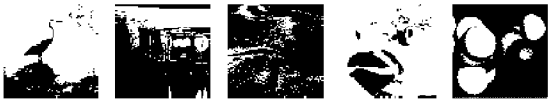

Review of PFOS Impairment in Mississippi River Pool 2

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1 Executive Summary

In March 2010, MPCA published a study investigating perfluorinated compounds (PFCs) in fish tissue and surface water in Pool 2 of the Mississippi River (MPCA, 2010). Minnesota Department of Health (MDH) issued a fish consumption (freshwater drum) advisory based on concentrations of perfluorooctane sulfonate (PFOS) in fish tissue documented in the study. Minnesota Pollution Control Agency (MPCA), in response, classified the 33-mile stretch of Pool 2 as impaired on its Clean Water Act Section 303(d) list of impaired waters. In order to address that impairment, MPCA has indicated that it is considering an approach that could ultimately include a numeric PFOS limitation in the National Pollutant Discharge Elimination System (NPDES) permit for the Metropolitan Council's Metropolitan Wastewater Treatment Plant (Metro WWTP), which discharges into Pool 2.

On behalf of Metropolitan Council, ENVIRON International Corporation (ENVIRON) reviewed the MPCA (2010) study and evaluated the initial permitting approach discussed with MPCA for the Metro WWTP. This review was conducted in light of MPCA (2010) Pool 2 data, additional publicly-available Pool 2 data, as well as the state-of-the-science with respect to PFOS ecotoxicology, environmental chemistry, and risk assessment.

As a result of the review and analysis, ENVIRON made the following key findings:

1. **Actual fish tissue PFOS impairment is limited to Section 4 in Pool 2.** The only area that exhibits impairment is Section 4, the most downstream study section of Pool 2 in the MPCA (2010) study. Over 99% of the 222 fish sampled in Sections 1, 2 and 3 are below the level indicative of impairment and are several orders of magnitude lower than concentrations in many of the Section 4 fish.
2. **A localized PFOS source within Section 4 is responsible for impairment.** Available sediment and water data from MPCA and other publicly available reports, as well as site-specific PFOS fish bioaccumulation modeling, indicates that localized conditions within Section 4 are responsible for the impairment.
3. **MPCA's proposed permit-based management response to PFOS in Pool 2 fish is not supported by the data.** Multiple lines of evidence indicate that the source of the observed PFOS impairment is limited to local sources within Section 4 and is not associated with Metro WWTP. First, the proposed MPCA approach focuses on surface water discharges and does not address PFOS present in sediment, which accounts for the majority of PFOS exposure to fish, as indicated by modeling. Second, the approach is inconsistent with the MDH fish tissue advisory level used to trigger environmental concerns. Third, addressing Metro WWTP through this approach will not be effective in removing the condition of impairment.

2 Introduction

In March 2010, the Minnesota Pollution Control Agency (MPCA) released a study of perfluorinated compounds (PFCs) in fish tissue and surface water in Mississippi River Pool 2 (MPCA 2010). Average concentrations of perfluorooctane sulfonate (PFOS) in fish tissue were evaluated by comparison to the Minnesota Department of Health (MDH) fish tissue advisory level derived to be protective of a one meal per week consumption rate, a value of 200 ng/g [1]. One of the five species of fish sampled (freshwater drum) exhibited an average PFOS tissue concentration greater than the MDH fish tissue advisory level, and MDH subsequently issued a fish consumption advisory for Pool 2. Based on the fish consumption advisory, Pool 2 was listed as "impaired" under 303(d) of the Clean Water Act. Based on this finding, MPCA proceeded with initial permit-based management actions for Metropolitan Council's Metropolitan (Metro) WWTP, which discharges to Pool 2.

On behalf of Metropolitan Council, ENVIRON International Corporation (ENVIRON) reviewed the MPCA (2010) study and evaluated the initial permitting approach discussed with MPCA for the Metro WWTP. This review was conducted in light of additional publicly-available PFOS chemistry data in Pool 2 surface sediment and water, as well as the state-of-the-science with respect to PFOS ecotoxicology, environmental chemistry, and risk assessment. The remainder of this report presents the synopsis of this review, and is organized into the following sections:

- Section 3: Review and Synthesis of Pool 2 PFOS Data
- Section 4: Considerations for PFOS Environmental Fate
- Section 5: Science-based Alternative Decision Making to Define and Address PFOS Impairment in Pool 2
- Section 6: Conclusions
- Section 7: References

[1] Concentrations of PFOS in fish tissue in the main text of this document are expressed on a nanograms PFOS per gram wet weight tissue basis.

3 Review and Synthesis of Pool 2 PFOS Data

This section presents a review and synthesis of publicly-available PFOS environmental data in Pool 2. Three primary environmental data sources were reviewed to understand the nature of PFOS in environmental compartments which are potentially-relevant to impairment in the Pool 2 aquatic environment:

1. Concentrations of PFOS in Pool 2 fish and water measured by MPCA (2010);
2. Concentrations of PFOS in Pool 2 sediment and water measured by MPCA (2006); and
3. Concentrations of PFOS in Mississippi River sediment and water near 3M Cottage Grove measured by Weston (2007, 2008, 2009).

Although the laboratory analytical techniques for PFCs during the time period of these studies were evolving and currently continue to improve (Malinsky, 2009 ; van Leeuwen et al., 2009), it was assumed that concentrations of PFOS in fish, surface sediment, and water among the studies were comparable such that a synthesis of the data from these studies would provide insight into the presence and behavior of PFOS in Pool 2 fish, surface water, and sediment.

3.1 Review of Concentrations of PFOS in Fish Sampled in the MPCA (2010) Pool 2 Study

3.1.1 MPCA (2010) Study Design

MPCA divided Pool 2 into four sections of varying lengths for their investigation of PFOS in fish and surface water (Figure 1): Section 1 (3.6 river miles) is the upper most section, Section 2 (9.5 river miles) receives discharge from Metropolitan Council's Metro WWTP, Section 3 (13.7 river miles), and Section 4 (4.7 river miles) at the lower end, which receives discharge from 3M's Cottage Grove Facility (3M Cottage Grove). In May 2009, Minnesota Department of Natural Resources (MDNR), on behalf of MPCA, collected five fish species from all sections: bluegill sunfish, carp, freshwater drum, smallmouth bass, and white bass. For each species, MDNR collected 15 fish per section for a total of 75 fish per section with the exception of bluegill sunfish in Section 1, where 12 fish were collected (72 fish for Section 1). In total, 297 fish samples were collected from Pool 2. MDNR also collected water samples from 12 stations (3 different collection sites within each section, 3 samples at each site). Water samples and 30 of the fish samples were concurrently analyzed by both the contracted lab and 3M as part of the quality assurance program.

3.1.2 Concentrations of PFOS in Fish Observed by MPCA (2010)

Average and 90th percentile concentrations[2] of PFOS in fish tissue were below the MDH fish tissue advisory level of 200 ng/g for all species of fish in Sections 1, 2 and 3 (Figures 2-4). Over 99% of the 222 fish sampled in Sections 1, 2 and 3 were below 200 ng/g. All fish in Sections 1 and 2 were below 200 ng/g. Only two fish samples were in excess of 200 ng/g in Section 3.

[2] 90th percentile values are conservative statistics that represent the extreme upper ranges for evaluating concentrations of PFOS in fish consumed by anglers, and are provided here for discussion purposes only. Using 90th percentile values in consideration of human health risks and/or fish tissue advisories would greatly overestimate typical exposures to PFOS.

These two fish were a male and a juvenile bluegill sunfish (204 and 201 ng/g, respectively). These fish were captured between river miles 833.5 and 834, which falls in the lower portion of Section 2 but were grouped with Section 3 samples by MPCA (MPCA 2010) as shown in Figure 4. The range of PFOS concentration for bluegill sunfish in this Section is 34 to 204 ng/g and the 90th percentile is 183 ng/g, suggesting that these two fish are outliers for the Section 3 sample grouping. The two exceedances of the 200 ng/g fish tissue advisory level represent only 0.9% of the fish sampled in Sections 1, 2 and 3. Concentrations of PFOS in fish in Sections 1, 2 and 3 do not exceed the MDH fish tissue advisory level. Data would not result in a MDH fish consumption advisory if this Sections 1, 2 and 3 had been addressed separately from Section 4 (either collectively as a combined Sections 1, 2 and 3 group or separately by section). The data demonstrates a clear absence of impairment in Sections 1, 2 and 3 of Pool 2.

Concentrations of PFOS in many of the fish from Section 4 were 1 to 2 orders of magnitude higher (i.e., approximately 10 to 100 times higher) than those in Sections 1, 2 and 3. Average concentrations of PFOS in four species of fish collected in Section 4 exceeded the 200 ng/g fish tissue advisory level (Figure 5). The average concentration of PFOS in white bass, 160 ng/g, was below the fish tissue advisory concentration. For all species, 90th percentile concentrations of PFOS in fish were greater than the fish tissue advisory level in Section 4, whereas in Sections 1, 2 and 3, all 90th percentile values were below the advisory level (Figure 6).

Within Section 4, data review indicates that it is possible that only a subset of fish exhibit elevated concentrations of PFOS. Only 36% of the sampled fish (27 of 75) exceeded the 200 ng/g fish tissue advisory level. The remainder of the fish exhibited concentrations of PFOS similar to that of Sections 1, 2 and 3, with an average concentration of 75 ng/g (standard deviation of 44 ng/g and median of 65 ng/g). The high standard deviations shown in the chart in Figure 5 and large range of values for Section 4 fish suggest that two populations of fish within Section 4 were sampled: one population of fish with a greatly elevated exposure to PFOS and one population of fish with a much lower exposure similar to that of fish in Sections 1, 2 and 3.

It should be noted that concentrations of PFOS in fish as close as 2 to 7 river miles downstream of Metro WWTP (Section 3 fish grouping, shown in Figure 4) do not indicate impairment. Average and 90th percentile values for concentrations of PFOS in fish (by species or all species combined) are below 200 ng/g. If the MDH fish consumption criteria were applied to sections of Pool 2, as opposed to the entirety of Pool 2, the data in Sections 1, 2 and 3 would not trigger a fish consumption advisory. Using the logic that PFOS exposure to fish from a particular point of discharge decreases with distance from the discharge point, fish tissue values support the hypothesis that PFOS released by Metro WWTP is not responsible for the high concentrations of PFOS in fish (impairment) observed in fish in Section 4. This hypothesis is confirmed by measured concentrations of PFOS in fish, surface water, and sediment (Section 3.2).

3.1.3 MPCA (2010) Data Analysis Approach

Taking into consideration the location of the fish that exceed the MDH advisory level, it is technically invalid to average the concentrations of PFOS in all Pool 2 fish samples. Based on the above discussion, the entire 33-mile length of the river should not be treated as a homogeneous unit for evaluating exposure to PFOS via consumption of fish, as concentrations of PFOS in Pool 2 fish are not at steady state. There is a large discrepancy between values for

a portion of the Section 4 fish compared to other fish in Sections 1, 2, 3 and the remainder of 4. Simple averages that include all samples from all four Sections of Pool 2 are skewed high by outliers of extremely high PFOS tissue concentrations from a portion of the fish obtained from Section 4.

The MPCA data analyses, which combined data from all fish samples from Pool 2 into a single average by species, do not yield representative values with which to address the impairment concerns associated with the consumption of wild fish caught throughout the Pool 2. For example, the Pool 2 average concentration for freshwater drum (229 ng/g; based on 60 samples in Sections 1, 2, 3 and 4) used to identify Pool 2 impairment status by MPCA (2010) does not accurately characterize human exposure to PFOS via fish consumption across the entirety of Pool 2. This average represents a gross overestimate of PFOS exposure for all of Pool 2 except for Section 4, where it may be an underestimate. More specifically, the average concentration of PFOS in freshwater drum in Sections 1, 2, and 3 is 59 ng/g (maximum of 139 ng/g); these values are not indicative of impairment and are not comparable to the Pool 2 average of 229 ng/g. Alternately, the average concentration of PFOS in freshwater drum in Section 4 is 740 ng/g (maximum of 3,600 ng/g), which is also not comparable to the Pool 2 average of 229 ng/g. The data indicate that only a portion of fish in Section 4 exhibit concentrations of PFOS which are indicative of impairment. As discussed in Section 5 of this document, the consequences of using the unrepresentative Pool 2 average fish tissue values in subsequent bioaccumulation factor (BAF) and fish consumption criterion (fCC) calculations leads to a conclusion that all of Pool 2 is impaired and needs to be addressed to be protective of human health. These conclusions are technically flawed, as they are not supported by the data and the current understanding of PFOS environmental fate.

3.2 Review of Concentrations of PFOS in Water and Surface Sediment Sampled in the MPCA and Weston Studies

3.2.1 Concentrations of PFOS in Water and Surface Sediment

Although fish sampling locations in the MPCA (2010) study are not sufficiently precise to evaluate the correlation of concentrations of PFOS in fish with concentrations of PFOS in water and/or sediment, data collected by MPCA and Weston indicate that concentrations of PFOS in water and sediment along the northern shoreline of Section 4 (adjacent to 3M Cottage Grove) are likely the source of the high concentrations of PFOS in Section 4 fish. Concentrations of PFOS in Pool 2 surface sediment and water are relatively low and uniform upstream of the 3M Cottage Grove Facility (Figures 7 and 8). Average concentrations in surface sediment and water samples collected near the 3M Cottage Grove shoreline (10 ng/g [3] and 88 ng/L [4], respectively) are 1 to 2 orders of magnitude higher than those upstream (0.7 ng/g and 4.5 ng/L, respectively), as shown in Figures 7 and 8. The upper ranges of the values also reflect this pattern: the concentrations in sediment and water upstream of 3M Cottage Grove (Sections 1, 2, 3 and a portion of 4) range from < 0.25 to 1.3 ng/g and < 5 to 10 ng/L, respectively, whereas

[3] Concentrations of PFOS in bulk sediment in the main text of this document are expressed on a nanograms PFOS per gram dry weight sediment basis.
[4] Concentrations of PFOS in WATER in the main text of this document are expressed on a nanograms PFOS per liter water basis

concentrations in sediment and water along the 3M Cottage Grove shoreline are as high as 220 ng/g and 530 ng/L, respectively.

The co-location of high concentrations of PFOS in surface sediment and water in Section 4 with 3M Cottage Grove indicates significant local contributions of PFOS to Pool 2. Soils and groundwater at 3M Cottage Grove are contaminated with PFOS to concentrations that are up to several orders of magnitude higher than concentrations observed in Pool 2 surface sediment and water. The Weston studies (Weston 2007, 2008, 2009) characterized the spatial resolution in substantial detail and concluded that ground water is a pathway for PFOS transport to Pool 2 from 3M Cottage Grove (Figures 9 and 10). Concentrations of PFOS in surface sediment and water increase substantially (relative to samples collected in upstream areas in Sections 1, 2, 3 and 4) at approximately the midpoint along the 3M Cottage Grove shoreline. At this location, concentrations in Pool 2 surface sediment concentrations increase to 27 ng/g (Figures 9) and concentrations in Pool 2 surface water increase to 172.5 ng/L (Figure 10). Concentrations in both surface sediment and water are elevated from this point proceeding downstream (eastward) along the 3M Cottage Grove shoreline. This area was noted by Weston (2007) as an area of uncontrolled groundwater movement from beneath 3M Cottage Grove into Pool 2 and represents a significant environmental pathway of 3M Cottage Grove PFOS to Pool 2.

The presence of elevated concentrations of PFOS in sediment and water near the nexus of East Cove and Section 4 of Pool 2 reveals a significant environmental pathway of 3M Cottage Grove PFOS to Pool 2. A MPCA (2006) study estimated that over a period of several decades, 3M Cottage Grove may have released approximately 50,000 lbs/year of PFCs to Pool 2, with recent estimates (circa 2006) of 3,500 lbs/year[5]. For example, concentrations of PFOS in water in 3M's East Cove (a small waterbody on 3M property that drains to Pool 2) are up to 5,600 higher than average concentrations in water upstream of 3M Cottage Grove. Also, concentrations of PFOS in surface sediment in 3M's East Cove are up to 1,600 times higher than average concentrations in surface sediment upstream of 3M Cottage Grove. East Cove has been and continues to be a receptacle for 3M Cottage Grove's NPDES-permitted discharges from the plant's wastewater treatment and cooling water system, with direct discharge to Section 4 of Pool 2 (Weston, 2007).

The influence of 3M Cottage Grove PFOS sources appears to extend to at least the farthest downstream sample collection stations for surface sediment and water in Pool 2, located approximately 1.5 miles downstream of the nexus of East Cove and the Mississippi River, just upstream from Lock and Dam Number 2 (the downstream boundary of Pool 2). A sample collected at a location approximately 1,500 feet downstream of the nexus exhibited concentrations of PFOS in water and sediment 9-22 times higher than average upstream concentrations, and indicates elevated levels of PFOS extending beyond the cluster of Weston samples collected in the immediate vicinity of the 3M Cottage Grove shoreline. Average concentrations of PFOS in surface sediment and water samples collected much farther downstream of 3M Cottage Grove (approximately 1.5 miles) were 4.9 ng/g and 27 ng/L, approximately 7 times higher than average values observed upstream of 3M Cottage Grove

[5] In contrast, the same report suggested Metro WWTP accounted for 123 lbs/year discharge, although the calculation is based on extremely limited PFC chemistry data.

