14.4	7.61	7.15	6.17	28.8	N/A	16.1	8.39	16.8
MS/WI-3	330	5.71	9.32	5.39	3.79	10.5	4.42	3.62	2.86	11.8	N/A	13.9	2.97	2.87
MS/WI-4	360	14.0	28.3	17.0	4.06	7.28	2.28	2.69	2.63	6.85	N/A	37.1	2.36	3.51
MS/WI-5	360	1.64	1.78	<1	1.41	7.37	2.16	2.83	2.69	12.0	N/A	6.46	1.78	3.34
MS/WI-6	380	<1	1.62	<1	1.49	6.75	3.11	2.16	2.28	7.51	N/A	10.5	1.59	2.36
MS/WI-7 ^b	–	<1	<1	4.31	9.68	30.7	7.19	21.5	12.5	16.7	N/A	18.4	8.90	2.28
MS/WI-8	–	1.03	<1	<1	1.07	6.18	8.60	3.48	2.74	11.6	N/A	6.94	1.76	<1
MS/WI-9	420	<1	1.04	1.47	1.23	6.76	6.98	3.03	<1	7.43	N/A	12.6	2.50	2.91
MS/WI-10	430	<1	1.29	<1	<1	5.47	1.73	2.32	2.42	8.86	N/A	7.78	2.72	1.43
MS/WI-11	480	<1	<1	<1	1.17	5.38	8.56	3.36	2.28	7.07	N/A	8.04	2.03	1.51
MS/WI-12 ^c	–	<1	<1	3.67	4.14	31.0	5.42	19.1	12.4	3.36	N/A	61.7	101	6.16
TR/WI-3	–	<1	<1	<1	<1	4.98	8.98	3.44	5.16	<1	N/A	3.91	<1	<1
TR/WI-4 ^d	–	<1	1.03	<1	<1	18.0	1.86	1.75	1.33	48.7	N/A	13.4	6.39	3.26

119 a: Three days average sandwiching each sampling day at the nearest gauging station in m³/s

120 b: La Crosse Wastewater Treatment Plant effluent

121 c: Prairie du Chien Wastewater Treatment Plant outfall
122 d: La Crosse Well #23

Table S6. Perfluorinated compounds in samples collected by Illinois State personnel

March

QCs, % accuracy	C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFHS	PFBS	
L-QC, 5.0 ng/L	91.2	97.1	91.4	106	97.0	80.2	100	116	109	111	82.7	96.8	106	
L-QC, 50 ng/L	91.8	100	99.0	111	111	102	95.9	109	88.7	102	95.6	111	90.0	
F-QC, 50 ng/L	101	106	96.4	102	96.9	93.4	90.6	NA	NA	97.1	75.2	86.9	79.8	
Samples, ng/L	Flow ^a	C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFBS	
IL/IL-7	970	<1	<1	<1	<1	3.89	2.35	2.75	1.89	4.60	ND	10.5	5.92	4.09
IL/IL-8	860	<1	<1	<1	1.42	4.63	1.92	2.69	2.08	5.46	ND	3.56	1.08	2.27
MS/IL-3	1200	<1	<1	<1	<1	7.94	2.61	4.37	31.5	325	ND	20.4	6.59	25.1
MS/IL-4	960	<1	<1	<1	<1	4.25	1.13	1.93	4.77	161	ND	5.46	1.59	4.24
MS/IL-9	4800	<1	ND	<1	<1	2.75	1.65	1.74	1.96	48.0	ND	3.94	<1	2.49
MS/IL-9D	4800	<1	<1	<1	<1	3.01	2.09	1.89	2.04	45.4	ND	4.32	<1	2.74

