Applying Statistical Analysis and Geographic Information Science (GIS) To Analyze The Level Of Perfluoroctane Sulfonate (PFOS) in Mississippi River Pool 2 between 2009 and 2012, Minnesota USA

Bezawit Hunegnaw
Department of Resource Analysis, Saint Mary's University of Minnesota, Minneapolis, MN 55404

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Abstract

Extensive screening analyses of perflurorocatanesulfonate (PFOS) and several other Perflurochemichals (PFCS) compounds from around the world have been identified as global pollutants. PFOS were measured in five fish species collected from Pool 2 (river impoundment) of Mississippi River, Minnesota USA in 2009 and 2012 in an effort to evaluate if levels decreased over time. To characterize the spatial distribution of PFCS in Pool 2, the pool was divided in to four sections. Section 1 was the most upstream and section 4 was the furthest downriver. Composite fish samples were analyzed for 10 PFC compounds. However, this study only focuses on PFOS. Samples were collected from areas of the Mississippi River near historical PFC sources. Fish from Pool 2 near Hastings, Minnesota USA had the highest concentration. On the other hand, locations upstream had PFOS concentrations below 200 ng/g; the concentration at which Minnesota issues a "one meal per month" fish consumption advisory. The highest PFOS concentrations in water coincided with the highest Fish concentrations observed, Section 4. A paired samples t-test was used to determine whether there was a statistically significant difference between fish species tested in 2009 and those tested in 2012. There was a significant difference in fish species for 2009 (M = 120.65ng/l, SD = 162.4) as opposed to fish species for 2012 (M= 73.15ng/l, SD = 111.90) ($p < .05$). There was no significant difference in the level of PFOS found in water for 2009 (M = 13.9242, SD = 24.159) and in 2012 (M =19.02, SD 41.31) ($p > .05$). Results suggest in comparison to 2012 PFOS, concentrations of PFOS in the fish species declined from 2009. PFOS concentrations in water from Pool 2 did not. Results from both years indicate higher levels of PFOS in water downstream in comparison to upstream.

Introduction

Perfluroalkylated substances (PFAS) are the collective name for majority of fluorinated compounds. Perfluroroctanoic acid (PFOA and Perflourooctane sulfonate (PFOS) molecules made up of hydrocarbons. The hydrogen atoms found in PFOS are replaced with fluorine atoms and are known as fluorocarbons. PFAS are environmental contaminants belonging to a chemical group known as perfluorinated compounds. Both PFOS and PFOA have unique properties and various applications

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including oil production, water repellency, and resistance to heat (Oliaei, Kriens, and Kessler, 2013).

Perfluorinated compounds were first produced in the late 1940's for the Manhattan project as a material to coat valves and seals Teng (2012). The production and use of Perfluorinated compounds grew from 1966 until the 1990's mainly due to their unique chemical attributes; they are stable in the environment and resistant to breakdown (Lau Anitole, Hodes, Lai, Pfahles-Hutchens, and Seed, 2007).

PFOS, PFOA, and other Perfluorinated compounds have been used extensively in industrial and consumer applications including stain and water-resistant coatings for furniture, pharmaceuticals, cosmetics, paper coatings, food wrappers, shampoos, paint, and non-stick surfaces for cooking utensils (Giesey and Kennan, 2001).

Various Perfluorinated compounds have been widely found in the environment, primarily resulting from human activity. These compounds have been shown to bioaccumulate in fish and experimental animals. Toxicology studies have shown that both PFOS and PFOA are readily absorbed after oral exposure and accumulate primarily in the kidney and liver (Benford, 2008). By 2001, it was discovered Perfluorinated compounds were accumulating in biota throughout the world and had been detected in varying tropic levels of the aquatic world including drinking waters, fish, mammals, and human beings (Giesey and Kennan, 2001).