(Figures 7 and 8). Concentrations of PFOS in surface sediment just upstream of Lock and Dam Number 2 (Figure 7) range from 0.6 to 2.6 ng/g, slightly higher than the range of values for samples upstream of Cottage Grove (< 0.25 to 1.3 ng/g). Concentrations in water are slightly elevated as well, as shown by a sample reporting a concentration of 10 ng/L (Figure 8) in the MPCA (2010) study. The remaining five samples had higher detection limits (50 ng/L), yielding inconclusive results.

Concentrations of PFOS in water and sediment indicate that Metro WWTP is not responsible for the high concentrations of PFOS in sediment and water observed in Section 4. Concentrations in water 2-7 miles downstream of Metro WWTP range from 8 to 10 ng/L (Figure 4), which is higher than results upstream of Metro of < 5 ng/L (Figures 2 and 3). This pattern of results suggests that Metro WWTP or another source of PFOS may be releasing PFOS mass at a rate sufficient to result in a slight elevation of the concentration of PFOS in Pool 2 water. This slight elevation of PFOS in Pool 2 water appears to be localized to this portion of Pool 2, as concentrations of PFOS in water further downstream are below detection limits (< 5 ng/L in upper Section 4, as shown in Figure 5). These data indicate attenuation of the slightly elevated PFOS concentrations observed 2-7 miles downstream of Metro WWTP to levels below the detection limit (< 5 ng/L). Thus, the data indicate that PFOS released from Metro WWTP attenuated with distance downstream, assuming it comprised a portion of the water samples bearing detectable concentrations of PFOS. The order of magnitude higher concentration of PFOS in water observed in middle and lower portions of Section 4 (e.g., as high as 530 ng/L, Figure 10) are not attributable to Metro WWTP.

Although sediment data are more limited, concentrations of PFOS in Pool 2 surface sediment samples also indicate that elevated levels of PFOS in Section 4 surface sediment are not attributable to Metro WWTP. It is possible that Metro PFOS contributes to the PFOS in Pool 2 sediment via the settling out of WWTP effluent suspended solids containing PFOS, as well as the partitioning of PFOS from Metro WWTP effluent to sediment. If this were occurring, however, a concentration gradient would be observed, with sediment nearest Metro WWTP exhibiting concentrations that are greater than sediments downstream. This would be expected to occur because suspended solids would tend to deposit nearer to the Metro WWTP discharge point. Also, PFOS released in the water column would tend to partition to sediments closer to the outfall because the highest concentrations of PFOS in surface water would occur in the effluent-river mixing zone. The nearest surface sediment samples downstream of Metro WWTP are located in the lower portion of Section 3, 11-13 miles downstream of Metro WWTP (2 farthest upstream samples shown in Figure 7). Concentrations in these samples are lower (< 0.25 and 0.5 ng/g) than samples farther downstream of Metro WWTP, which were collected in the upper portion of Section 4 upstream of 3M Cottage Grove. There is no concentration gradient present in these samples (0.3 to 1.6 ng/g) that would support a conclusion that Metro WWTP is a source or causative factor in Section 4 impairment. That is, if PFOS released from Metro WWTP represented a significant source to sediment in this area, concentrations in the upper portion of Section 4 would be less than concentrations in the lower portion of Section 3 because some attenuation would be expected between these locations. Additionally, the overall range of all of the lower Section 3 and upper Section 4 samples (< 0.25 to 1.6 ng/g) is much lower than the concentrations of PFOS in sediment adjacent to the 3M Cottage Grove shoreline (Figure 9), which are as high as 220 ng/g. It is not valid to attribute the extremely high

concentrations in the 3M Cottage Grove shoreline sediment to Metro WWTP since these sediments exhibit concentrations that are much higher than sediments closer to Metro WWTP.

Additionally, the range of concentrations of PFOS in Pool 2 sediment observed downstream of Metro WWTP is reflective of the range of concentrations of PFOS in sediment that may be attributable to ambient, non-point watershed PFOS sources. MPCA observed an average (SD) concentration of 0.84 (0.58) ng/g in sediment from stormwater collection ponds in the Minneapolis/St. Paul metropolitan area, with sampling locations within the Pool 2 watershed (MPCA-Crane & Hennes, 2010). These stormwater ponds receive a stormwater from a wide variety of industrial and non-industrial sources and indicate PFOS is present in stormwater at a concentration sufficient to result in the accumulation of PFOS in sediment at concentrations as high as approximately 1-2 ng/g. Thus, the concentrations the lower Section 3 and upper Section 4 samples (< 0.25 to 1.6 ng/g) are similar to that observed in the stormwater pond sediment, indicating that PFOS in this location represents PFOS associated with watershed sources.

In addition to the absence of Metro WWTP contributions to the impairment observed in Section 4, PFOS data in fish and water indicates Metro WWTP does not cause impairment in the nearest fish and water sampling locations 2 to 7 miles downstream of Metro WWTP. As discussed in Section 3.1.1 and shown in Figure 4, concentrations of PFOS in fish this area (Section 3) are below levels associated with impairment. Concentrations of water (8 to 10 ng/L) and sediment (unknown due to lack of samples) are clearly below levels required to cause elevated concentrations of PFOS in fish.

3.2.2 Spatial Relationships between PFOS in Water and Surface Sediment to PFOS in Fish

Elevated concentrations of PFOS in sediment and water in a portion of Section 4 are likely to result in a higher localized exposure of PFOS to fish. Qualitatively, higher concentrations in sediment and water in these areas explain higher concentrations of PFOS in a portion of the Section 4 fish samples. The spatial co-occurrence of elevated concentrations of PFOS in surface sediment and water correspond with the observation that concentrations of PFOS in a portion of Section 4 fish are an order of magnitude higher than the majority of fish sampled in the study.

The spatial and statistical pattern of fish, sediment, and water PFOS data can be explained by either: 1) fish caught in Sections 1, 2 and 3 are lower because their spatial ranges of movement (home ranges) do not include areas of elevated PFOS exposure in Section 4; or 2) fish caught in Sections 1, 2 and 3 include some fish that may have been exposed to Section 4, but concentrations of PFOS have decreased following their movement to the less contaminated study sections. Either possibility, or a combination, is possible. For example, four of the five studies fish species, freshwater drum, bluegill sunfish, smallmouth bass and carp have relatively small home ranges (~30 – 900 meters^2; Minns, 1995; Parr, 2002; Jones and Stuart, 2008); nearly all fish sampled within each of the MPCA (2010) study sections were likely exposed to PFOS sources within that study section. For example, it is extremely unlikely given the spatial scales associated with the above estimates that the movement range of the fish sampled in Section 4 includes the stretch of Section 2 containing the Metro WWTP discharge location,

approximately 24,000 meters (approximately 16 miles) upstream. Concentrations of PFOS in most fish reflect local PFOS exposures on a spatial scale much smaller than that of the MPCA (2010) study sections.

In contrast, white bass may move as far as 40 river miles (Morgan, 2006), suggesting that PFOS exposure in white bass could be derived from more than one study section across the 33-mile length of Pool 2. The data corroborate this hypothesis, as concentrations of PFOS in white bass exhibit the least variation and most comparability among the four study sections (Figures 2-6). The difference in the lowest and highest average concentrations among the study sections is only two-fold, indicating a relative amount of homogeneity in the exposure of white bass to PFOS in Pool 2. In comparison, the difference between the lowest average concentrations of PFOS in freshwater drum (Section 2) is 15 times lower than that of the average concentration in Section 4. A simple averaging of all Pool 2 white bass makes the most sense for any of the species sampled by MPCA; however, the validity of this approach remains unclear given that concentrations of PFOS in white bass in Section 4 were still higher than those in other Sections, suggesting that a possible localized elevated PFOS exposure within Section 4 could be elevating concentrations in a portion of the Section 4 white bass.

Fish movement is variable and site-specific, and is best quantified by individual studies on the local fish populations of interest. For example, a study conducted in Missouri streams by Funk (1957) revealed that approximately half of a sample population of 11 freshwater drum moved 10 miles or more during a period of approximately a year. If a minimum annual movement range of 10 miles is assumed for Pool 2 freshwater drum, it is conceivable that a substantial portion of freshwater drum would be exposed to more than one study section over a one-year time period since the length of the study sections are approximately 4 to 14 miles in length. Thus, fish body burden of PFOS accumulated in one Section would cross Section lines as the fish migrated. Fish collected in a study section would represent PFOS exposure conditions from more than one study section (as hypothesized above for white bass). Under this hypothetical scenario, concentrations of PFOS in fish would be expected to be uniform among the study sections (as in the actual white bass dataset), even if there was a single area of elevated PFOS exposure within one of the study sections. With exposure averaging across larger areas, the MPCA assumption of a homogeneous exposure unit (and practice of averaging samples from more than one study section) would be supported by the data. However, the robust MPCA (2010) study of 297 fish samples does not support this hypothesis due to the extremely elevated concentrations of PFOS in Section 4 fish, as illustrated in Figures 2-6.

A more likely explanation for the discrepancy among concentrations of PFOS in fish among the MPCA (2010) study sections (if large home ranges are assumed) lies in the time scales for PFOS uptake and elimination in fish. Is it likely that PFOS accumulated by fish in an area with elevated PFOS exposure conditions is eliminated during movement to a less contaminated area. For example, fish exposed to an elevated PFOS point source within Section 4 would accumulate PFOS to concentrations much higher than those in other study sections, but, upon moving to other sections, would eliminate PFOS from tissue to maintain steady state with lower PFOS concentrations in sediment, water, and diet. This time scale for elimination is supported by a bioaccumulation study in fish where fish were exposed to PFOS-contaminated water, then moved to clean water (Martin et al., 2003). Results indicated that the half-life for PFOS

measured was approximately 2-3 weeks (13 days for carcass and 20 days for liver; Martin et al., 2003a). According to the study results, concentrations in fish would decrease to reach steady state (decreasing or increasing) within a few weeks upon moving to areas with different PFOS exposures. Although this hypothesis enables a consideration for very far fish movements (e.g., miles), it requires the presence of a source of elevated PFOS exposure to fish within Section 4 to elicit the observed pattern of greatly different concentrations between Section 4 and the remainder of Pool 2. It provides additional justification that impairment (i.e., fish exhibiting concentrations of PFOS greater than 200 ng/g) would be limited to an area near this elevated exposure source, as concentrations in fish tissue would decrease as the fish migrate to less contaminated sections of Pool 2.

4 Considerations for PFOS Environmental Fate

This section presents a state-of-the-science review for PFOS behavior in aquatic ecosystems and includes an application of quantitative fate and bioaccumulation modeling to understand the exposure of fish to PFOS in Pool 2.

4.1 State-of-the-Science Review

The behavior of PFOS and other PFCs does not follow the general scientific paradigm for the chemical behavior or fate of bioaccumulative organic compounds. Most bioaccumulative compounds are hydrophobic, strongly attracted to organic carbon in sediment and lipids within aquatic organisms after release to aquatic environments. The behavior of these compounds has been numerically predicted by models relying on a physical chemical property known as the octanol-water partition coefficient (K_{OW}; Gobas, 1993; Arnot and Gobas, 2003; Gobas et al., 2003). For a large proportion of modern organic compounds, scientists and policy makers take advantage of the existing paradigm (using K_{OW}) to predict chemical fate such that environmental risks can be more efficiently and effectively managed (Muir and Howard, 2006).

K_{OW} values for PFCs are difficult to measure because they possess surfactant properties that interfere with the measurement of K_{OW}, making evaluation with the existing paradigm not feasible (Tolls et al., 1994; Giesy and Kannan, 2002). Coupled with the initial analytical difficulty in measuring PFCs in environmental samples and the inability to fully evaluate fate, the bioaccumulative potential of these compounds went largely untested until the early 2000s, when field research revealed that many of the compounds were present in organisms at concentrations exceeding those in abiotic environmental media such as water, soil, and sediment (Giesy and Kannan, 2001). PFCs were soon found to behave differently than most bioaccumulative organic compounds, as they were found to be strongly attracted to proteins (rather than lipids) in organisms (Conder et al., 2008). Controlled laboratory experiments confirmed that chemical fate (and bioaccumulation) of PFCs could not be predicted using the general K_{OW}-based approaches used for other bioaccumulative chemicals (Martin et al., 2003a; Martin et al., 2003b). Through several field experiments, PFOS was determined to bioaccumulate to concentrations in tissue several orders of magnitude higher than concentrations in water (Conder et al., 2008).

As environmental chemists and toxicologists adapt or create a new paradigm to understand PFCs, the existing K_{OW}-based approach is not directly applicable, necessitating that the understanding of PFOS fate be built "from scratch" using data from empirical field and laboratory studies and newly-derived models. Despite its use for several decades, the field of environmental chemistry and toxicology is only just beginning to understand PFOS chemical fate, bioaccumulation, and sources to watersheds. Nakayama et al. (2010) in the May 27, 2010 issue of the environmental chemistry journal *Environmental Science & Technology* stated "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."

Aside from the lack of a basic scientific paradigm, a primary issue limiting understanding of PFOS is that acceptable analytical laboratory performance approaching a level comparable to that of other major chemicals of concern has been attained only in the past two to three years (van Leeuwen et al., 2009; Malinsky, 2009). The limited number of field studies prior to this time

are difficult to interpret and compare, making the development of fate theory extremely difficult. Recent field studies are few, with only a handful of studies on PFOS fate and sources in rivers and streams (Becker et al., 2008a; Becker et al., 2008b; Zushi et al., 2008; Nakayama et al., 2010). As with the cutting edge of most scientific issues, these papers often raise as many (or more) questions than they resolve, and many of the studies are focused more on understanding environmental levels rather than gaining advanced understanding of chemical fate mechanisms. For example, none of these studies examine quantitative relationships between PFOS sources, abiotic environmental compartments (e.g., sediment, carbon, surface water), and aquatic organisms.

4.2 Role of Sediment in Aquatic Fate of PFOS

A consistent narrative is beginning to emerge from the available field and laboratory studies: sediment is an important environmental compartment influencing the accumulation of PFOS in aquatic organisms. Controlled laboratory studies have documented that PFOS is attracted to organic carbon (OC) in aquatic sediments, with partition coefficients of approximately 400 L/kg OC, dry weight (Higgins et al., 2006). Ahrens et al. (2009) observed much higher OC partition coefficients (approximately 10x higher) than that observed by Higgins et al. (2006) using sediment and sediment pore water from field collected sediment in Tokyo Bay. Results clearly document that organic carbon in sediments has a significant capacity to adsorb PFOS.

Simple relationships between concentrations of PFOS in water and sediment also confirm that sediment is a key source and/or sink for PFOS in aquatic systems. Becker et al. (2008) observed that concentrations of PFOS in surface sediment were approximately 20 to 40 times higher than concentrations in surface water in the Roter River (Germany), and Lin (2010) reported concentrations in sediment were 16-26 times higher than water in the Nanmen River (Taiwan). Other studies have reported much higher ratios. Concentrations in sediment were observed to be an average of 220 times higher than that of water in 21 major lakes, rivers, and canals in the Netherlands (Kwadijk et al., 2010). Surface water and surface sediment data collected upstream, near, and downstream of the 3M Cottage Grove facility in Section 4 of Pool 2 reveal that average concentrations in sediment are two orders of magnitude (100-200 times) higher that of water (MPCA, 2006; Weston, 2007; Weston, 2008; Weston, 2009). On a total mass basis alone, sediment-associated PFOS in aquatic systems is likely to be a significant portion of the total PFOS in aquatic systems, and especially in Pool 2, and cannot be overlooked in terms of environmental management.

4.3 Relevance of Sediment-associated PFOS to Pool 2 Fish

A significant pathway for sediment-associated PFOS to enter aquatic food webs is via bioaccumulation in benthic invertebrates that are consumed by fish and other organisms. Laboratory studies have confirmed that sediment-associated PFOS bioaccumulates in benthic invertebrates, with a Biota-Sediment Accumulation Factor (BSAF) of 1.22 g, OC/g (Higgins et al., 2007). In the field, consumption of PFOS in benthic invertebrates by benthivorous fish may be an important exposure pathway. Although field studies have not yet attempted mechanistic or quantitative investigations regarding this exposure pathway, two of the most comprehensive aquatic food web studies conducted to date have both noted that sediment is a potentially major source of PFOS to fish, as many of the benthic fish sampled in those studies expressed elevated concentrations of PFOS compared to other species (Martin et al., 2004; Houde et al.,

2008). It should be noted that exposure to benthic fish from sediment porewater (via absorption during contact with sediment) and ingestion of sediment-associated plants may also be a source of benthic PFOS exposure, although these exposure mechanisms have not yet been evaluated.