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QCs, % accuracy	C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFHS	PFBS	
L-QC, 5.0 ng/L	82.3	81.3	81.1	79	85.8	91.6	105	NA	NA	86	94.9	91.4	89	
L-QC, 50 ng/L	96.6	108	107.0	116	104	105	93.2	NA	NA	95	97.9	106	93.6	
F-QC, 50 ng/L	101	117	107.9	114	117.4	121.9	109.1	NA	NA	102.0	100.4	111.9	97.0	
Samples, ng/L	Flow ^a	C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFBS	
IL/IL-1	71	<1	<1	1.56	5.79	14.4	10.9	13.4	5.95	6.85	ND	17.6	4.25	2.35
IL/IL-2	71	<1	<1	1.16	3.34	15.6	9.82	12.6	7.34	9.17	ND	16.7	3.64	2.47
IL/IL-3	—	<1	<1	1.00	3.63	11.7	4.09	7.38	5.50	21.6	ND	13.7	3.60	2.35
IL/IL-3D	—	<1	<1	1.07	3.72	12.0	4.75	7.20	5.68	21.3	ND	14.6	3.91	2.19
TR/IL-1	140	<1	ND	<1	<1	<1	2.29	1.20	ND	ND	ND	<1	ND	<1

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QCs, % accuracy		C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFHS	PFBS
L-QC, 5.0 ng/L		94.3	96.6	86.5	86.2	91.6	114	99.6	97.6	102	104	102	106	95.6
L-QC, 50 ng/L		92.3	82.2	82.9	91.3	83.9	96.4	86.9	107	102	84.1	92.6	96.1	90.0
F-QC, 50 ng/L		77.0	82.1	108	119	125	75.9	82.3	110	107	95.6	100	101	97.8
Samples, ng/L	Flow ^a	C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFHS	PFBS
IL/IL-1	63	<1	<1	2.14	4.61	26.9	8.99	17.3	11.6	12.8	<1	27.4	4.18	13.7
IL/IL-2	63	<1	<1	2.80	5.52	22.6	8.92	15.9	10.1	8.70	<1	21.9	6.01	5.00
IL/IL-2D	63	<1	<1	2.66	5.77	23.3	8.87	15.6	9.86	8.71	<1	23.8	5.50	5.04
IL/IL-3	—	<1	<1	1.48	4.29	16.5	7.02	13.9	10.0	6.85	ND	17.1	5.50	3.87
IL/IL-7	950	<1	<1	<1	1.15	3.58	2.73	4.38	2.74	3.98	<1	2.81	1.17	1.00
IL/IL-8	910	<1	<1	1.07	1.63	5.09	3.79	4.62	1.90	4.56	<1	6.48	1.80	1.33
MS/IL-3	4200	<1	<1	<1	<1	4.86	3.48	4.53	12.2	420	<1	8.33	2.18	4.65
MS/IL-4	4400	<1	<1	<1	1.00	3.99	3.13	3.09	3.42	160	ND	5.53	1.13	3.13
MS/IL-9	8400	<1	<1	<1	1.04	3.81	2.70	2.59	1.87	22.1	<1	3.50	1.04	2.07
MS/IL-9D	8400	<1	<1	<1	<1	3.57	2.66	2.58	1.91	23.7	<1	3.23	<1	2.06
TR/IL-2	120	<1	<1	<1	<1	1.88	3.30	1.60	<1	2.01	<1	<1	<1	<1