Use of these compounds has been detected not only in industrial and populated areas but even the Arctic (Bossi, Ridget, Dietz, Sonne, Fauser, Dam and Vorkamp, 2005). Concerns regarding Mississippi River pollution first emerged after World War II as significant impacts to water quality began to accrue from the increased use of agricultural chemicals and continuous industrial development. As a result of manufacturing activities, accompanying waste disposal in lakes and rivers brought about a direct impact on aquatic ecosystem and a downstream impact on drinking water.

The Minnesota Pollution Control Agency (MPCA) conducted investigations on PFOS/PFOA levels in drinking water and discovered that some residential areas had exposure to PFOS (MPCA, 2008).

The toxicity of PFOS and PFOA has been studied extensively in rodents with several effects. Carcinogenic effects are not highlighted in human studies. However, in a draft risk assessment, the Environmental Protection Agency concludes evidence was suggestive that PFOA is carcinogenic in humans (EPA, 2005).

Multiple studies and research show accumulated level of PFOS and PFOA have adverse health effects from the exposure (Cui, Zhou, Liao, Fu, and Jiang, 2009). Rats were exposed to PFOS and PFOA for 28 days and observed for weight loss changes, abnormal behavior, and damage to the liver and lungs were found. Most studies have involved the analysis on fish livers as a target organ or on the blood as according to Giesey and Kennan (2001), PFOS compounds accumulate preferentially in livers rather than in muscle tissues of fish.

Fish not only represent an important food source for humans but are also environmental Bioindicators. Reports on PFC levels in edible fish have shown that PFOS are usually the dominant PFC with elevated concentration. According to the MPCA (2008), in April 2007 the MPCA found elevated concentration of PFOS in fish collected from Lake Calhoun in Minneapolis.

According to Giesey and Kennan (2001), the lack of data on fillets is a great concern due to the potential of human PFOS exposure through the consumption of contaminated fish. The existence of PFOS in the environment was deemed of such importance that the Environmental Protection Agency (EPA) launched a program where companies were required to reduce emissions and product content of PFCS (EPA, 2002).

No epidemiological studies have been carried out to assess increase in illness incidence associated to exposures to PFCS. According to (Oliaei *et al.*, 2013), PFOS and PFOA blood levels in residents affected by contaminated drinking water in the Minnesota East Metro were generally found to be higher than the general population level.

For more than 40 years, a Minnesota based company was the primary global producer of PFOS based materials. According to Oliaei *et al.* (2006), the company produced 7.33 million pounds at its plants in the United States and Europe. However, current production of PFOA and PFOS is much less as a result of regulation and companies using alternatives for this chemical. Large quantities of PFC, including PFOS containing wastes, were deposited at several sites in Minnesota. Companies began phasing out manufacturing 8-carbon chain PFC related products. The phase out process was completed by 2002 (Giesy and Kannan, 2001). By and large, the longer the carbon chain length, the longer PFCS persist in the human body. While terminating the production of eight- carbon PFOS and PFOA, it reformulated its chemistry to produce a four-carbon chain. According to Betts (2007) it takes four carbon chains 1 month to be eliminated, PFOS takes 5.4 years; therefore, levels of PFOS and PFOA representative of past discharges continue to be present.

Prior to the 2009 study, limited sampling was conducted on fish for the presence of PFOS in Pool 2. When studied, the low number of fish species and water samples had inconsistencies (MPCA, 2008). Given the uncertainties surrounding the extent of potential contaminants in the area and importance of fish in the diet of some of the region's population, a complete comparison was deemed necessary. It is possible to compare the levels in this study because it focuses on same set of fish species in one river segment.

The objectives of this study were to compare the extent of PFOS in five fish species and river water collected in 2009 and 2012 from Mississippi River Pool 2 and to examine if the chemical have declined over the years. Fish consumption advisories were issued to warn the public of possible toxicological threats from consuming certain fish species. Do the levels of PFOS observed in the species pose a risk to human consumption? To answer this, PFOS concentrations found within Pool 2 were compared to consumption advisory benchmarks. The consumption of fish may be a pathway by which Minnesota residents are exposed to PFOS. This study does not investigate human dietary exposure through fish consumption; nor does it investigate the potential source of perfluornated compounds.