To quantitatively investigate the potential importance of sediment-associated PFOS to Pool 2 fish, ENVIRON developed a bioaccumulation model to explicitly account for the accumulation of sediment-associated PFOS through the consumption of invertebrates living in PFOS-contaminated sediment. The model assumes PFOS is accumulated by fish via two exposure pathways (Figure 11): 1) a Sediment Exposure Pathway that begins with the accumulation of PFOS in sediment by absorption into benthic invertebrates that are then consumed by fish that accumulate PFOS via dietary absorption; and 2) a Water Column Exposure Pathway that comprises the direct absorption of PFOS into the fish across the body wall (including gills).

The model makes the following primary assumptions:

- Concentrations of PFOS in water and surface sediment are at steady state on a localized scale and that concentrations in water and sediment are independent of one another.
- Fish diets are derived from epibenthic and/or benthic invertebrates that absorb or ingest PFOS from sediment or sediment porewater.
- Bioaccumulation constants derived from laboratory data from water-only and food-only exposures to fish, and from data from laboratory exposures of benthic invertebrates to sediment are applicable to Pool 2 organisms and conditions.
- Fish are restricted to the area modeled in each of the three modeling scenarios and/or the accumulation kinetics for PFOS in fish are such that concentrations of PFOS in fish would change and reach steady state when moving to a new location exhibiting different concentrations of PFOS in sediment, water, and/or surface sediment invertebrates.
- Water and surface sediment data obtained from the various studies (samples collected 2005-2009) approximate PFOS exposure conditions to fish at the time of fish sampling (2009) in the MPCA (2010) study.

Model inputs included two site-specific Pool 2 parameters that were varied among localized exposure areas in Pool 2: 1) average concentration of PFOS in surface sediment; and 2) average concentration of PFOS in surface water. Concentrations of PFOS in sediment and surface water were obtained from available MPCA and Weston studies. The model input also includes an assumed average concentration of OC in surface sediment (0.01 g OC/g, sediment) because OC was not measured in the studies from which PFOS data were obtained. This assumed value is commonly used to derive sediment benchmarks and model bioaccumulation (NOAA, 2008), and is with the range of values (0.01 to 0.10) generally observed for sediment in inland waters of the United States (USEPA, 1993).

Three modeling scenarios were investigated for localized sections of Pool 2 according to PFOS sediment and water sample groupings by area as summarized in Figures 7 and 8, with raw data summarized in Tables 1, 2 and 3:

1. **Upstream of 3M Cottage Grove (Table 1)**: The Upstream of 3M Cottage Grove scenario represents areas of Pool 2 that are not likely to be impacted directly from PFOS adjacent to 3M Cottage Grove. Data were obtained from Pool 2 from the first MPCA water sample location #1 (approximately river mile 847) proceeding to the north-south transect of water samples collected by Weston (2007) that depict concentrations of PFOS below the detection limit (50 ng/L; approximately river mile 818.7). This area includes MPCA study Sections 1, 2, 3, Metro WWTP in Section 2, and the upper 25% of Section 4.

2. **3M Cottage Grove Shoreline (Table 2)**: The 3M Cottage Grove Shoreline scenario represents an area of Pool 2 that reflects the elevated concentrations of PFOS in surface sediment and water observed in Pool 2 adjacent to 3M Cottage Grove. Data were obtained from Pool 2 (Section 4) from the samples collected outside of the 3M Cottage Grove West Cove outfall (approximately river mile 818.5) to samples collected outside of the 3M Cottage Grove East Cove outfall (approximately river mile 817.5). This area includes an area directly adjacent to 3M Cottage Grove, extending approximately 200 meters into the river. It should be noted that the entire area does not appear to be contaminated with PFOS relative to upstream areas because concentrations are highest in an area downstream of the midpoint of 3M Cottage Grove as discussed above (Figures 9 and 10). It should also be noted that the concentration of PFOS in sediment and water samples obtained from East and West Coves were not used to derive the average concentrations for these scenarios, as it was unclear whether MPCA (2010) sampled fish directly from these areas and whether fish can move freely from the river into these coves.

3. **Downstream of 3M Cottage Grove (Table 3)**: The Downstream of 3M Cottage Grove scenario represents an area of Pool 2 that demonstrates PFOS impacts that may be associated with downstream transport of PFOS in sediment and water from 3M Cottage Grove and/or the areas adjacent to 3M Cottage Grove. Data were obtained from Pool 2 (Section 4) samples collected downstream of the 3M Cottage Grove East Cove outfall (approximately river mile 817.2) to samples collected upstream of the Pool 2 dam (approximately river mile 816).

Fish PFOS bioaccumulation model calculations for all three scenarios, including all mathematical operations required to use the three input parameters to derive the total concentration of PFOS in fish and the percentage of the accumulated PFOS derived from the Sediment Exposure Pathway for the three scenarios are shown in Tables 4, 5 and 6. Comparison of the predicted concentrations of PFOS in fish to those observed in the MPCA study (2010) reveals good model performance, with model predictions falling within the range of the observed averages for the species in each of the relevant sections (Figure 12).

Key model findings include:

- For the Upstream of 3M Cottage Grove scenario, the model predicts that concentrations in fish are not expected to result in concentrations of PFOS in fish above 200 ng/g (prediction of 32 ng/g; Table 4). The model prediction was consistent with the observed data for Sections 1, 2 and 3 fish, where species averages ranged from 24 to 100 ng/g, over 99% (220 of 222) of the Section 1, 2 and 3 fish samples were below the MDH fish tissue

advisory level, and all 90th percentile values were below the MDH fish tissue advisory level (Figures 2, 3 and 4).

- For the 3M Cottage Grove Shoreline scenario, the model predicts that concentrations in fish are expected to be greater than 200 ng/g (prediction of 490 ng/g; Table 5). The model prediction was consistent with the observed data for Section 4 fish, where species averages ranged from 160 to 740 ng/g. Concentrations above 200 ng/g were observed in 36% (27 of 75) of the Section 4 fish samples, and all 90th percentile values among species in Section 4 were above 200 ng/g (Figure 5).
- For the Downstream of 3M Cottage Grove scenario, the model predicts concentrations are expected to remain above 200 ng/g (prediction of 220 ng/g; Table 6). This suggests impairment conditions (concentrations in fish greater than 200 ng/g) are likely downstream of 3M Cottage Grove, an area representing at least 50% of the downstream portion of Section 4.
- For all model scenarios, the model predicts that a majority (80-86%) of PFOS accumulated by fish is derived from ingesting sediment invertebrates (i.e., Sediment Exposure Pathway; Tables 4, 5 and 6); thus, the majority of PFOS in fish tissue is derived from sediment-associated PFOS.

The concentration of organic carbon is sediment is an important factor in estimating the proportion of sediment-associated PFOS accumulated by fish. As mentioned above, due to a lack of data from MPCA and Weston studies, a default value of 0.01 g OC/g sediment was used for the OC concentration in Pool 2 sediment. Sensitivity analysis of the fish PFOS bioaccumulation model revealed that if lower values for OC concentrations are assumed, model predictions indicated that a higher percentage of PFOS would be derived from sediment-associated PFOS. For example, if an assumed concentration of OC in sediment was lowered from 0.01 to 0.0025 g OC/g sediment, 94-95% of PFOS accumulated by fish is predicted to be derived via the Sediment Exposure Pathway PFOS for the three model scenarios. The predicted concentrations of PFOS increase to 100-1,700 ng/g, which is still comparable to the actual values observed by MPCA (2010). If the OC input value is increased from the default 0.01 to 0.05 g OC/g sediment, 45-56% of fish PFOS is attributed to sediment-associated PFOS, indicating that sediment-PFOS is still an important source (roughly half) of PFOS accumulated by fish. Model performance suffers if this assumption is made, however, as the range of predicted total concentrations of PFOS in fish decreases to 10-180 ng/g. This range of predicted values is low compared to actual values observed in the MPCA (2010) study.

5 Science-based Alternative Decision Making to Define and Address PFOS Impairment in Pool 2

The following section reviews MPCA's initial management response (MPCA, 2010) to address PFOS impairment in Pool 2 and proposes an alternate path forward based on a review of PFOS science and the subsequent integration with Pool 2-specific data.

5.1 MPCA Management Response to the MPCA (2010) Pool 2 Study

Following the impairment determination that was based on a Pool 2-wide average concentration of PFOS in freshwater drum of 229 ng/g, MPCA adopted a management strategy aimed at addressing the impairment by establishing discharge limits for Metro WWTP. MPCA first used concentrations of PFOS in water and fish tissue to estimate site-specific fish consumption criterion (fCC) for PFOS in Pool 2. The fCC represents a hypothetical upper limit for the concentration of PFOS in surface water assumed to be associated with an acceptable dose of PFOS from ingestion of Pool 2 fish and incidental ingestion of Pool 2 surface water. Based on a bioaccumulation factor (BAF) derived from the MPCA (2010) data, as well as other policy-defined human health risk assessment parameters, MPCA calculated a fCC of 7 ng/L. MPCA subsequently applied the 7 ng/L fCC to permit modeling for Metro WWTP. Based on permit modeling, MPCA concluded that Metro WWTP has a Reasonable Potential to Exceed (RPE) water quality standards for PFOS.

Although MPCA's proposed permitting-focused approach could be an appropriate first step in managing many traditional chemicals of concern, the available site-specific data and unique environmental aspects of PFOS indicate that an alternate approach may be more effective in addressing the impairment of Pool 2. Specifically, an alternate approach can be supported scientifically as described below:

- **Impairment is Limited to Section 4**

  The available Pool 2 data demonstrate that PFOS-associated impairment is limited to or within Section 4. If considered on a section-by-section basis, human exposure to PFOS in fish tissue beyond Section 4 is not sufficient to result in an impairment status because average fish tissue concentrations in fish sampled in Sections 1, 2 and 3 were below the MDH fish tissue advisory level of 200 ng/g (MPCA, 2010). Several additional lines of evidence, including MPCA and Weston sediment and water PFOS chemistry data, peer-reviewed research on the fate of PFOS in aquatic systems and fish, as well as site-specific fish bioaccumulation modeling demonstrate that the source of the impairment is associated with local Section 4 PFOS sources, primarily contaminated sediment. The data do not support treating Pool 2 as a single unit due to the large differences in PFOS concentrations in fish, surface water, and sediment between Section 4 and Sections 1, 2 and 3. Although there are no barriers to prevent movement of fish exposed to PFOS sources within Section 4 to other Sections of Pool 2, uptake and elimination kinetics of PFOS in fish tissues suggest that concentrations of PFOS in any fish emigrating from Section 4 will decrease to levels below 200 ng/g within weeks of leaving high-exposure areas.

  It is understood that regulatory policy requires the entirety of Pool 2 to be listed as impaired for 303(d) purposes; however, when developing a permitting approach to

address the impairment, MPCA has the regulatory latitude to use the data and other supporting evidence to manage a water body reach by stretches rather than an a homogeneous unit. The data indicate that the actual source of the impairment is located in Section 4, that the contribution of Metro WWTP PFOS to impairment is irrelevant and insignificant, and that PFOS limits for Metro WWTP will not help MPCA address that impairment by reducing fish tissue concentrations in Section 4 fish. The data indicate that effluent limits for PFOS at the Metro WWTP will not resolve the impairment that is concentrated in Section 4. Focusing clean-up and restoration efforts on the section of Pool 2 (Section 4) with a demonstrated human health concern is more effective (cheaper, quicker, cleaner) than treating the entire Pool as if it were homogeneous, which essentially dilutes the efforts and may not address the core problem. A focused approach to Section 4, or a portion thereof, is supported by the data.

- **Calculation of the MPCA Fish Consumption Criterion is Inconsistent with the Methodology of the MDH Fish Tissue Advisory**
  In implementing the mitigative strategy for the impairment in Pool 2, MPCA appears to have assumed that it needs to evaluate risks to human health via calculation of a water quality criterion for PFOS in the form of a fCC. However, MDH has already evaluated the risks to human health, and has established an acceptable fish tissue level of 200 ng/g. In order to remove the fish tissue impairment identified by MDH, the mitigative strategy needs to target those actions that will reduce average fish tissue PFOS levels below 200 ng/g. Calculation of a fCC using the MPCA methodology targets a fish tissue level of 37 ng/g, which is five times lower than appropriate to address the impairment.

  Of specific interest in the calculation of the fCC is the use of the Relative Source Contribution (RSC) value, which accounts for the allowable percentage of exposure from the particular source of interest (in this case, Pool 2 fish and incidental ingestion of Pool 2 water). The RSC value used by MPCA to derive the fCC is 0.2; a value prescribed by MPCA policy for use in absence of chemical-specific data (MPCA, 2008). This value assumes that exposure from Pool 2 PFOS sources can be no more than 20% of the reference exposure dose that represents an upper limit for a PFOS dose with no adverse effects. In contrast, the RSC used to derive the MDH fish tissue advisory level of 200 ng/g is 1.0. Although this is less conservative than using 0.2, state and federal agencies take this approach because it is assumed that positive health benefits associated with fish consumption partly outweigh risks associated with potentially adverse effects from chemical exposure (OEHHA, 2008).

  The use of a RSC value of 0.2 results in a target concentration of PFOS in water and fish that is 5 times lower than to the level effective in removing the observed impairment. Interpreting MPCA fCC calculations (MPCA, 2010), at a water concentration equal to the fCC value of 7 ng/L, a maximum concentration of 37 ng/g in fish tissue is the control limit. By using 7 ng/L as the criterion in permitting calculations, the effective concentration of PFOS in fish tissue is calculated to be 37 ng/g or lower, which is unnecessary for appropriately addressing the impairment by lowering fish tissue concentrations below 200 ng/g.

- **The MPCA Fish Consumption Criterion Does not Account for the Major PFOS Source - Sediments**
  Applying the BAF to waters and effluents associated with a point source discharge (as in the derivation of the fCC) explicitly precludes consideration of sediment as a source of PFOS (i.e., calculation of the fCC value does not include concentrations of PFOS in sediment). The current permit-focused approach to mitigating the impairment is to reduce discharges to the water column. This approach assumes that the concentration in the water column will also decrease, resulting in a concurrent proportional decrease in fish tissue concentrations (a tenet of a water column BAF-based criterion). Using the bioaccumulation modeling described above (Tables 4-6), water column-associated PFOS accounts for only approximately 15% of the PFOS in fish tissue, while sediment-associated PFOS accounts for approximately 85% of PFOS in fish tissue. Since the majority (i.e., 85%) of fish PFOS exposure originates from sediment sources, even if PFOS discharges to the water column were removed completely and all other conditions remained the same, concentrations of PFOS in fish are likely to remain relatively constant, resulting in no change in the impairment status for fish in Section 4 of Pool 2. Alternatively, a more specific targeted approach to mitigation of impairment in Section 4 to address the impairment of Pool 2 is supported by the data and other scientific information.

5.2 Alternative PFOS Management Strategies Relative to Metro WWTP

Based on the previous sections, it is clear that a permit-focused mitigative approach to addressing PFOS impairment in all sections of Pool 2 is not warranted, nor will it be effective in addressing the Pool 2 impairment. Instead, Pool 2 data and ecotoxicological information on PFOS support the implementation of a section-by-section approach to mitigating the impairment. Only Section 4 fish exhibit fish tissue concentrations exceeding the MDH fish tissue concentration limits. A section-by-section consideration of the data and ecotoxicological information on PFOS provides a holistic approach for addressing and prioritizing the many sources of PFOS in the Pool 2 watershed, including legacy sediment contamination, groundwater, nonpoint source runoff, precipitation, and other industrial point sources, even in the absence of a completed TMDL.

A more appropriate approach would be to tailor the fCC and subsequent calculations to properly set the fish tissue concentration endpoint, accounting for the discrepancy in the RSC values used by MPCA and MDH, and to adjust the approximately 85% of PFOS in fish tissue that is derived from sediment while only 15% is derived from the water column. Alternative permitting calculations (described below), properly adjusting for data, conclude that there is no Reasonable Potential to Exceed the water quality criterion for PFOS.

First, ENVIRON used a RSC value to of 1.0, which is consistent with the derivation of the MDH fish tissue advisory level for PFOS as discussed previously (allows an end result of up to 200 ng/g in fish tissue) and the level which will address the fish impairment. After applying this modification, the resulting fCC value is 34 ng/L. This value targets fish exhibiting concentrations of PFOS in fish of 187 ng/g and higher, which approximates the 200 ng/g fish tissue advisory level. Second, a modification was made to explicitly account for the contribution of sediment-associated PFOS by using ENVIRON's fish PFOS bioaccumulation model to estimate the concentration of PFOS in the water column that would be necessary to elicit a concentration of

approximately 187 ng/g in fish, assuming a concentration of PFOS of 0.69 ng/g in surface sediment (average value for Pool 2 upstream of Section 4). The resulting alternate fCC is 145 ng/L (Table 7), and would be applicable to Sections 1, 2, 3 and 4 upstream of 3M Cottage Grove.