QCs, % accuracy	C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFHS	PFBS	
L-QC, 5.0 ng/L	94.3	96.6	86.5	86.2	91.6	114	99.6	97.6	102	104	102	106	95.6	
L-QC, 50 ng/L	92.3	82.2	82.9	91.3	83.9	96.4	86.9	107	102	84.1	92.6	96.1	90.0	
F-QC, 50 ng/L	78.4	81.6	118	115	125	79.2	80.9	115	107	80.1	99.4	102	107	
Samples, ng/L	Flow ^a	C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFHS	PFBS
IL/IL-7	610	<1	<1	<1	2.23	8.45	2.68	6.02	3.01	2.98	ND	4.86	2.02	1.33
IL/IL-8	730	<1	<1	<1	2.27	7.28	2.62	5.41	2.65	3.45	<1	5.28	1.88	1.44
IL/IL-9	—	<1	<1	<1	1.76	6.62	2.12	4.79	2.19	3.70	ND	5.24	1.85	1.32
IL/IL-10	1000	<1	<1	<1	1.91	6.77	2.54	4.81	2.52	2.68	<1	3.33	1.56	1.27
IL/IL-11	1000	<1	<1	<1	1.35	5.45	2.22	4.24	1.80	2.35	<1	3.78	1.89	1.28
MS/IL-1	3700	<1	<1	<1	<1	2.91	1.43	2.68	<1	3.95	<1	3.37	1.09	1.14
MS/IL-2	4100	<1	<1	<1	<1	3.12	1.01	1.30	<1	4.09	<1	2.94	<1	1.06
MS/IL-3	4100	<1	<1	<1	<1	5.43	2.42	2.56	10.5	458	<1	8.33	2.11	2.68
MS/IL-4	4200	<1	<1	<1	<1	2.95	1.56	2.11	1.82	73.9	<1	3.01	1.19	<1
MS/IL-5	4700	<1	<1	<1	<1	3.66	1.34	1.59	2.78	158	<1	4.63	<1	1.02
MS/IL-6	—	<1	<1	<1	<1	2.01	1.67	1.08	<1	16.5	<1	2.03	<1	<1
MS/IL-7	7600	<1	<1	<1	<1	2.93	<1	1.67	1.22	47.6	ND	2.98	<1	1.57
MS/IL-8	8000	<1	<1	<1	<1	2.41	<1	1.24	<1	30.3	ND	3.06	<1	<1
MS/IL-9	9100	<1	<1	<1	<1	3.07	1.72	2.43	<1	28.6	<1	3.30	<1	1.30
TR/IL-1	570	<1	<1	<1	<1	2.19	1.24	3.23	1.44	4.27	<1	1.39	<1	<1

QCs, % accuracy	C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFHS	PFBS	
L-QC, 5.0 ng/L	104	91.5	92.2	92.9	89.4	117	97.9	106	94.0	91.4	89.5	98.8	95.3	
L-QC, 50 ng/L	90.2	83.4	85.9	89.5	82.6	90.6	87.3	109	102	85.7	91.8	95.2	90.4	
F-QC, 50 ng/L	77.7	106	123	116	99.7	80.5	77.4	116	103	87.8	99.8	98.3	90.7	
Samples, ng/L	Flow ^a	C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFHS	PFBS
IL/IL-1	110	<1	<1	1.32	3.28	11.7	10.1	9.31	6.52	5.20	<1	50.8	7.10	2.32
IL/IL-2	110	<1	<1	1.43	5.52	16.3	5.26	10.6	7.39	5.44	<1	15.0	4.27	1.81
IL/IL-3	—	<1	<1	1.38	4.29	16.3	4.89	10.0	7.89	5.69	<1	14.4	4.22	2.27
IL/IL-4	520	<1	<1	1.24	2.82	6.66	3.05	5.45	3.11	2.78	<1	6.76	2.06	1.68
IL/IL-5	740	<1	<1	<1	1.92	7.96	2.93	4.72	2.88	3.45	ND	6.43	1.57	1.74
IL/IL-6	740	<1	<1	1.04	2.44	9.35	3.54	5.88	3.60	3.45	<1	6.69	1.75	1.34
TR/IL-2	80	<1	<1	<1	<1	2.88	1.23	1.70	<1	<1	ND	1.50	<1	1.31