Methods

Study Area

The Mississippi River (3,731 km) is the largest river in North America, flowing from its source at Lake Itasca, Minnesota USA through the center of the continental

United States to the Gulf of Mexico. The Mississippi River Pool 2 (Figure 1) stretches 33 miles through the metro corridor of Saint Paul, Minnesota (Ford Dam) to Lock and Dam 2 Hastings, Pool 2 plays a vital role in the landscape and ecosystem as well as being central to recreational activities such as fishing and swimming. According to a study published by the Upper Mississippi River Conservation Committee, close to 15 million people rely on the Mississippi River or its tributaries for daily water supply (Beaulieu, 2010). Given the high population density in the areas surrounding Pool 2 and the year round accessibility, the river is generally more vulnerable to contamination, especially with the nearby presence of industrial and commercial activities.

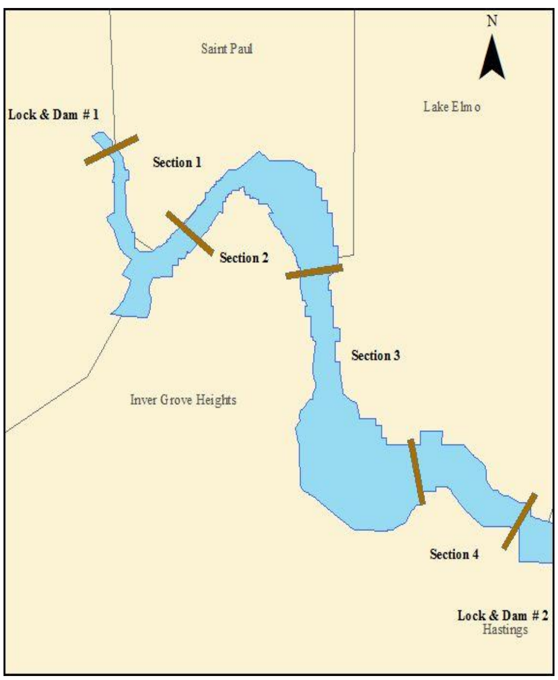

Figure 1. Mississippi River Pool 2. A 33 mile river section between Ford Dam in St. Paul and Hastings, MN.

Fish Collection

Fish were collected using electro-shocking equipment at four sections of Pool 2. As part of the MPCA study, fish species were sampled at four geographic locations to evaluate possible geographical differences. Average PFOS concentrations were compared among sections for all of Pool 2. Description of the four Pool 2 sections:

Section 1: Upper Mississippi River located between Minneapolis and Saint Paul, MN by Lock and Dam one.

Section 2: Adjacent to Holman Field north of Pigs Eye Lake.

Section 3: South of Pigs Eye Lake including Moers lake, Spring Lake and Lower Grey Cloud Area in Cottage Grove.

Section 4: Located on Mississippi River, upstream of Hastings, MN by Lock and Dam two.

Sampling locations in Pool 2 were chosen due to the proximity of known historical sources of PFCS (MPCA, 2010). Rain and high water precluded sampling in one continuous period. Thus, sampling was conducted in two rounds during 2009: July 2 and September 24; samples concluded with three rounds in 2012: May 28, 29 and June 2.

A total of 237 fish were collected by the Minnesota Department of Natural resources and the Minnesota Pollution Control Agency (MPCA, 2010). Species selected for the survey were freshwater drum, smallmouth bass, white bass, bluegill sunfish, and the common carp. These species typically have the following characteristics:

- Common edible fish caught by anglers
- Have been previously assessed
- Are of commercial and recreation value

Samples were packed in coolers separated by species, measured for length, wrapped in aluminum foil, and frozen prior to shipment for analysis by Analytical Ltd. Analytical Ltd and Minnesota Department of Natural resources assisted the MPCA staff in fish sampling procedure. However, analysis of 13 PFCS including PFOS and PFOA were performed by third party AXYS Analytical, Ltd. using liquid chromatography-electro tandem mass spectrometry LC/MS/MS (MPCA, 2010) (Table 1).