Third, ENVIRON used a conservative background concentration of 5 ng/L for alternate permitting calculations based on observed instream values. The current MPCA permit calculations use a Mississippi River background PFOS concentration of 7 ng/L, a value that is not based on the actual instream PFOS measurements that are available. Instead, by unwritten policy, the value is set in the MPCA permit calculations to be equal to the fCC. If the background concentration and fCC are equivalent, then there is no assimilative (dilution) capacity in the receiving water and, effectively, the fCC is the end-of-pipe permit limitation. MPCA's rationale for this approach is that the receiving water is listed as impaired for PFOS and applying this approach is "established practice" toward not causing or contributing to further impairment. ENVIRON modified the applicable background concentration to reflect actual instream measurements of PFOS from the official MPCA database. The actual instream results (<5.07 ng/L, <5.11 ng/L, and <4.93 ng/L) indicate that PFOS is not detected in upstream Mississippi River water at an approximate method detection limit of 5 ng/L. These values are also consistent with the 2010 MPCA sampling conducted in Sections 1 and 2 upstream of the Metro WWTP discharge (see Table 1).

To numerically assess the RPE status of the Metro WWTP, ENVIRON used the standard MPCA spreadsheet with the two alterations as described above: 1) an alternate fCC of 145 ng/L (in the spreadsheet this is referred to as the continuous standard - cs), and 2) a background concentration of 5 ng/L. A reproduction of this spreadsheet for PFOS is given in Table 8. No other input parameters to the spreadsheet were changed from the original MPCA calculations (including WWTP flow, river 7Q10 value, etc.). With these two input modifications, the resulting alternate water quality based effluent limits (WQBELs) are 1,856 ng/L (daily maximum) and 1,071 ng/L (monthly average). To assess the RPE status, the projected effluent quality (PEQ) is compared to the alternate daily maximum WQBEL; if the PEQ is less than the daily maximum WQBEL, then there is no RPE and no further permitting action (such as implementation of numeric limits) is warranted.

The original PEQ value (650 ng/L in Metro WWTP permitting calculations) is a statistical projection of the maximum expected effluent concentration and essentially applies a multiplying factor (2.6 – based on the number and variability of the database, i.e., 4 samples and a coefficient of variation of 0.6) to the maximum value. MCES has more representative PFOS effluent data (July, 2010), which results in an updated PEQ (discussed below). Since the original PEQ (650 ng/L) is less than the alternate daily maximum WQBEL (1,856 ng/L), the Metro WWTP does not exhibit a RPE. Also, the original PEQ (650 ng/L) is less than the monthly average WQBEL (1,071 ng/L), further supporting this finding. The conclusion of no RPE is based directly on MPCA calculation methodologies and input parameters except for two alternate parameters: a more appropriate continuous standard (fCC) of 145 ng/L and a Mississippi River background concentration of 5 ng/L derived from instream data.

More recent Metro WWTP effluent PFOS data are available as alternate values to those presented above. Results from a 7-day, consecutive 24-hour composite sampling program conducted in July 2010 are presented in Table 9, which indicate values well below the previous maximum effluent concentration of 250 ng/L (maximum daily value of 56.3 ng/L). Given the more representative sample type (24-hour composite versus single grab) and recent changes to contributing industrial users, Metropolitan Council believes this data set better characterizes the current Metro WWTP discharge.

Daily average values from the July 2010 database ranged from 42.2 to 56.3 ng/L and reflect a decrease in PFOS associated with influent, resulting in lower Metro WWTP effluent PFOS concentrations due to changes in wastes received at the Metro WWTP. These changes are likely related to changes at industrial electroplating facilities and source control measures implemented by 3M Oakdale groundwater (Spring, 2010). Also, more confidence can be placed in the July 2010 dataset because it is comprised of 24-hour composite samples. Previous Metro WWTP effluent data are derived from grab samples that provide a less-representative "snapshot" of effluent quality. Using only the July 2010 data, 7 samples with a default coefficient of variation of 0.6 yields a multiplying factor of 2.0 and an updated PEQ value of 2.0 × 56.3 ng/L = 112.6 ng/L. The updated PEQ (112.6 ng/L) yields a value significantly less than the original PEQ calculated in the MPCA spreadsheet (650 ng/L). The updated PEQ is more representative of current Metro WWTP effluent due to the recent changes in influent quality and the more robust sampling approach.

Both the original (650 ng/L) and updated (112.6 ng/L) PEQs result in a finding of no RPE for WQBELs derived from an fCC of 145 ng/L and a Mississippi River background concentration of 5 ng/L. Further, for the better representative July 2010 database, use of any alternative background concentration up to a level equal to the fCC (145 ng/L) will also result in no RPE.

6 Conclusions

ENVIRON independently and critically analyzed publicly-available PFOS chemistry data in Pool 2, reviewed and evaluated the state-of-the-science regarding PFOS fate in aquatic systems relative to Pool 2, and assessed the existing permit-based management approach for addressing impairment conditions attributed to the discharge of PFOS from Metro WWTP. Based on this independent research and analysis, ENVIRON makes the following key findings:

1. **Actual fish tissue PFOS impairment is limited to Section 4 in Pool 2.** When evaluated on a section-by-section basis, the only Section of Pool 2 that exhibits impairment is Section 4 (or a portion thereof). Section 4 is the most downstream study section of Pool 2 in the MPCA (2010) study. Over 99% of the 222 fish sampled in Sections 1, 2 and 3, along with their average and 90 percentile values, are below the level indicative of impairment, and do not trigger a fish advisory. MPCA's impairment calculations improperly combine data from all four Sections, resulting in a scope of the impairment that is not supported by the data. The data and other evidence indicate that the impairment is limited to Section 4 only, as fish movement patterns and PFOS bioaccumulation in fish are such that fish exhibiting elevated concentrations at levels of concern are located within Section 4. The available data and current knowledge of PFOS environmental chemistry indicate that it is most efficient to selectively apply mitigative strategies to each section based on the specific contributions and sources.
2. **A localized PFOS source within Section 4 is responsible for impairment.** Available sediment and water data from MPCA and other publicly-available reports, as well as site-specific PFOS fish bioaccumulation modeling, indicate that localized conditions within Section 4 are responsible for the impairment. Concentrations of PFOS in water and surface sediment along a portion of the 3M Cottage Grove shoreline approximately 1 mile or more in length are orders of magnitude higher than average upstream values. Fish bioaccumulation modeling reveals that concentrations of PFOS in sediment and water in this area, as well as the remainder of the downstream portion of Section 4, are likely to elicit concentrations in fish that exceed the MDH fish tissue advisory level for PFOS. Throughout Pool 2, modeling identifies sediment as the primary source of PFOS to fish in Pool 2, representing approximately 85% of PFOS exposures.
3. **MPCA's proposed permit-based management response to PFOS in Pool 2 fish is not supported by the data.** Application of MPCA's proposed numerical permit-based approach beyond Section 4 is not supported by Pool 2 data and the current scientific understanding of PFOS environmental chemistry. Metropolitan Council does not deny that Metro WWTP discharges PFOS to Pool 2; however, PFOS released from Metro WWTP does not result in the impairment that has been observed only in Section 4 of Pool 2. Concentrations of PFOS in fish as close as 2 to 7 river miles downstream of Metro WWTP are below fish advisory levels. Concentrations of PFOS in surface water and sediment also indicate that the PFOS in the Metro WWTP discharge does not result in the impairment observed in Section 4.

   MPCA's proposed numerical permit-based approach for Metro WWTP does not explicitly consider sediment as a source of PFOS despite the significant (~85%) contribution of sediment-associated PFOS to PFOS impairment. Concentrations of PFOS in sediment

are not explicitly accounted for in the current BAF and its subsequent use to generate a water quality criterion applicable to point source discharges. The current water column- and point-source discharge-based approach will not address PFOS in sediment, and thus will likely be ineffective in addressing impairment in Section 4 fish.

MPCA's proposed approach to determining the numerical permit-based management of PFOS in Pool 2 is inconsistent with the MDH fish tissue advisory level used to trigger it. MDH has already evaluated the risks to human health via consumption of PFOS in fish, and has established an acceptable fish tissue level of 200 ng/g. In order to remove the fish tissue impairment identified by MDH, the mitigative strategy needs to target those actions that will reduce fish tissue PFOS levels below 200 ng/g. MPCA methodology targets a fish tissue level of 37 ng/g, which is five times lower than what will be effective in removing the impairment.

Even with an end-of-the-pipe permitting management paradigm, it is clear that permitting action is not required for Metro WWTP and will not be effective in reducing fish tissue concentrations, and thus addressing the impairment. Using a modified permitting approach that is more consistent with actual data and the MDH fish tissue advisory used to identify impairment, as well as a water-column criterion that explicitly accounts for PFOS in sediment, a Reasonable Potential to Exceed by Metro WWTP does not exist.

In conclusion, levels of impairment identified by MPCA (2010) are based on elevated PFOS found solely in Section 4 fish tissue. Impairment is and will likely continue to be restricted to Section 4 or a portion thereof given fish movement patterns and the time scale for PFOS uptake and elimination in fish. Multiple lines of evidence indicate that local sources of PFOS in Section 4, especially PFOS in Section 4 surface sediment, are responsible for the impairment. The proposed permit-focused approach, as applied to Metro WWTP, is likely to be ineffective in addressing the impairment, and may later impede a more effective TMDL-focused approach to understand and manage the contributions of the multitude of sources and define complex environmental processes involved with the fate of PFOS in Pool 2.

7 References

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Tables

Table 1. Concentrations of PFOS in surface sediment and water samples obtained from Sections 1, 2, 3, and 4 upstream of 3M Cottage Grove.

Sediment Sample	[Sediment PFOS] (ng/g, dw)	Reference	Note	Water Sample	[Water PFOS] (ng/L)	Reference	Note
XS-01a	0.837	Weston, 2007	Section 4 upstream of 3M Cottage Grove	Miss-up	5.14	MPCA, 2006	Section 4
XS-01b	1.34	Weston, 2007	Section 4 upstream of 3M Cottage Grove	1	2.56	MPCA, 2010	Value represents 1/2 DL; Section 1
XS-01c	0.289	Weston, 2007	Section 4 upstream of 3M Cottage Grove	2	2.53	MPCA, 2010	Value represents 1/2 DL; Section 1
XS-01d	0.343	Weston, 2007	Section 4 upstream of 3M Cottage Grove	3	2.53	MPCA, 2010	Value represents 1/2 DL; Section 1
XS-01e	0.472	Weston, 2007	Section 4 upstream of 3M Cottage Grove	4	2.53	MPCA, 2010	Value represents 1/2 DL; Section 2
Sediment upstream	1.57	MPCA, 2006	Section 4 upstream of 3M Cottage Grove	5	2.52	MPCA, 2010	Value represents 1/2 DL; Section 2
LS-821	0.125	Weston, 2007	Value represents 1/2 DL; Section 3	6	7.71	MPCA, 2010	Section 2
LS-824	0.524	Weston, 2007	Section 3	7	10.3	MPCA, 2010	Section 3
				8	8.51	MPCA, 2010	Section 3
				9	2.54	MPCA, 2010	Value represents 1/2 DL; Section 3
				10	2.5	MPCA, 2010	Value represents 1/2 of detection limit; Sample from Section 4 upstream of 3M Cottage Grove

Mean [PFOS Surface Sediment] (ng/g, dw)	0.69

Mean [PFOS Water] (ng/g, dw)	4.5

Abbreviations

DL: Detection Limit
dw: dry weight
g: gram
L: Liter
ng: nanogram
PFOS: perfluorooctane sulfonate
ww: wet weight

Note

Sediment samples reported at "NR" (Not Reported) and/or "NQ" (Not Quantifiable) by Weston were not included due to lack of numerical values.

Water samples from locations LS-821, LS-824, XS-01a, XS-01b, XS-01c, XS-01d, and XS-01e (Weston, 2007) were not used to derive the average concentration of PFOS in water, as all results from these stations were below the detection limit of 50 ng/L. Data from other studies (MPCA, 2006; MPCA, 2010) expressed lower detection limits, and these datasets were considered sufficient to characterize this area of Pool 2. Inclusion of the non-detect Weston (2007) data (values of half the detection limit) artificially skewed the mean concentration of PFOS in water from 4.5 ng/L to 15 ng/L.

Table 2. Concentrations of PFOS in surface sediment and water samples obtained from Section 4 adjacent to 3M Cottage Grove shoreline, excluding East Cove and West Cove.

Sediment Sample	[Sediment PFOS] (ng/g, dw)	Reference	Note	Water Sample	[Water PFOS] (ng/L)	Reference	Note
IW01	0.458	Weston, 2007		IW01	25	MPCA, 2006	Value represents 1/2 DL; The DL (50 ng/L) for water analysis in Weston (2007) is 10X higher than other studies examined in this modeling effort.
IW02	0.321	Weston, 2007		IW01	25	Weston, 2007	Value represents 1/2 DL
IW03	0.363	Weston, 2007		IW02	25	Weston, 2007	Value represents 1/2 DL
IW04	0.23	Weston, 2007		IW02	25	Weston, 2007	Value represents 1/2 DL
IW05	0.32	Weston, 2007		IW03	25	Weston, 2007	Value represents 1/2 DL
IW06	0.469	Weston, 2007		IW03	25	Weston, 2007	Value represents 1/2 DL
IW07	0.502	Weston, 2007		IW04	25	Weston, 2007	Value represents 1/2 DL
IW08	0.753	Weston, 2007		IW04	25	Weston, 2007	Value represents 1/2 DL
IW09	0.589	Weston, 2007		IW05	25	Weston, 2007	Value represents 1/2 DL
IW09a	27	Weston, 2007		IW05	25	Weston, 2007	Value represents 1/2 DL
IW09b	1.6	Weston, 2007		IW06	25	Weston, 2007	Value represents 1/2 DL
IW09c	0.802	Weston, 2007		IW06	25	Weston, 2007	Value represents 1/2 DL
IW09d	0.358	Weston, 2007		IW07	25	Weston, 2007	Value represents 1/2 DL
IW09e	0.279	Weston, 2007		IW07	25	Weston, 2007	Value represents 1/2 DL
IW09f	0.737	Weston, 2007		IW08	25	Weston, 2007	Value represents 1/2 DL
IW10	1.37	Weston, 2007		IW08	25	Weston, 2007	Value represents 1/2 DL
IW11	4.84	Weston, 2007		IW09	162	Weston, 2007	
IW12	4.12	Weston, 2007		IW09	183	Weston, 2007	
IW13	3.62	Weston, 2007		IW09a	25	Weston, 2007	Value represents 1/2 DL
IW14	4.2	Weston, 2007		IW09a	25	Weston, 2007	Value represents 1/2 DL
IW14a	74.5	Weston, 2007		IW09b	25	Weston, 2007	Value represents 1/2 DL
IW14c	10.4	Weston, 2007		IW09b	25	Weston, 2007	Value represents 1/2 DL
IW14d	0.125	Weston, 2007	Value represents 1/2 DL	IW09c	25	Weston, 2007	Value represents 1/2 DL
IW14e	0.125	Weston, 2007	Value represents 1/2 DL	IW09c	25	Weston, 2007	Value represents 1/2 DL
IW14f	0.513	Weston, 2007		IW09d	25	Weston, 2007	Value represents 1/2 DL
IW15	1.31	Weston, 2007		IW09d	25	Weston, 2007	Value represents 1/2 DL

Sediment Sample	[Sediment PFOS] (ng/g, dw)	Reference	Note	Water Sample	[Water PFOS] (ng/L)	Reference	Note
IW16	0.654	Weston, 2007		IW09e	25	Weston, 2007	Value represents 1/2 DL
IW17	1.47	Weston, 2007		IW09e	25	Weston, 2007	Value represents 1/2 DL
IW18	3.17	Weston, 2007		W09f	25	Weston, 2007	Value represents 1/2 DL
IW19	3.53	Weston, 2007		W09f	25	Weston, 2007	Value represents 1/2 DL
IW19a	44.3	Weston, 2007		IW10	25	Weston, 2007	Value represents 1/2 DL
IW19b	6.86	Weston, 2007		IW11	113	Weston, 2007	
IW19c	1.81	Weston, 2007		IW12	25	Weston, 2007	Value represents 1/2 DL
IW19d	0.295	Weston, 2007		IW12	25	Weston, 2007	Value represents 1/2 DL
IW19e	0.535	Weston, 2007		IW13	53.9	Weston, 2007	
IW19f	1.42	Weston, 2007		IW13	59.4	Weston, 2007	
IW20	1.42	Weston, 2007		IW14	25	Weston, 2007	Value represents 1/2 DL
IW21	1.35	Weston, 2007		IW14a	111	Weston, 2007	
IW23	17.4	Weston, 2007		IW14a	130	Weston, 2007	
IW24	30.7	Weston, 2007		IW14b	63.1	Weston, 2007	
R3	8.28	Weston, 2008		IW14b	57.8	Weston, 2007	
SAB01	0.125	Weston, 2009		IW14c	25	Weston, 2007	Value represents 1/2 DL
SAB03	0.125	Weston, 2009		IW14d	25	Weston, 2007	Value represents 1/2 DL
SAB04	219	Weston, 2009		IW14d	25	Weston, 2007	Value represents 1/2 DL
SAB05	0.125	Weston, 2009		IW14e	25	Weston, 2007	Value represents 1/2 DL
SAB06	0.125	Weston, 2009		IW14e	25	Weston, 2007	Value represents 1/2 DL
SAB07	0.125	Weston, 2009		IW14f	25	Weston, 2007	Value represents 1/2 DL
SAB08	0.125	Weston, 2009		IW14f	25	Weston, 2007	Value represents 1/2 DL
				IW15	60.2	Weston, 2007	
				IW15	25	Weston, 2007	Value represents 1/2 DL
				IW16	155	Weston, 2007	
				IW17	116	Weston, 2007	
				IW17	122	Weston, 2007	
				IW18	115	Weston, 2007	
				IW18	110	Weston, 2007	
				IW19	105	Weston, 2007	
				IW19	96.6	Weston, 2007	
				IW19a	214	Weston, 2007	
				IW19a	206	Weston, 2007	
				IW19b	127	Weston, 2007	