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May

QCs, % accuracy		C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFHS	PFBS	
L-QC, 5.0 ng/L		79.8	84.5	85.6	95.9	96.2	117	103	97.4	91.9	110	95.7	95.5	96.9	
L-QC, 50 ng/L		90.7	90.7	85.6	93.7	86.9	90.1	84.4	109	116	91.0	95.4	99.3	100	
F-QC, 50 ng/L		104	124	76.6	90.8	87.5	97.9	94.7	107	86.4	76.5	92.4	96.8	89.2	
Samples, ng/L		Flow ^a	C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFHS	PFBS
MS/IL-10		15000	<1	<1	<1	<1	2.29	1.12	1.64	1.15	38.5	<1	2.23	<1	1.25
MS/IL-11		15000	<1	<1	<1	<1	1.67	<1	1.46	1.00	17.6	<1	2.32	<1	1.71
MS/IL-11D		15000	<1	<1	<1	<1	1.93	<1	1.47	<1	19.9	<1	3.86	<1	1.26
MS/IL-12		16000	<1	<1	<1	<1	2.16	<1	1.41	<1	20.6	ND	1.76	<1	1.35

134 a: Three days average sandwiching each sampling day at the nearest gauging station in m³/s

Table S7. Perfluorinated compounds in samples collected by US EPA Region 7 personnel

April														
QCs, % accuracy	C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFHS	PFBS	
L-QC, 5.0 ng/L	84.5	92.3	84.7	111	93.6	81.4	101	118	109	99.3	90.5	96.8	84.4	
L-QC, 50 ng/L	91.7	103	97.2	116	109	103	96.5	104	92.6	110	96.2	104	84.8	
F-QC, 50 ng/L	100	120	111	119	119	115	119	94.5	92.2	103	96.7	108	101	
Samples, ng/L	Flow ^a	C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFBS	
MO/MO-1 ^b	1400	<1	<1	<1	<1	<1	<1	<1	ND	ND	<1	2.73	<1	ND
MO/MO-2 ^b	1800	1.04	<1	<1	ND	<1	<1	<1	ND	ND	ND	7.05	1.22	ND
MO/MO-3 ^b	1800	<1	ND	<1	ND	<1	<1	<1	ND	ND	ND	11.0	<1	<1
MO/MO-3D	1800	<1	ND	<1	<1	<1	<1	<1	ND	ND	ND	9.70	<1	<1
MO/MO-4 ^b	1800	<1	<1	<1	<1	1.61	2.30	1.27	ND	ND	ND	9.11	<1	ND
MO/MO-5 ^b	6100	<1	<1	<1	ND	<1	<1	<1	ND	ND	ND	2.51	<1	ND
MO/MO-5D ^b	6100	<1	<1	<1	<1	<1	<1	<1	ND	ND	ND	3.04	<1	ND
TR/IA-1	89	<1	<1	<1	<1	<1	ND	<1	ND	ND	ND	1.14	<1	ND
TR/IA-2	—	<1	<1	<1	ND	ND	ND	ND	ND	ND	<1	<1	ND	ND
TR/IA-3	37	<1	ND	<1	ND	ND	ND	ND	ND	ND	<1	ND	ND	ND
TR/IA-4	240	<1	ND	<1	ND	ND	ND	<1	ND	ND	ND	<1	<1	ND
TR/IA-5	970	<1	<1	<1	ND	<1	<1	<1	ND	ND	ND	<1	ND	ND
TR/IA-6	350	<1	<1	<1	ND	ND	ND	<1	ND	ND	ND	<1	ND	ND
TR/IA-7	720	<1	<1	<1	ND	<1	ND	<1	ND	ND	ND	1.83	<1	ND
TR/IA-7D	720	<1	<1	<1	ND	<1	<1	<1	ND	ND	ND	1.65	<1	ND
TR/MO-1 ^b	190	<1	<1	<1	<1	2.01	1.05	1.34	ND	ND	<1	15.2	1.62	ND
TR/MO-2	830	<1	<1	<1	ND	<1	ND	<1	ND	ND	ND	1.57	<1	ND