Sixty samples of each fish species for a total of 237 samples were analyzed for the 13 types of perfluorochemichals (PFOA, PFOS, PFOSA, PFBS, PFEA, and PFDA). Only data pertaining to PFOS was utilized for this study. Arithmetic mean results by species and year are summarized in (Table 2).

Table 1. PFOS in fish tissues (ng/l) for each section by year.

Species	2009				2012			
Section	1	2	3	4	1	2	3	4
Bluegill	24	41	99	260	28	27	32	98
Carp	30	16	39	224	11	11	50	438
Drum	55	49	72	739	36	21	32	347
Small Mouth Bass	40	26	49	260	30	26	26	59
White Bass	76	72	83	159	46	47	39	59

Table 2. Mean PFOS concentrations (ng/l) for each fish species and year from Pool 2.

Species	2009	2012
Bluegill	110	46
Carp	77	127
Drum	229	109
Small Mouth Bass	94	35
White Bass	97	48

Water Collection

In conjunction with the collection of the fish samples, water samples were collected on July 02, 2009 and September 24, 2012. A total of 32 water samples, 3 from each of the 12 stations were completed and analyzed for PFOS (Table 3). All water samples were collected using clean 2 liter polyethylene bottles and shipped to AXYS for analysis. All river water samples were collected below the river surface and Global Position System (GPS) was used to determine the position of samples taken. According to MPCA, Temperature, Oxygen and water depths were also collected to characterize each site.

The 2012 MPCA study was designed with the dual objective of replicating and building upon the 2009 MPCA study. The same protocols were used enabling comparisons over time.

Table 3. Mean level of PFOS (ng/l) in water by section and station.

Section	Station	2009	2012
1	1	5.11	4.99
1	2	5.06	4.86
1	3	5.05	4.91
2	4	5.05	4.94
2	5	5.03	5.06
2	6	7.71	5.01
3	7	10.3	4.92
3	8	8.51	9.84
3	9	5.08	5.42
4	10	5.03	5
4	11	90	149
4	12	15.16	24.4

Statistical Analysis

Statistical analyses were performed using SPSS Version 12. The PFOS data were normally distributed in all five species. Potential differences in PFOS concentrations between species and among water samples were tested using the Students Paired t-test with a significance level set at .05.

Software Used

Geographic Information Systems were used to map the current study. Shapefiles for Hennepin, Ramsey, Dakota, and Washington county boundaries were downloaded from the Minnesota Department of Natural Resources (MnDNR) GeoSpatial Commons website.

To accomplish goals of this study, the Statistical Package for Social Science (SPSS 12.0) was used to analyze the level of perflorochemichals. It was also used to generate descriptive statistics, charts and graphs. ArcGIS® 10.1 and Microsoft Office Spreadsheet Application Excel® were also used extensively during the work.

Results and Discussion

Fish Hypothesis

PFOS reductions between 2009 and 2012 were examined for Pool 2. A one-tailed paired data t-test was used to compute statistical significance between 2009 and 2012 as shown in (Table 4).

Table 4. Paired sample t-test.

Paired Sample Statistics					
		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	Fish09	120.65	20	164.4001	36.76098
	Fish12	73.15	20	111.9066	25.02307

Hypotheses were as follows:

Ho: Fish2012 = Fish2009
Ha: Fish2012 < Fish2009

The null hypotheses (Ho) states that there is no difference between the two population means. Ho was rejected and the alternative hypothesis that the Fish2012 population means is less than Fish2009 ($p < .05$) was supported. This is likely the result of manufacturing companies located near the Mississippi River no longer manufacturing PFOS. Since new PFOS products are being produced around compounds containing fewer carbons, potential impacts are reduced.

Water Hypothesis

A one-tailed paired data t-test was used to compute statistical significance between 2009 and 2012 as shown in Table 5.
To determine whether the level of PFOS in Pool 2 changed between 2009 and 2012, the data were compared using a paired *t*-test.