Sediment Sample	[Sediment PFOS] (ng/g, dw)	Reference	Note	Water Sample	[Water PFOS] (ng/L)	Reference	Note
				IW19b	88.9	Weston, 2007	
				IW19c	54.5	Weston, 2007	
				IW19d	25	Weston, 2007	Value represents 1/2 DL
				IW19d	25	Weston, 2007	Value represents 1/2 DL
				IW19e	25	Weston, 2007	Value represents 1/2 DL
				IW19e	25	Weston, 2007	Value represents 1/2 DL
				IW19f	25	Weston, 2007	Value represents 1/2 DL
				IW19f	25	Weston, 2007	Value represents 1/2 DL
				IW20	112	Weston, 2007	
				IW20	118	Weston, 2007	
				IW21	413	Weston, 2007	
				IW21	436	Weston, 2007	
				IW22	523	Weston, 2007	
				IW22	539	Weston, 2007	
				IW23	323	Weston, 2007	
				IW23	350	Weston, 2007	
				IW24	114	Weston, 2007	
				IW24	466	Weston, 2007	
				IW25	94.5	Weston, 2007	
				IW25	102	Weston, 2007	
				R2	25	Weston, 2008	
				R3	25	Weston, 2008	
				R4	25	Weston, 2008	
				11	90.07	MPCA, 2010	

Mean [PFOS Surface Sediment] (ng/g, dw)	10

Mean [PFOS Water] (ng/g, dw)	88

Abbreviations

DL: Detection Limit
dw: dry weight
g: gram
L: Liter
ng: nanogram
PFOS: perfluorooctane sulfonate
ww: wet weight

Note

Sediment samples reported at "NR" (Not Reported) and/or "NQ" (Not Quantifiable) by Weston were not included due to lack of numerical values.

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Table 3. Concentrations of PFOS in surface sediment and water samples obtained from Section 4 downstream of 3M Cottage Grove.

Sediment Sample	[Sediment PFOS] (ng/g, dw)	Reference	Note	Water Sample	[Water PFOS] (ng/L)	Reference	Note
XS-02a	2.31	Weston, 2007		Miss-down #1	14.5	MPCA, 2006	
XS-02a	2.66	Weston, 2007		Miss-down #2	6	MPCA, 2006	
XS-02b	0.603	Weston, 2007		Miss-down #3	2.555	MPCA, 2006	Value represents 1/2 DL
XS-02c	0.798	Weston, 2007		12	15	MPCA, 2010	
XS-02d	0.702	Weston, 2007		R5	98	Weston, 2008	
XS-02e	1.24	Weston, 2007					
Sed-Miss-down #1	27.9	MPCA, 2006					
Sed-Miss-down #2	8.26	MPCA, 2006					
Sed-Miss-down #3	1.71	MPCA, 2006					
R5	6.13	Weston, 2008					
R6	1.35	Weston, 2008					

Mean [PFOS Surface Sediment] (ng/g, dw)	**4.9**

Mean [PFOS Water] (ng/g, dw)	**27**

Abbreviations

DL: Detection Limit
dw: dry weight
g: gram
L: Liter
ng: nanogram
PFOS: perfluorooctane sulfonate
ww: wet weight

Note

Sediment samples reported at "NR" (Not Reported) and/or "NQ" (Not Quantifiable) by Weston were not included due to lack of numerical values.

Water samples from locations XS-02a, XS-02b, XS-02c, XS-02d, and XS-02e (Weston, 2007) were not used to derive the average concentration of PFOS in water, as all results from these stations were below the detection limit of 50 ng/L. Data from other studies (MPCA, 2006; Weston, 2008; MPCA, 2010) expressed lower detection limits, and these datasets were considered sufficient to characterize this area of Pool 2. Inclusion of the non-detect Weston (2007) data (values of half the detection limit) did not greatly alter the mean concentration of PFOS in water (i.e., 26 ng/L instead of 27 ng/L).

Table 4. Fish bioaccumulation model for Sections 1, 2, 3, and 4 upstream of 3M Cottage Grove.

Model Input Variables					
Item	**Abbre-viation**	**Value**	**Units**	**Note**	**Reference**
Measured [Water PFOS]	Wat	4.5	ng/L	Average of water samples in Sections 1-4, upstream of Cottage Grove.	Table 1
Measured [Sediment PFOS]	Sed	0.69	ng/g, dw	Average of Section 3 and 4 surface sediment samples upstream of Cottage Grove.	Table 1
Total organic carbon (OC) in sediment	TOC	0.01	g, OC/g, dw	Organic carbon not measured or data unavailable for sediment samples from Pool 2 investigations of PFOS in sediment. 0.01 (i.e., 1% TOC) represents a standard default modeling assumption for sediment.	

Model Constants					
Item	**Abbre-viation**	**Value**	**Units**	**Note**	**Reference**
Biota-Sediment Accumulation Factor (BSAF)	BSAF	1.22	g, OC/g, ww	Lab-derived steady state estimate with invertebrates and spiked sediment.	Higgins et al., 2007
Bioaccumulation factor (BAF)	BAF	0.32	kg prey, ww/kg predator, ww	Lab-derived steady state estimate (fish carcass) for trout and PFOS-spiked food only exposure.	Martin et al., 2003a
Bioconcentration Factor (BCF)	BCF	1,100	L/kg, ww	Lab-derived steady state estimate with trout (fish carcass) and PFOS-spiked water only exposure.	Martin et al., 2003b

Model Predictions				
Item	**Abbre-viation**	**Value**	**Units**	**Note**
[Sediment PFOS], OC-normalized	SedOC	69	ng/g, OC	Sed ÷ TOC
Predicted [Sediment invertebrate PFOS]	Inv	84	ng/g, ww	SedOC × BSAF
[Fish PFOS] from Dietary (Sediment invertebrate) Source	Fsed	27	ng PFOS/g, ww	Inv × BAF
Predicted [Fish PFOS] from Direct Absorption from Water	Fwat	4.9	ng PFOS/g, ww	Wat × BCF ÷ 1,000 g, ww/kg, ww
Total [PFOS Fish]	**F**	**32**	**ng PFOS/g, ww**	**Fsed + Fwat**
Percentage of [Fish PFOS] from sediment	**%Fsed**	**84**	**%**	**100% × Fsed / F**
Percentage of [Fish PFOS] from water	**%Fwat**	**16**	**%**	**100% × Fwat / F**

Abbreviations

dw: dry weight
g: gram
kg: kilogram
L: Liter
ng: nanogram
OC: organic carbon
PFOS: perfluorooctane sulfonate
ww: wet weight

Table 5. Fish bioaccumulation model for Section 4 adjacent to 3M Cottage Grove shoreline.

Model Input Variables					
Item	**Abbre-viation**	**Value**	**Units**	**Note**	**Reference**
Measured [Water PFOS]	Wat	88	ng/L	Average of water samples in Section 4 adjacent to 3M Cottage Grove shoreline.	Table 2
Measured [Sediment PFOS]	Sed	10	ng/g, dw	Average of surface sediment samples in Section 4 adjacent to 3M Cottage Grove shoreline	Table 2
Total organic carbon (OC) in sediment	TOC	0.01	g, OC/g, dw	Organic carbon not measured or data unavailable for sediment samples from Pool 2 investigations of PFOS in sediment. 0.01 (i.e., 1% TOC) represents a standard default modeling assumption for sediment.	

Model Constants					
Item	**Abbre-viation**	**Value**	**Units**	**Note**	**Reference**
Biota-Sediment Accumulation Factor (BSAF)	BSAF	1.22	g, OC/g, ww	Lab-derived steady state estimate with invertebrates and spiked sediment.	Higgins et al., 2007
Bioaccumulation factor (BAF)	BAF	0.32	kg prey, ww/kg predator, ww	Lab-derived steady state estimate (fish carcass) for trout and PFOS-spiked food only exposure.	Martin et al., 2003a
Bioconcentration Factor (BCF)	BCF	1,100	L/kg, ww	Lab-derived steady state estimate with trout (fish carcass) and PFOS-spiked water only exposure.	Martin et al., 2003b

Model Predictions				
Item	**Abbre-viation**	**Value**	**Units**	**Note**
[Sediment PFOS], OC-normalized	SedOC	1,006	ng/g, OC	Sed ÷ TOC
Predicted [Sediment invertebrate PFOS]	Inv	1,227	ng/g, ww	SedOC × BSAF
[Fish PFOS] from Dietary (Sediment invertebrate) Source	Fsed	393	ng PFOS/g, ww	Inv × BAF
Predicted [Fish PFOS] from Direct Absorption from Water	Fwat	97.0	ng PFOS/g, ww	Wat × BCF ÷ 1,000 g, ww/kg, ww
Total [PFOS Fish]	**F**	**490**	**ng PFOS/g, ww**	**Fsed + Fwat**
Percentage of [Fish PFOS] from sediment	**%Fsed**	**80**	**%**	**100% × Fsed / F**
Percentage of [Fish PFOS] from water	**%Fwat**	**20**	**%**	**100% × Fwat / F**

Abbreviations

dw: dry weight
g: gram
kg: kilogram
L: Liter
ng: nanogram
OC: organic carbon
PFOS: perfluorooctane sulfonate
ww: wet weight

Table 6. Fish bioaccumulation model for Section 4 Section 4 downstream of 3M Cottage Grove.

Model Input Variables					
Item	**Abbre-viation**	**Value**	**Units**	**Note**	**Reference**
Measured [Water PFOS]	Wat	27	ng/L	Average of water samples in Section 4 adjacent to 3M Cottage Grove shoreline.	Table 3
Measured [Sediment PFOS]	Sed	5	ng/g, dw	Average of surface sediment samples in Section 4 adjacent to 3M Cottage Grove shoreline	Table 3
Total organic carbon (OC) in sediment	TOC	0.01	g, OC/g, dw	Organic carbon not measured or data unavailable for sediment samples from Pool 2 investigations of PFOS in sediment. 0.01 (i.e., 1% TOC) represents a standard default modeling assumption for sediment.	

Model Constants					
Item	**Abbre-viation**	**Value**	**Units**	**Note**	**Reference**
Biota-Sediment Accumulation Factor (BSAF)	BSAF	1.22	g, OC/g, ww	Lab-derived steady state estimate with invertebrates and spiked sediment.	Higgins et al., 2007
Bioaccumulation factor (BAF)	BAF	0.32	kg prey, ww/kg predator, ww	Lab-derived steady state estimate (fish carcass) for trout and PFOS-spiked food only exposure.	Martin et al., 2003a
Bioconcentration Factor (BCF)	BCF	1,100	L/kg, ww	Lab-derived steady state estimate with trout (fish carcass) and PFOS-spiked water only exposure.	Martin et al., 2003b

Model Predictions				
Item	**Abbre-viation**	**Value**	**Units**	**Note**
[Sediment PFOS], OC-normalized	SedOC	488	ng/g, OC	Sed ÷ TOC
Predicted [Sediment invertebrate PFOS]	Inv	595	ng/g, ww	SedOC × BSAF
[Fish PFOS] from Dietary (Sediment invertebrate) Source	Fsed	190	ng PFOS/g, ww	Inv × BAF
Predicted [Fish PFOS] from Direct Absorption from Water	Fwat	29.9	ng PFOS/g, ww	Wat × BCF ÷ 1,000 g, ww/kg, ww
Total [PFOS Fish]	**F**	**220**	**ng PFOS/g, ww**	**Fsed + Fwat**
Percentage of [Fish PFOS] from sediment	**%Fsed**	**86**	**%**	**100% × Fsed / F**
Percentage of [Fish PFOS] from water	**%Fwat**	**14**	**%**	**100% × Fwat / F**

Abbreviations

dw: dry weight
g: gram
kg: kilogram
L: Liter
ng: nanogram
OC: organic carbon
PFOS: perfluorooctane sulfonate
ww: wet weight

Table 7. Fish bioaccumulation model applied to estimate PFOS water criterion at a given concentration of PFOS in surface sediment.

Model Input Variables					
Item	**Abbre-viation**	**Value**	**Units**	**Note**	**Reference**
PFOS reference dose	RFD	8E-05	mg/kg*d		MPCA, 2010
Human angler body weight	BW	70	kg, bw		MPCA, 2010
Relative Source Contribution Factor	RSC	1		Value consistent with that used by MDH to indentify water body impairment and derive a fish consumption criterion for PFOS (200 ng/g, ww).	MPCA, 2010
Incidential ingestion of water	IW	0.01	L/d		MPCA, 2010
Fish tissue consumption rate	CR	30	g, ww/d		MPCA, 2010
Measured [Sediment PFOS]	Sed	0.69	ng/g, dw	Average of Section 3 and 4 surface sediment samples upstream of Cottage Grove.	Table 1
Total organic carbon (OC) in sediment	TOC	0.01	g, OC/g, dw	Organic carbon not measured or data unavailable for sediment samples from Pool 2 investigations of PFOS in sediment. 0.01 (i.e., 1% TOC) represents a standard default modeling assumption for sediment	

Model Constants					
Item	**Abbre-viation**	**Value**	**Units**	**Note**	**Reference**
Biota-Sediment Accumulation Factor (BSAF)	BSAF	1.22	g, OC/g, ww	Lab-derived steady state estimate with invertebrates and spiked sediment.	Higgins et al., 2007
Bioaccumulation factor (BAF)	BAF	0.32	kg prey, ww/kg predator, ww	Lab-derived steady state estimate (fish carcass) for trout and PFOS-spiked food only exposure.	Martin et al., 2003a
Bioconcentration Factor (BCF)	BCF	1,100	L/kg, ww	Lab-derived steady state estimate with trout (fish carcass) and PFOS-spiked water only exposure.	Martin et al., 2003b

Model Predictions				
Item	**Abbre-viation**	**Value**	**Units**	**Note**
[Sediment PFOS], OC-normalized	SedOC	69	ng/g, OC	Sed ÷ TOC
Predicted [Sediment invertebrate PFOS]	Inv	84	ng/g, ww	SeOC × BSAF
[Fish PFOS] from Dietary (Sediment invertebrate) Source	Fsed	27	ng PFOS/g, ww	Inv × BAF
Dose from consumption of sediment-derived PFOS in fish	Dfsed	1.2E-05	mg/kg*d	CR × Fsed ÷ 1,000,000 ng, ww/ng, ww ÷ BW
Allowable maximum dose from ingestion of water and ingestion of fish	Dwat	6.8E-05	mg/kg*d	(RFD - Dfsed) × RSC
PFOS fish consumption criterion	**FCC**	**145**	**ng/L**	**1,000,000 ng/mg × (Dwat × BW) ÷ ((IW + (BCF × CR ÷ 1,000 g, ww/kg, ww))**
Predicted [Fish PFOS] from Direct Absorption from Water	Fwat	160	ng PFOS/g, ww	Wat × BCF ÷ 1,000 g, ww/kg, ww
Total [PFOS Fish]	F	187	ng PFOS/g, ww	Fsed + Fwat

Abbreviations

dw: dry weight
g: gram
kg: kilogram
L: Liter
ng: nanogram
OC: organic carbon
PFOS: perfluorooctane sulfonate
ww: wet weight

Table 8. Alternate PFOS permit calculations for Metro.