QCs, % accuracy	C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFHS	PFBS	
L-QC, 5.0 ng/L	94.3	96.6	86.5	86.2	91.6	114	99.6	97.6	102	104	102	106	95.6	
L-QC, 50 ng/L	92.3	82.2	82.9	91.3	83.9	96.4	86.9	107	102	84.1	92.6	96.1	90.0	
F-QC, 50 ng/L	90.3	106	103	87.9	97.8	91.1	82.5	112	99.3	95.2	105	112	113	
Samples, ng/L	Flow ^a	C12	C11	C10	C9	C8	C7	C6	C5	C4	PFDS	PFOS	PFHS	PFBS
MO/IA-1 ^b	590	<1	<1	<1	<1	<1	1.13	1.06	ND	1.89	<1	1.69	<1	<1
MO/IA-2 ^b	620	<1	<1	<1	<1	<1	<1	<1	ND	1.76	<1	1.67	<1	ND
MO/IA-2D ^b	620	<1	<1	<1	<1	<1	1.59	<1	ND	1.70	<1	1.62	<1	ND
MO/IA-3 ^b	850	<1	<1	<1	<1	<1	<1	<1	ND	2.02	<1	1.65	<1	ND
TR/MO-3 ^b	28	<1	<1	<1	<1	1.09	<1	<1	ND	1.98	<1	4.05	1.81	1.12
TR/MO-3D	28	<1	<1	<1	<1	1.16	<1	<1	ND	1.88	<1	2.93	1.88	<1

138 a: Three days average sandwicheing each sampling day at the nearest gauging station in m³/s
139 b: Collected from the Missouri River Basin including Missouri (R7-1, 3-5, 13, 16-18), Kansas (R7-2), and Marmaton Rivers (R7-15).
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Figures

Figure captions

Figure S1. Detailed map for samples collected by Minnesota State personnel

TR/MN-1 was from a creek to Wild Rice Lake Reservoir (not included in the Upper Mississippi River Basin); TR/MN-2 from Snake River; TR/MN-3 from Elk River; TR/MN-4 from Rum River; MN/MN-1–6 from Minnesota River and all others from Upper Mississippi River.

Figure S2. Detailed map for samples collected by Wisconsin State personnel

TR/WI-1 was from Chippewa River; TR/WI-2 from Black River; WI/WI-1 from Wisconsin River; TR/WI-3 from Halfway Creek; TR/WI-4 from Well #23 in La Cross; all others from Upper Mississippi River