Table 5. Descriptive statistics from water samples in Mississippi River Pool 2.

Paired Sample Statistics					
		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	River09	13.9242	12	24.15917	6.97415
	River12	19.0292	12	41.31277	11.92597

Data for water in station 1 and 4 were Missing; therefore, the average was calculated for this analysis. Although the sample size does not meet the requirements of normal distribution, the paired t-test was run for the sample size (N) =12. The following hypotheses were tested:

Ho: River2012 = River2009
Ha: River 2012 > River2009

The null hypotheses (Ho) states that there is no difference between the two population means. Ho was not rejected ($p > .05$) and concluded 2009 and 2012 were not statistically different though the level was noticeably higher in 2012 water samples. This was likely influenced by the sample size being too small (N) = 12 and a larger sampling might well have shown a statistical significance.

Discussion

The purpose of this research was to determine if PFOS levels in fish and water in Mississippi River Pool 2 changed from 2009 to 2012. A paired sample t-test was used to determine whether there was a statistically significant difference between the fish species tested in 2009 and again in 2012 (Table 6). Results supported the hypothesis. The mean difference was statistically significant. Fish species collected in 2009 had higher PFOS *M* = 120.65ng/l, *SD* = 162.4) as opposed to Fish 2012 (*M*= 73.15ng/l, *SD* = 111.90).

Table 6. Paired Samples t-test at 95% confidence interval.

Paired Samples Test					
	Paired Differences				
		Mean	Std.Deviation	td. Error Mea	95% Confidence Interval of the Difference Lower
Pair 1	River09 - River12	-5.105	17.29911	4.99382	0.076
Paired Samples Test					
		95% Confidence Interval of the Difference Upper	t	df	sig. (2-tailed)
Pair 1	River09-River12	5.88633	-1.022	11	0.329

The most significant level of PFOS concentration found in fish species in 2009 and 2012 was found in the lower parts of Pool 2. These collection sites were identified along locations of various known waste discharge sites. Paired t-test results showed there was no significant difference in the mean concentration of PFOS in water between 2009 and 2012 ($p > .05$) though 2012 values were notably higher.

In this study, the inverse relationship between the increase of PFOS in water sample and the decrease of PFOS in fish sample has not been answered. However, based on statistical inferences, the level of PFOS in water increased in 2012. This may be due to unobserved variables affecting the outcome. Suspected variables might include the existence of an industrial complex historically emitted PFOS and the uptake of the diverse species sampled in the study. Due to limitations that were inherent in to data availability, more robust data is needed to reach a more refined exploration especially in the lower parts of Pool 2 where level of PFOS are found to be extremely high. Lower reaches of Pool 2 received wastewater discharges before the PFOS phase-out. It is in this area of river along where manufacturing companies exist that the numbers are noticeably higher.

Lower fish tissue concentration of PFOS was found throughout Pool 2 for all five species. The decrease in PFOS level was most apparent for the freshwater drum, which had the highest average concentration of PFOS in 2009 (i.e. 229 g/g) and 109 ng/g in 2012. This is a significant decline and is well below the 200 ng/g threshold for human consumption of one meal per week (MDH, 2009) (Figure 2).

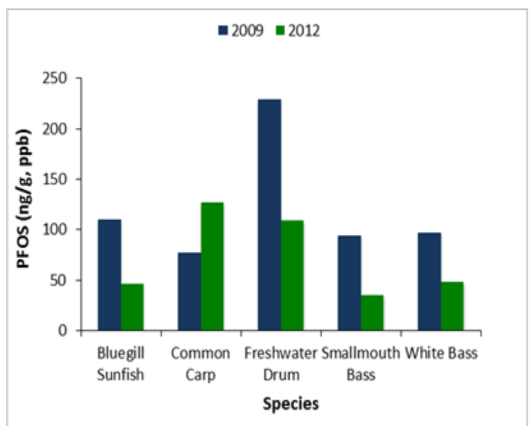

Figure 2. Comparison of average PFOS levels in Fish tissues in 2009 and 2012.