Metropolitan Council Environmental Services (MCES) Water Quality-Based Effluent Limits (WQBELs)

Parameter	Value	Units	Note
Plant Flow	950.04	mliters/d	(ADW)
	251.00	mgd	
River 7Q10	4,197.87	mliters/d	(Class 2B)
	1716		
	0.646317		
	1,109.08	mgd	
Background Conc.	5.0000	ng/l	PFOS; S000-266
Continuous Std (cs)	145.0000	ng/l	
Maximum Std (ms)	85,000.00	ng/l	
Final Acute Value	170,000.00	ng/l	

Waste Ld Allocation:	
WLAcs	763.61
WLAms	460,562.76

Coeff of Variation-CV	0.6000
Variance	0.3075
Std. Dev.	0.5545
Duration (n days)	30.00

Long Term Ave.-LTA	
u_4/u_{30}	6.38
u	6.24
LTAcs	595.84
u_1	11.75
LTAms	147,884.58
Use LTAcs < LTAms:	TRUE

WQBEL: Daily Max.	1,855.6511
s^2_n	0.17
s_n	0.41
u_n	6.31
Mo.Av. (2x)	1,071.13

Max Meas Effl Value	250.00
# data points	4.00
PEQ factor	2.60
Proj Effl Qual.(PEQ)	650.00

PEQ > Daily Max	FALSE
PEQ > FAV	FALSE
Reasonable Potential	no

NOTE:
Table was modified from a file obtained from MPCA.

Table 9. Concentrations of PFOS in effluent from the Metropolitan Wastewater Treatment Plant, July 2010.

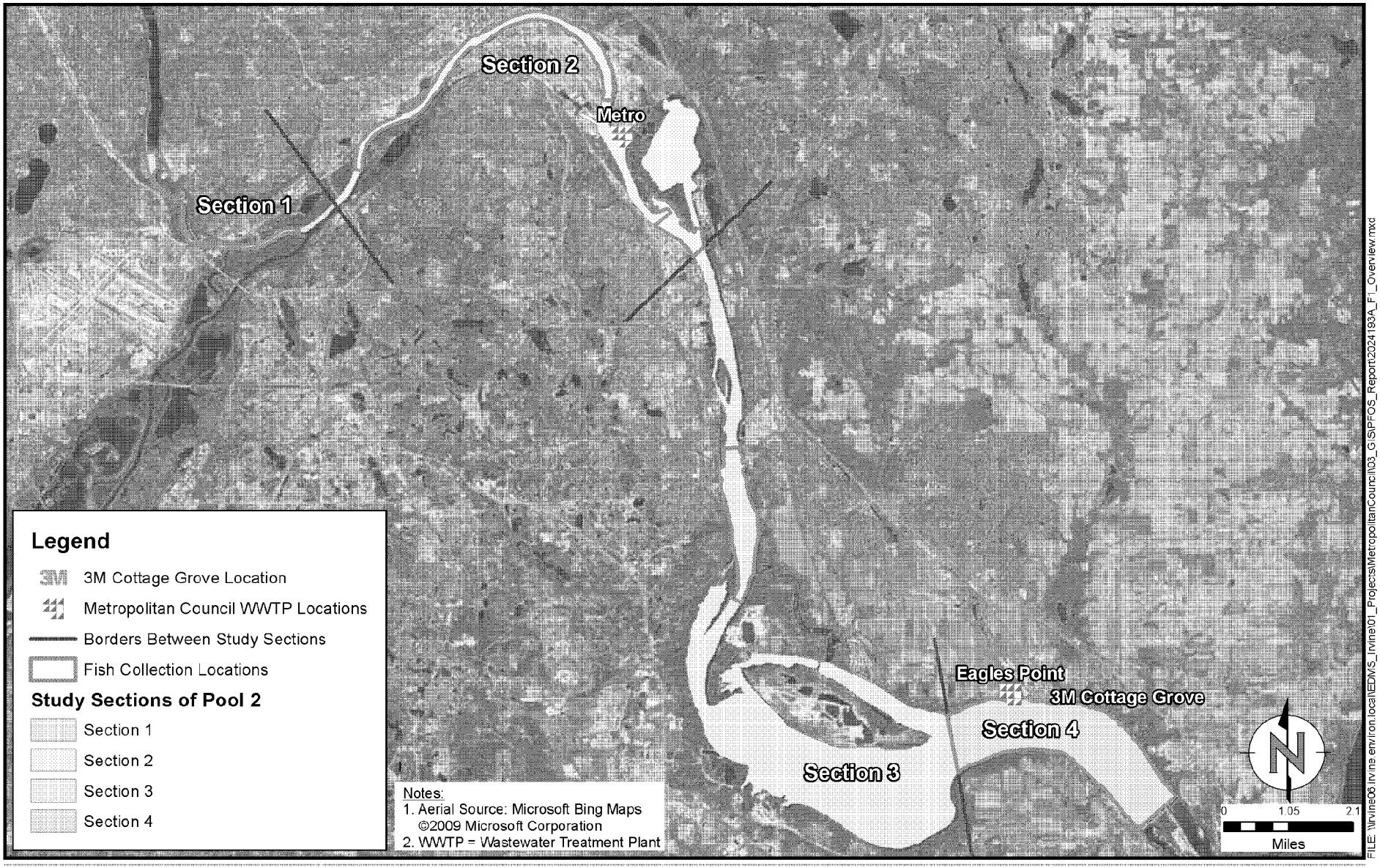
Raw Data [1]			
Day	**Date**	**Sample ID**	**PFOS Concentration (ng/L)**
Thursday	7/22/2010	PF4-1	51.2
Thursday	7/22/2010	PF5-1	51.6
Thursday	**7/22/2010**	**Average**	**51.4**
Friday	7/23/2010	PF4-2	57.7
Friday	7/23/2010	PF5-2	53.8
Friday	**7/23/2010**	**Average**	**55.75**
Saturday	7/24/2010	PF4-3	39.2
Saturday	7/24/2010	PF5-3	48
Saturday	**7/24/2010**	**Average**	**43.6**
Sunday	7/25/2010	PF4-4	47
Sunday	7/25/2010	PF4-4 (Duplicate analysis)	43.6
Sunday	7/25/2010	PF4-4 Average	45.3
Sunday	7/25/2010	PF5-4	62
Sunday	**7/25/2010**	**Average**	**53.65**
Monday	**7/26/2010**	**PF4-5**	**42.2**
Tuesday	**7/27/2010**	**PF4-6**	**54.3**
Wednesday	7/28/2010	PF4-7	54.8
Wednesday	7/28/2010	PF4-7 (Duplicate analysis)	57.8
Wednesday	**7/28/2010**	**PF4-7 Average**	**56.3**

Sample Data for Permitting Uses [2]	
Sampling Date	**PFOS Concentration (ng/L)**
7/22/2010	51.4
7/23/2010	55.75
7/24/2010	43.6
7/25/2010	53.65
7/26/2010	42.2
7/27/2010	54.3
7/28/2010	56.3
Average	**51.0**
Median	**53.7**
Count	**7**
Maximum	**56**

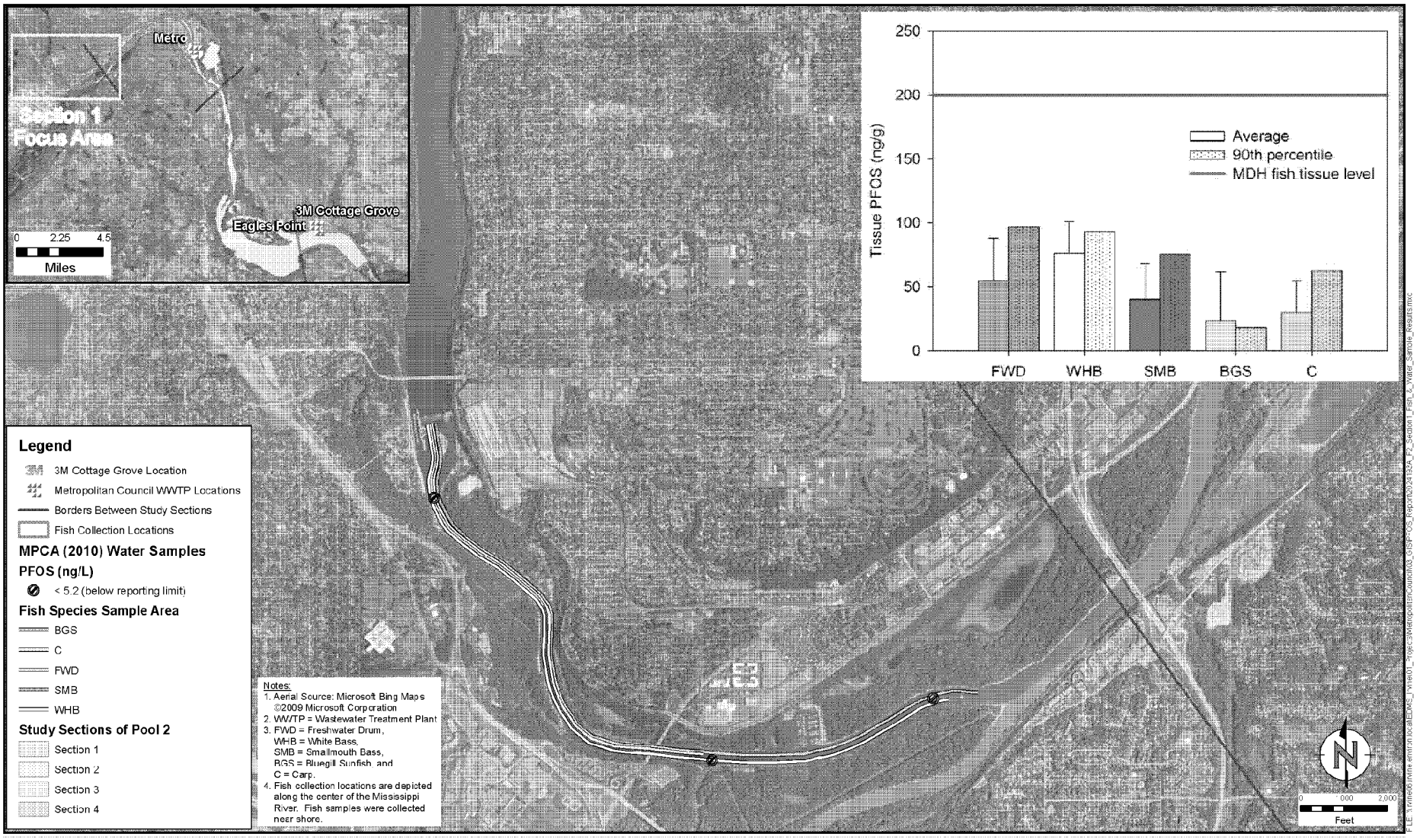
NOTE:

1. One sampler (PF4) was operated for one week (Thursday, July 22-Wednesday, July 28); two samples from this sampler (July 25 and July 28) were analyzed in duplicate. The other sampler (PF5) was operated for four days (Thursday, July 22-Sunday, July 25). All samples were analyzed for PFOS at AXYS Analytical Services (Sidney, BC, Canada) by SPE/LC/MS/MS using appropriate isotopic standards to correct for analyte recoveries.
2. Raw data was combined to provide a single value for the concentration of PFOS in effluent per day. Results of duplicates samples were averaged, then results from the two samplers were averaged for a given day.

Figures



ENVIRON	Minnesota Pollution Control Agency (MPCA) Mississippi River Pool 2 Study Area	Figure 1
DRAFTED BY: MMcMeechan DATE: 9/10/2010		PROJECT: 20-24193A



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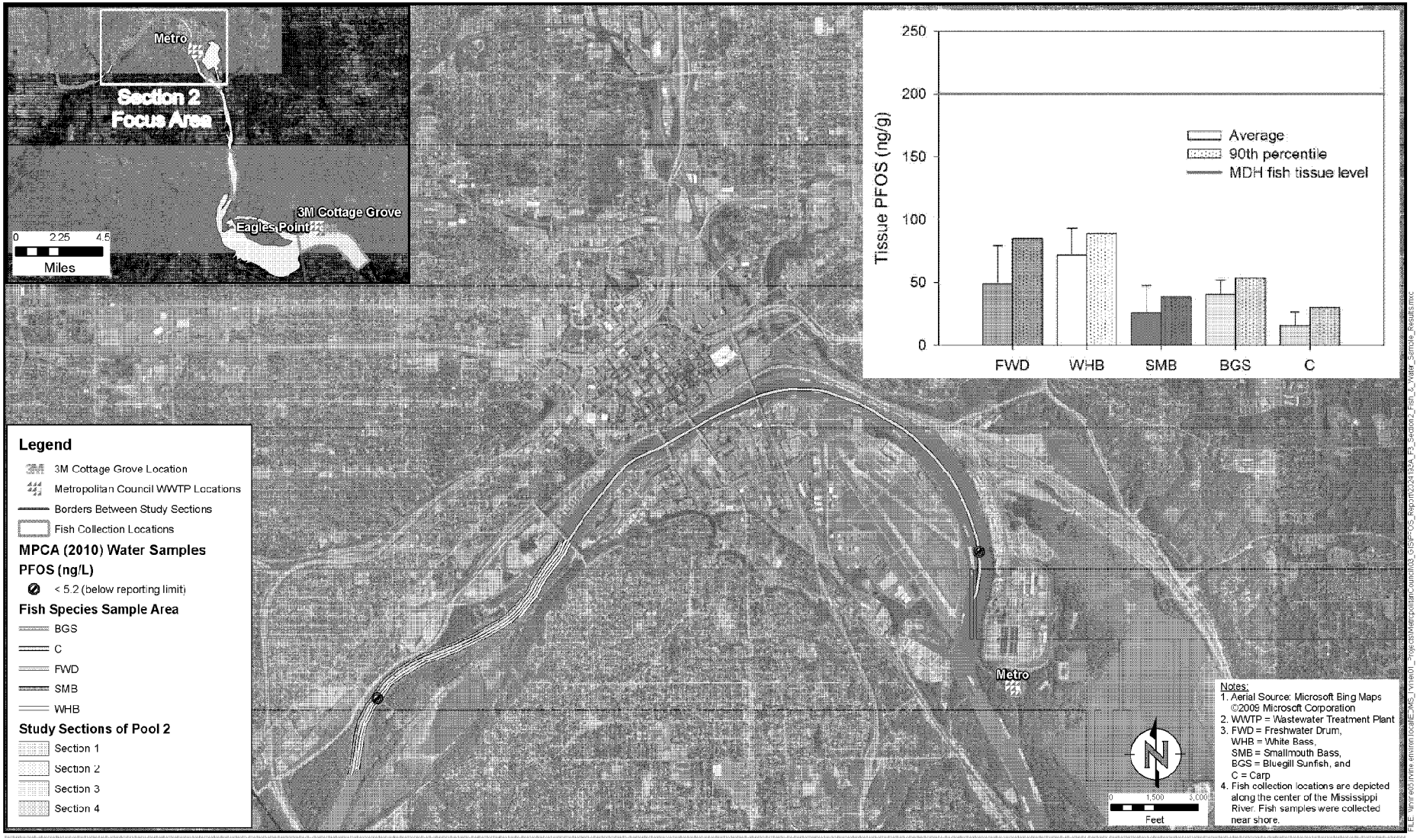
Minnesota Pollution Control Agency (MPCA) Mississippi River Pool 2
Section 1 Fish and Water Sample Results

Figure 2

PROJECT: 20-24163A



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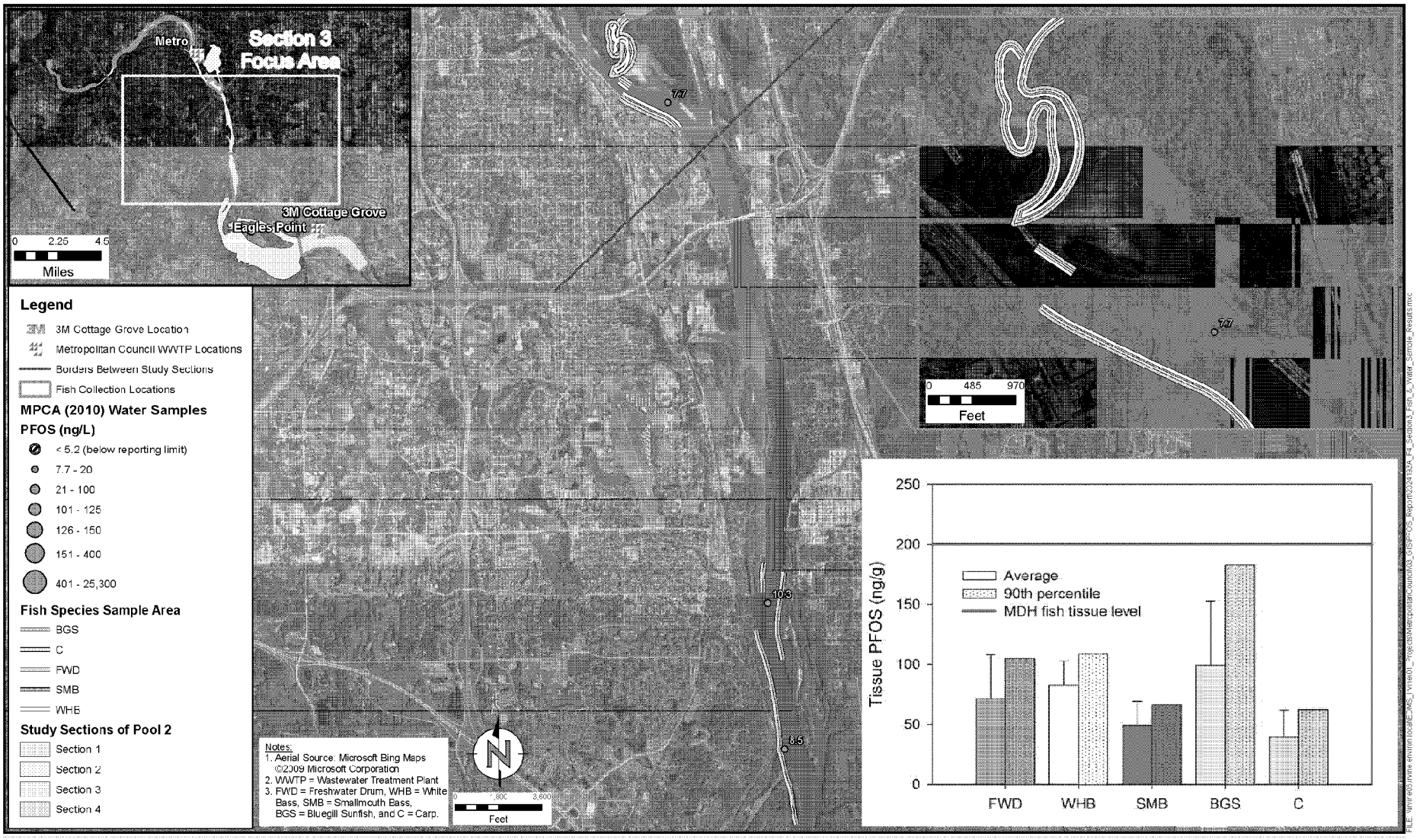
Minnesota Pollution Control Agency (MPCA) Mississippi River Pool 2
Section 2 Fish and Water Sample Results