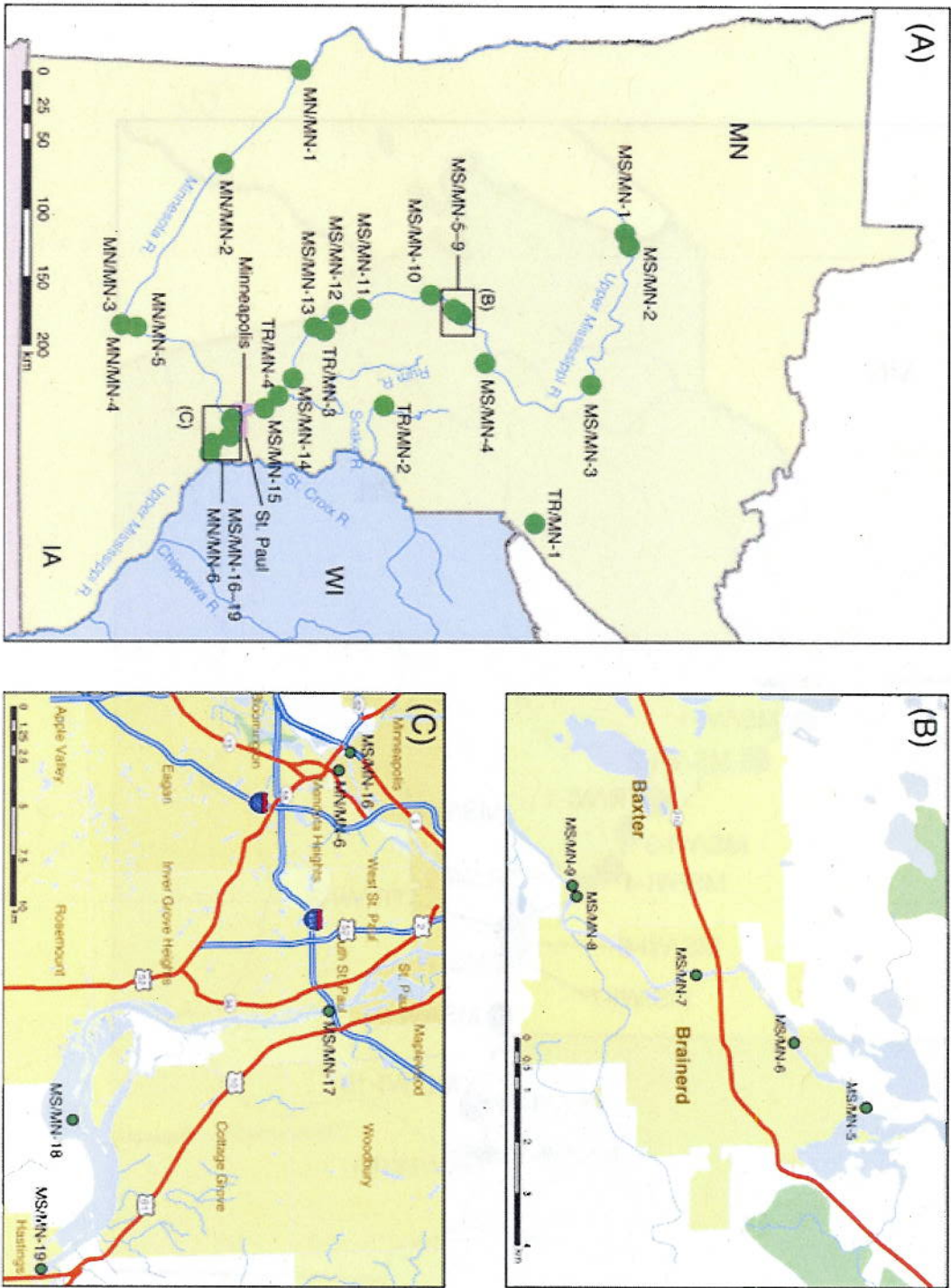
Figure S3. Detailed map for samples collected by Illinois State personnel