Minnesota Department of Health guidelines are presented in Table 7. It is clear to see the acceptable levels vary greatly per the frequency of consumption.

Table 7. Statewide fish consumption advisory.

Consumption	PFOS (ppb) Minnesota Department Of Health
Unrestricted	<40
1 meal/week	>40-200
1 meal/month	>200-800
Do not eat	>800

Perfluoroctane sulfonate (PFOS) is the PFC that accumulates to levels of concern in fish. Minnesota Department of Health has site specific meal advice for fish from waters where fish have been tested for PFOS. By following the state wide fish consumption advisory, People can reduce their exposure to PFOS caught in specific Minnesota Rivers such as Pool 2. As shown in Table 7, concentrations levels help provide information on fish consumption. Spacing out meals over time is the way to keep exposure to a safe level.

A variety of health effects occur in laboratory animals exposed to high doses of PFOS. According to (MDH, 2009) the health effects seen were a decrease in high density lipoprotein (HDL or good cholesterol and changes in thyroid hormone levels in some animals. PFOS concentration in Pool 2 showed an overall decrease between 2009 and 2012. The most significant level of PFOS concentration found in fish species in 2009 and 2012 was found in the lower parts of Pool 2 (section 4). The collection sites were identified along locations of various known discharge sites.

PFOS values for 2009 and 2012 were examined overall for Pool 2. A comparison of fish species within each section and all sections combined shows the PFOS concentrations for both 2009 and 2012 were generally below (100 ng/g ppb) in all sampled sections of the river except for Section 4 (Figure 3, 4, and 5).

Except for white bass, the highest concentrations for each species occurred in the southern most section of Pool 2 (Section 4) adjacent to manufacturing plants.

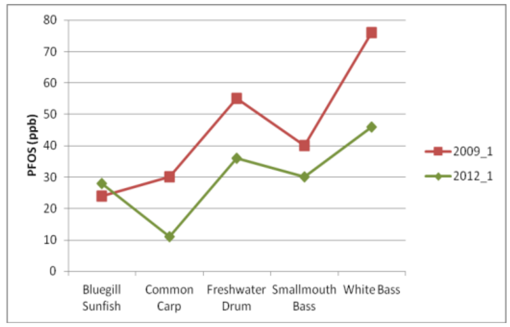

Figure 3. Section 1 distribution of PFOs by species and section.

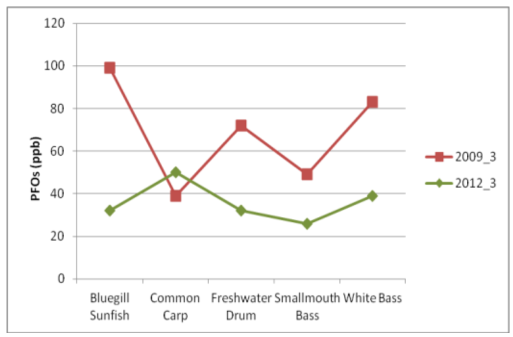

Figure 4. Section 2 distribution of PFOs by species and section.

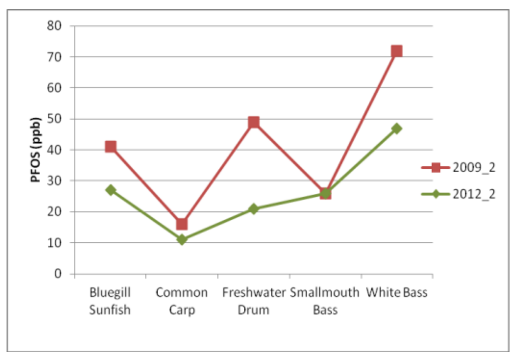

Figure 5. Section 3 distribution of PFOs by species and section.