Figure 3

PROJECT: 20 24193A



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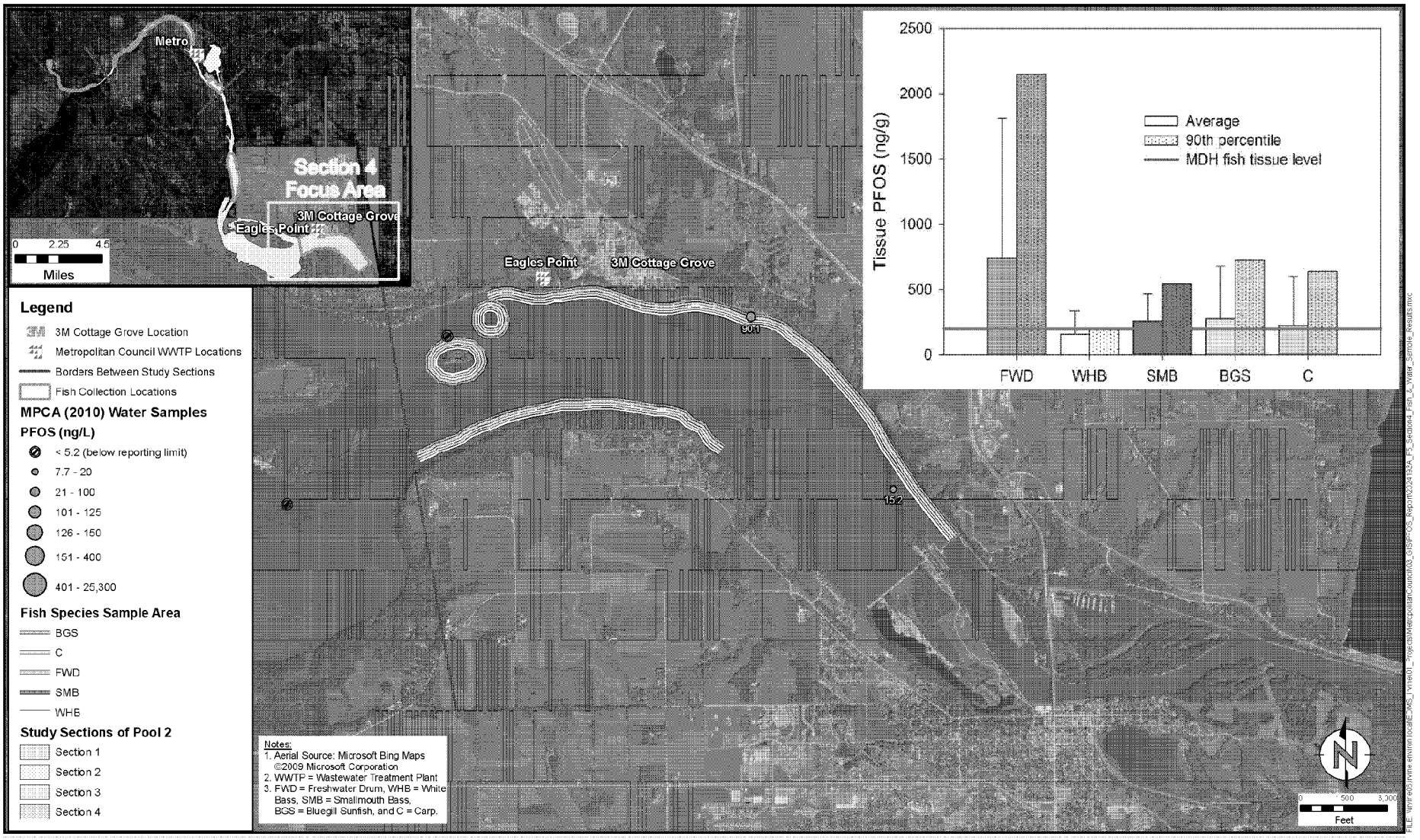
Minnesota Pollution Control Agency (MPCA) Mississippi River Pool 2
Section 3 Fish and Water Sample Results

Figure 4

PROJECT: 20 24193A



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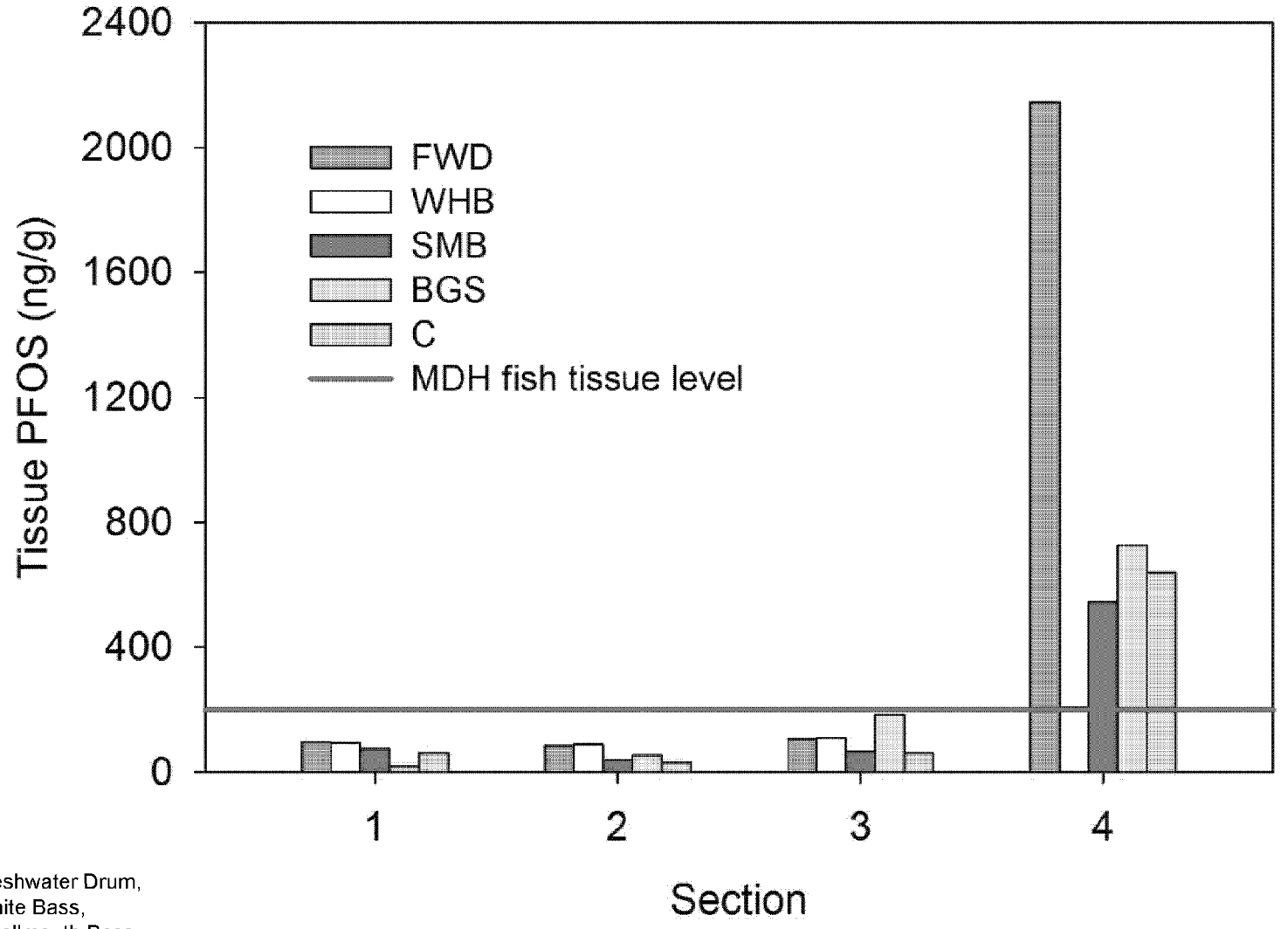
Minnesota Pollution Control Agency (MPCA) Mississippi River Pool 2
Section 4 Fish and Water Sample Results

Figure 5

PROJECT: 30 24193A



Notes:
1. FWD = Freshwater Drum,
   WHB = White Bass,
   SMB = Smallmouth Bass,
   BGS = Bluegill Sunfish, and
   C = Carp.

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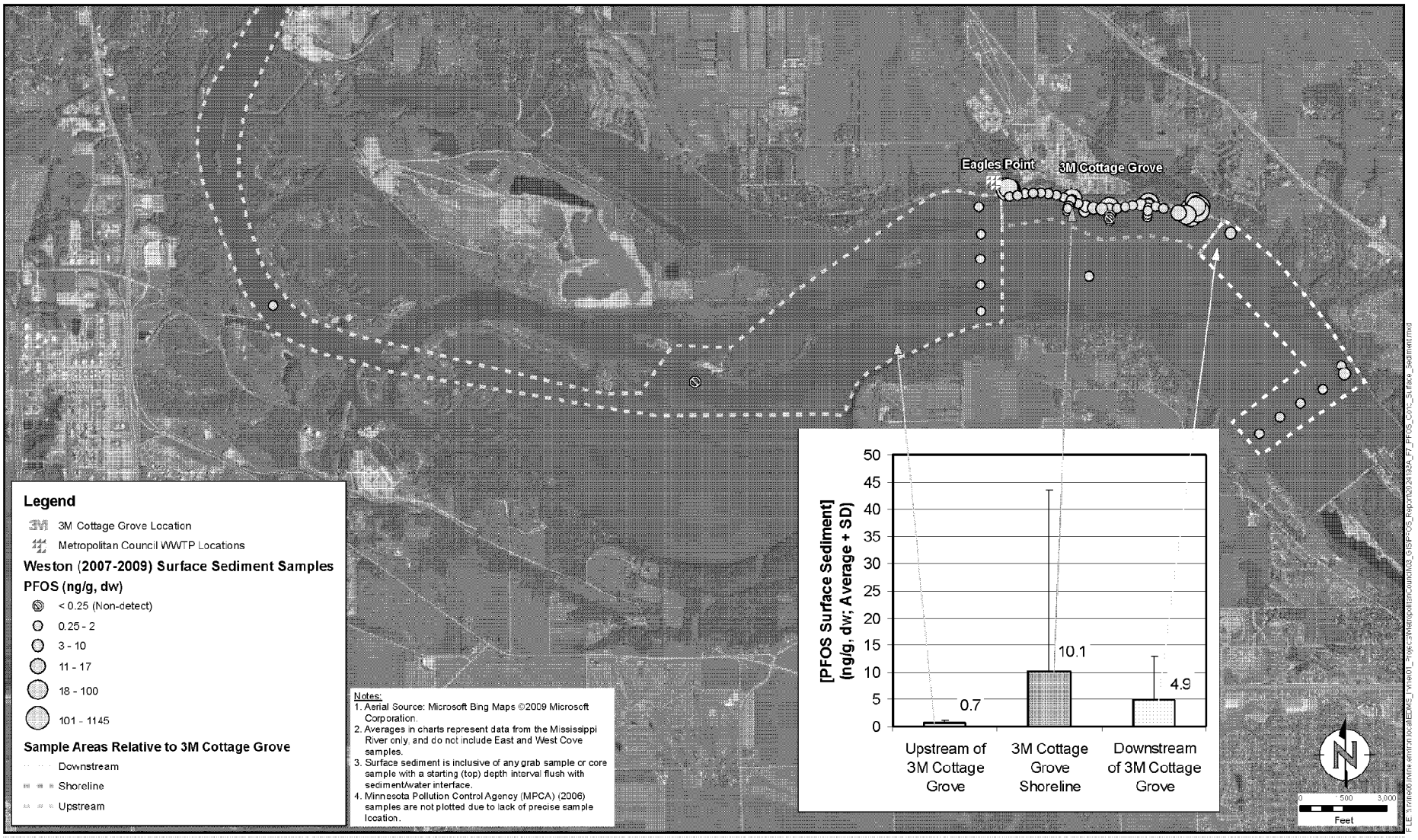
90th Percentile Concentrations of Perfluorooctane Sulfonate (PFOS) in Fish Fillet by Species

Figure 6

PROJECT: 20-24193A



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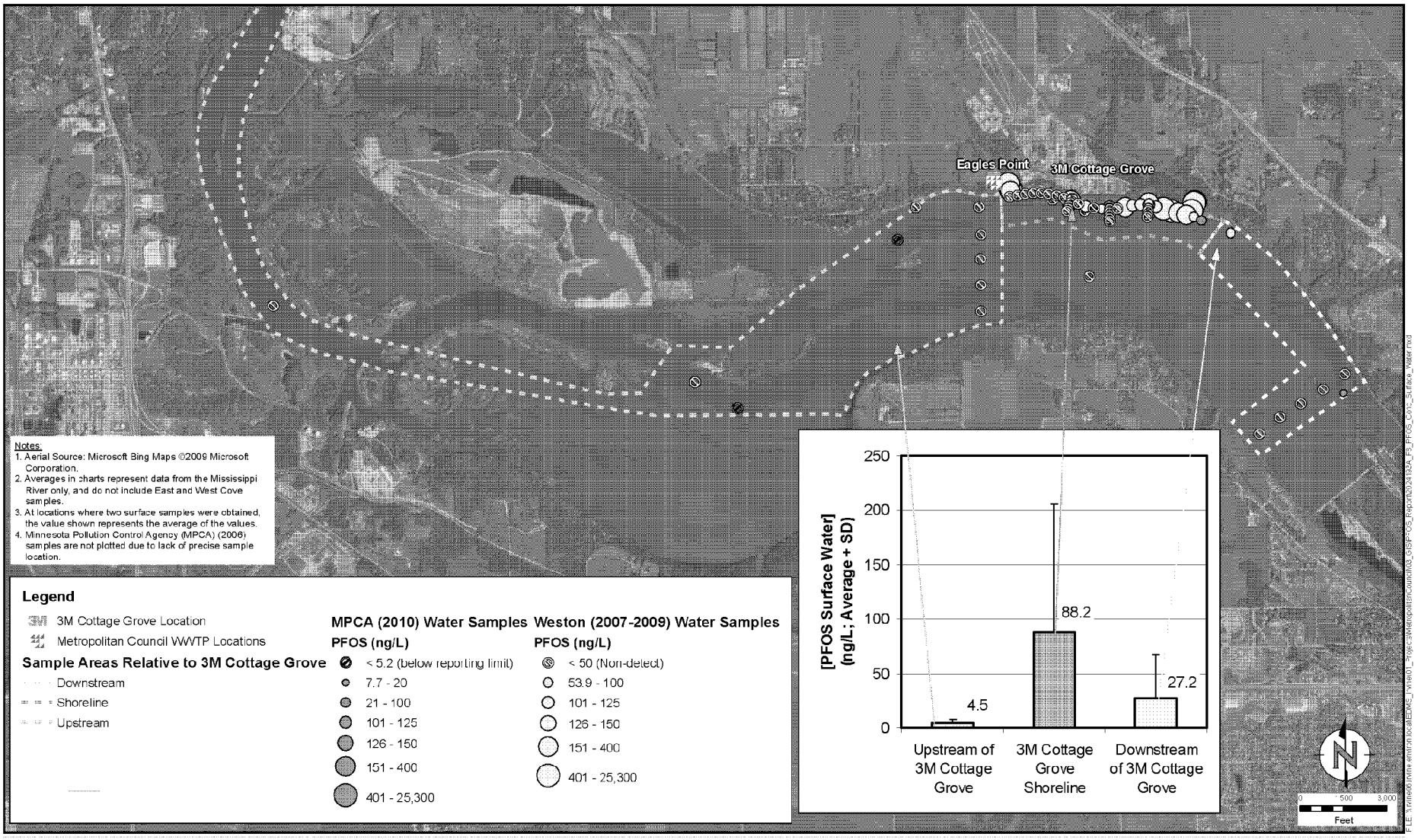
Concentrations of Perfluorooctane Sulfonate (PFOS) in Lower Mississippi River Pool 2 Surface Sediment