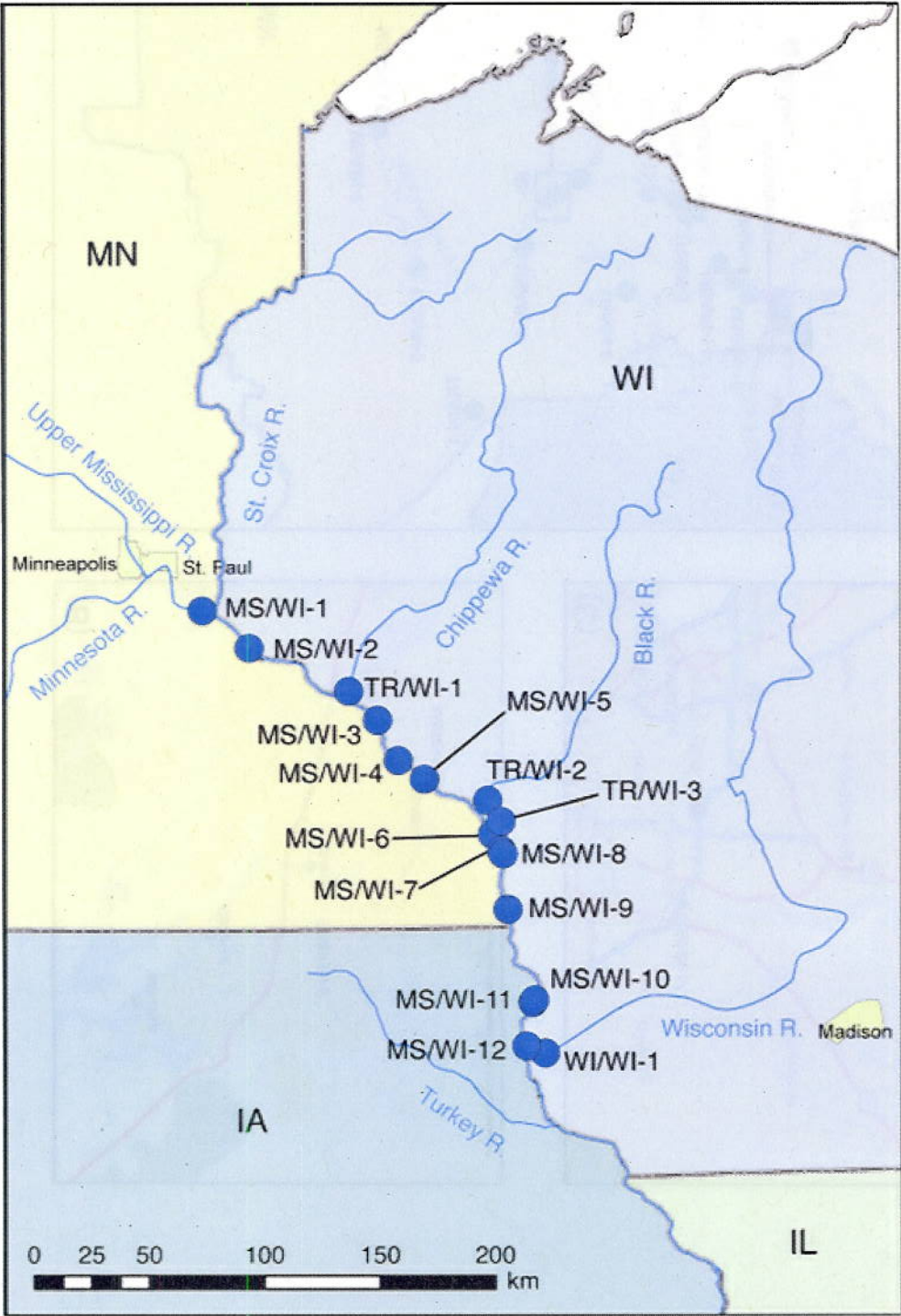
IL/IL-4–11 were from Illinois River; IL/IL-1 from Cal Sag Channel; IL/IL-2 from Chicago Ship Canal; IL/IL-3 from Des Plaines River; TR/IL-1 from Rock River; TR/IL-2 from Kankakee River; all others from Upper Mississippi River.