Manufacturing plants in the study area were producing 8-Carbon PFCs. Although manufacturing plants, which discharges waste water to the Mississippi River, terminated all production of 8-carbon PFCS by the end of 2002. These flurochemichal wastes likely contributed to higher contamination in section 4 relative to 1, 2, and 3. Distribution of PFOS by species in section 4 (most downstream area) indicates level of PFOS substantially greater than 200 ng/g. For fish fillets with PFOS concentrations in the range 200-800 ng/g ppb), the advice is one meal per month (MDH, 2009).

White bass PFOs distributions remain relatively similar from section 1 to 3 and the ranges of PFOS concentrations are lower in white bass in comparison to other species. White bass are predators; they are prone to travel long distances and have limited home ranges. Unlike most bottom feeders, white bass do not obtain their food from the bottom of the water source, which they reside in. They can be found throughout the water column and are good indicator of PFC contamination (MDNR, 2015). This may help explain why white bass had relatively constant PFOS levels.

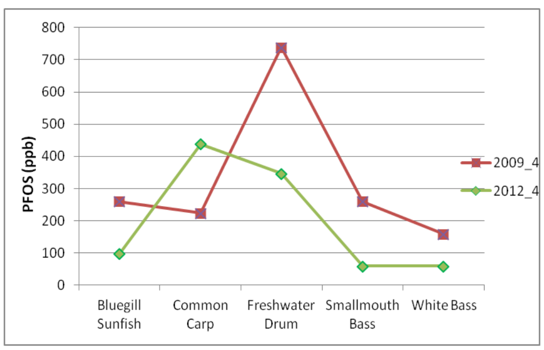

Figure 6. Section 4 distribution of PFOs by species and section.

2012 results indicate an overall reduction in PFOS levels in fish tissue for the four of the five species sampled in Pool 2. Only carp showed an increase in the mean PFOS concentration (Figures 4 and 6). The overall increase in carp in the study is greatly impacted by the higher readings noted for carp in section 4. Common carp are a large omnivorous fish that live in a variety of habitats and are noted for their tolerance to pollution. Common carp are generally found closer to the bottom of the water and likely accumulate PFC contaminants from direct physical contact with contaminated sediment or by consuming benthic invertebrates such worms, insects and crawfish that live in contaminated sediments (Nico, Maynard, Schofield, Cannister, Larson, Fusaro, and Neilson, 2012).

The overall trend for all fish species is very similar except for freshwater drum. Freshwater drum PFOS levels in 2009 for all sections were extremely high. Freshwater drum is a bottom feeder that eats mollusks, insects and fish. It prefers clear water, but it is tolerant of turbid conditions (Fuller, 2015). For bottom feeders such as freshwater drum, sediment may pose a more significant source of PFCS.

2012 data for freshwater drum indicates PFOS concentrations are generally below100 ng/g ppb) and the less variation for freshwater drum within this area indicate greater confidence that exposures have decreased in this area.

In general, by comparing the distribution of PFOS by species and section for 2009 and 2012, there were less PFOS in 2012. Comparison of fish species within each section shows that the PFOS concentrations were generally below 100 ng/g (ppb) except for section 4. Results suggest individuals who consume fish caught in (section 4) maybe exposed to higher level of PFOS.

Conclusions

PFCS have a number of beneficial uses in industrial, commercial, and consumer products due to their ability to repel both water and oil, and are resistant to breakdown. However these same properties also contribute to their persistence, toxicity, and ability to travel long distances and to bioaccumulate in animal and humans.

Results suggest the level of PFOS in Pool 2 of the Upper Mississippi River fish species have declined. Results of PFOS found in water increased in 2012 and does not support the initial hypothesis. This may be due to the sample size being too small and the existence of production plant by the river with waste water discharges may have influenced results.

Levels of PFOS in water and fish were highest in section 4. Section 4 is the most downstream section of Pool 2. These findings should help Minnesota residents better understand the extent of PFOS levels in fish and water, and determine areas of focus for future sample collections. Additional studies with more data would be encouraging, particularly in the lower parts of Pool 2 where concentrations were high; it would be helpful to explore and monitor current levels of PFOS.

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