Figure 7

PROJECT: 20-24103A



ENVIRON	Concentrations of Perfluorooctane Sulfonate (PFOS) in Lower Mississippi River Pool 2 Water	Figure 8
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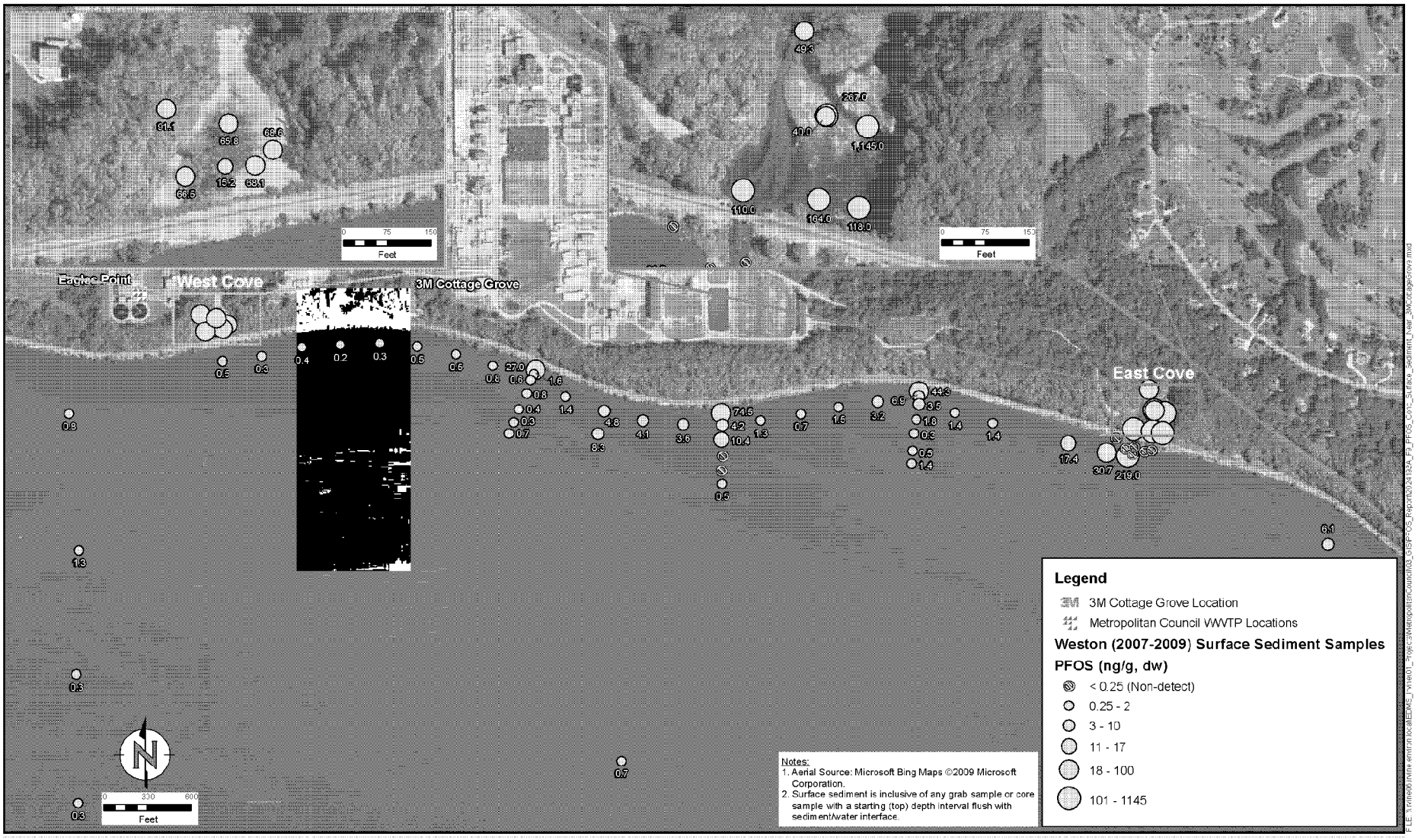

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Concentrations of Perfluorooctane Sulfonate (PFOS) in Lower Mississippi River Pool 2 Surface Sediment Near 3M Cottage Grove

Figure 9

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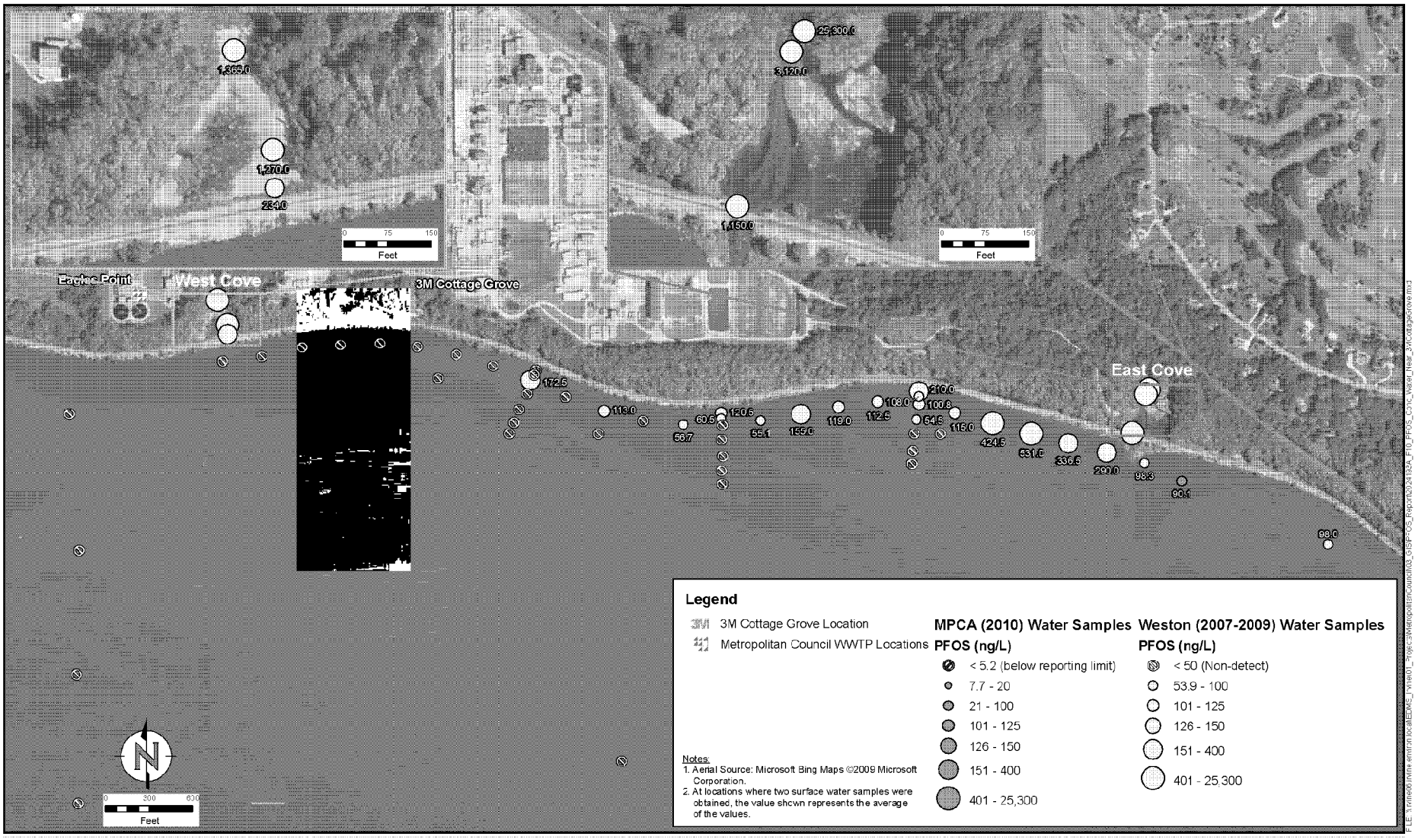
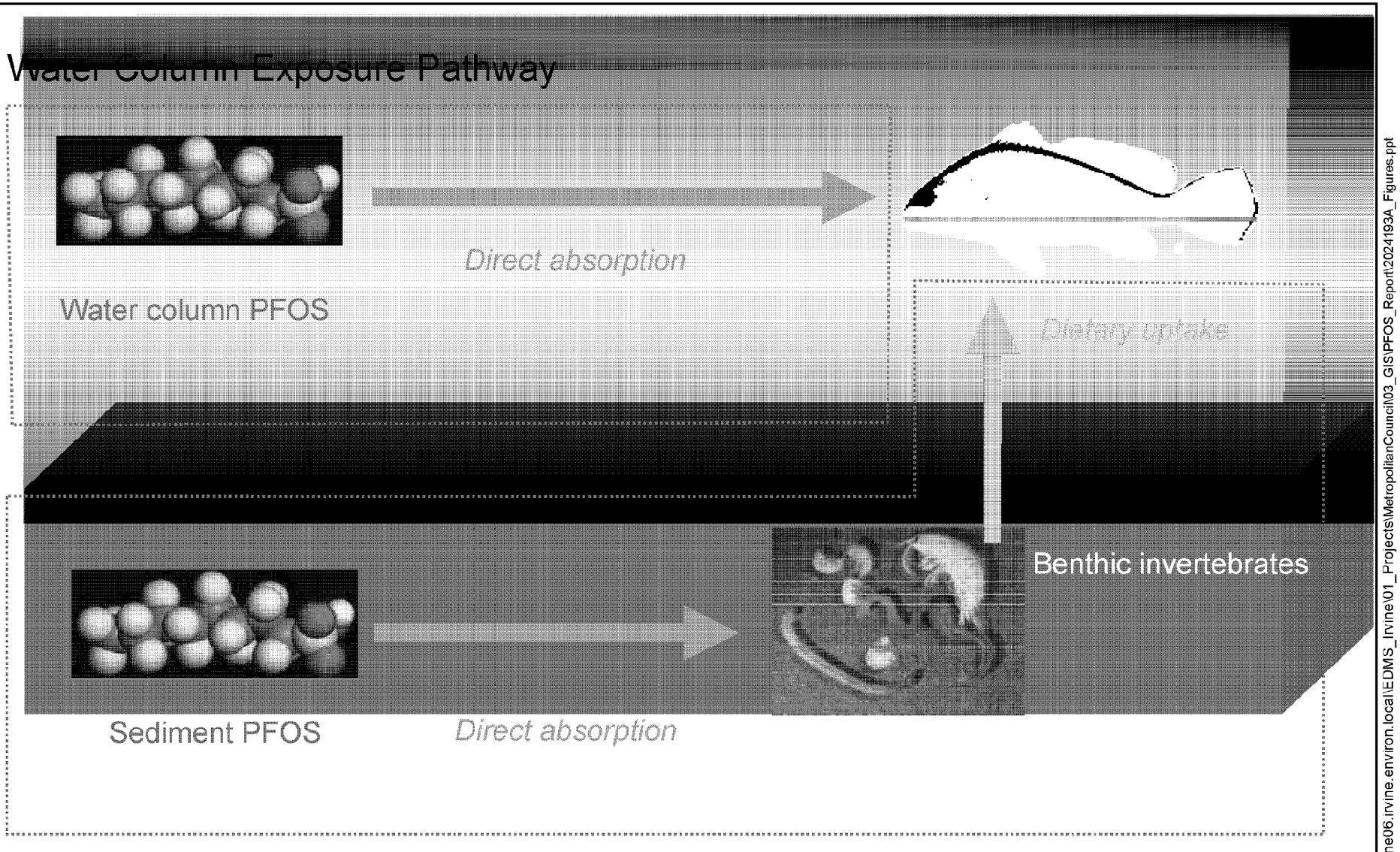


ENVIRON	Concentrations of Perfluorooctane Sulfonate (PFOS) in Lower Mississippi River Pool 2 Water Near 3M Cottage Grove	Figure 10
DRAFTED BY: MMcMeechan DATE: 10/19/2010		PROJECT: 20-24103A



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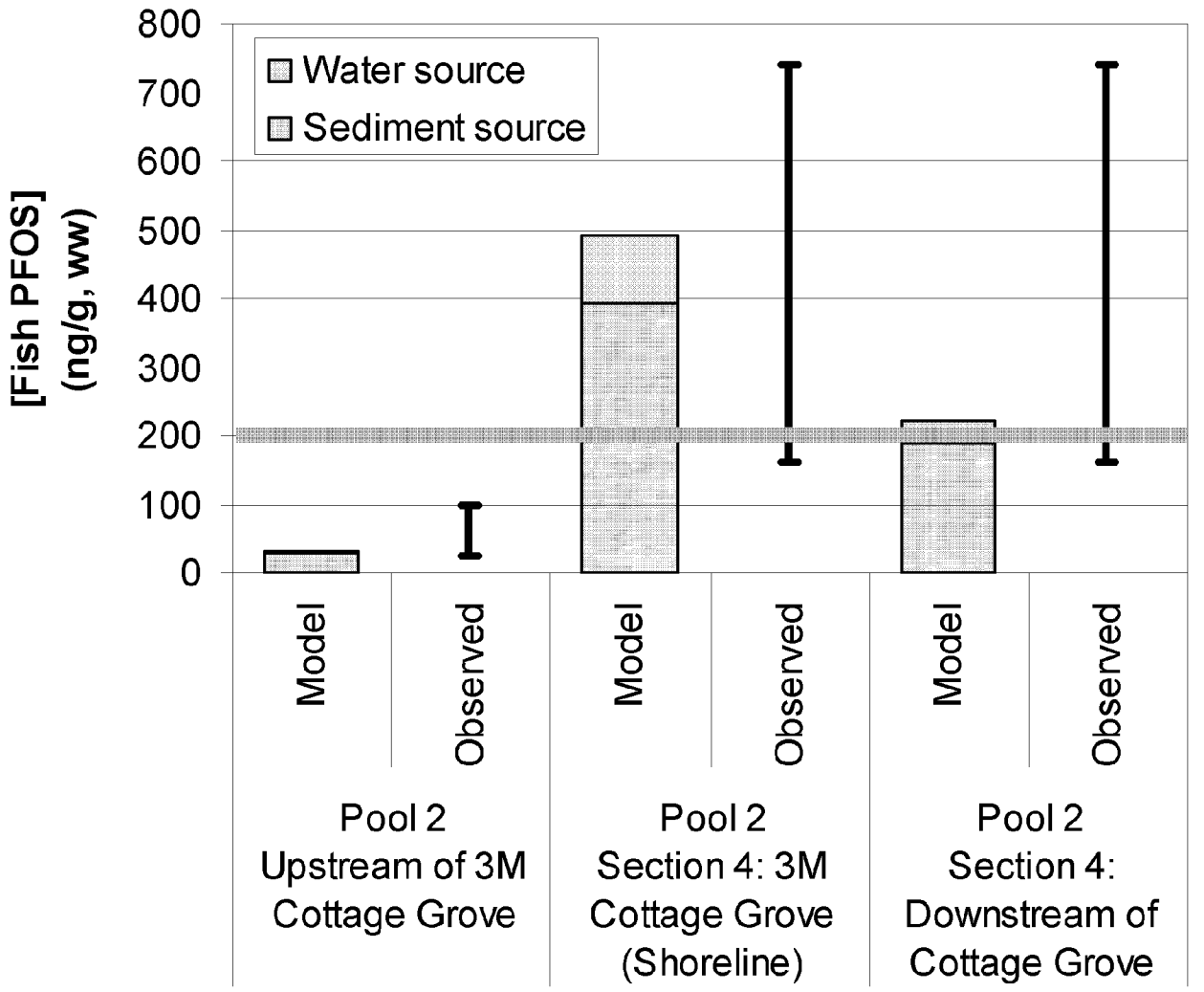
Conceptual Model Design for the Pool 2 PFOS Fish Bioaccumulation Model

Figure 11

PROJECT: 20-24193A



Notes:
1. PFOS = Perfluorooctane Sulfonate
2. Red line represents MDH PFOS fish tissue advisory level.

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PFOS Bioaccumulation Model Predictions Compared to Ranges of Observed Average PFOS Concentrations in Fish

Figure 12

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