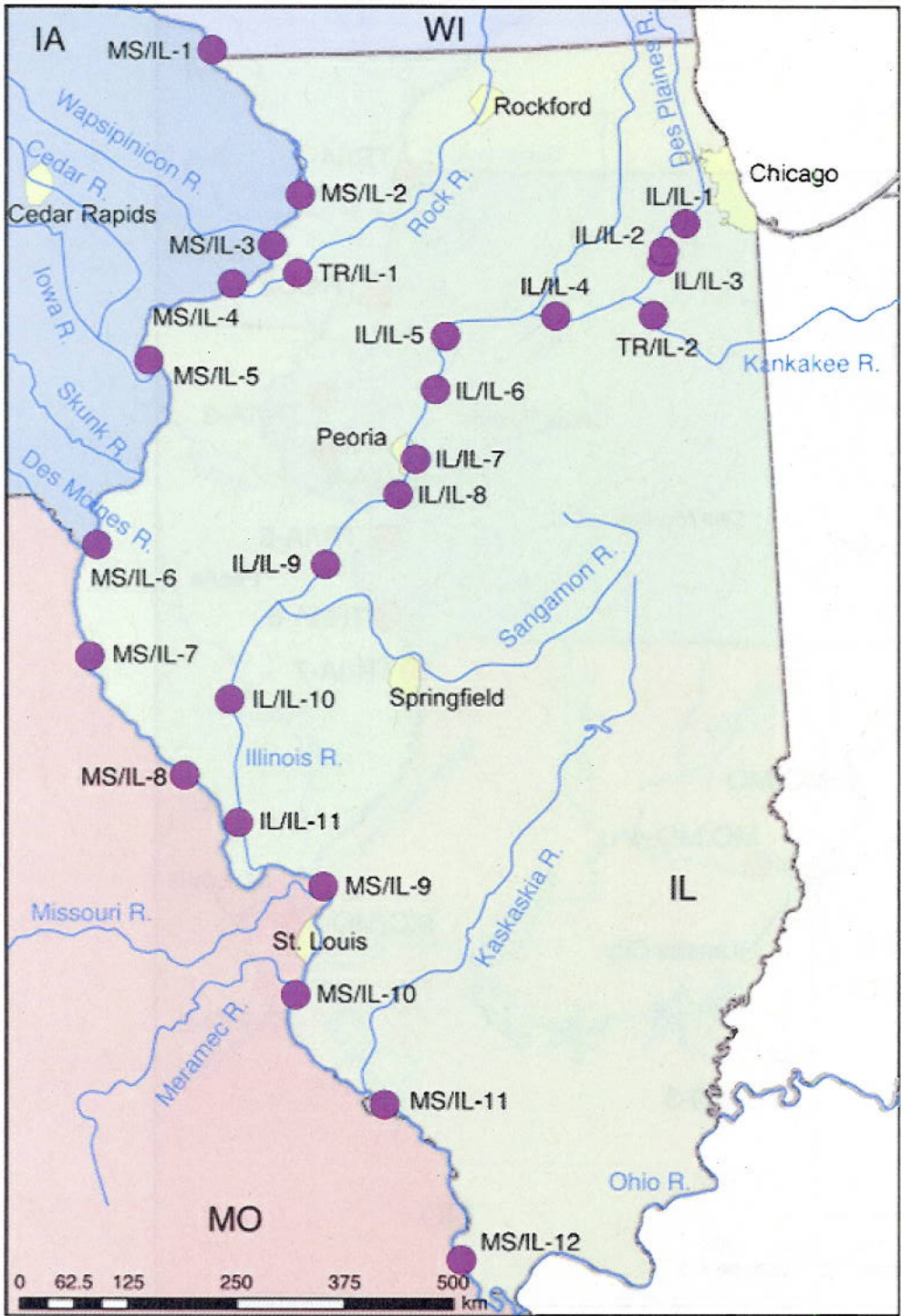
Figure S4. Detailed map for samples collected by US EPA Region 7 State personnel

TR/IA-1 from Upper Iowa River; TR/IA-2 from Turkey River; TR/IA-3 from Maquoketa River; TR/IA-4 from Wapsipinicon River; TR/IA-5 from Iowa River; TR/IA-6 from Skunk River; TR/IA-7 from Des Moines River; TR/MO-1 was from Kansas River; TR/MO-2 from Meramec River; TR/MO-3 from Marmaton River; all others from Missouri River. Missouri, Kansas, and Marmaton Rivers belong to the Missouri River Basin.

Figure S5. Mass flux for C4 (or PFBA), C8 (or PFOA), PFBS, and PFOS in the Upper Mississippi River (0 kilometer point at the confluence of the Mississippi and Ohio Rivers). Three-day averaged flow is depicted as the dotted line, with flow measured in $\text{m}^3/\text{s} \times 10^3$.







181 Figure S4
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