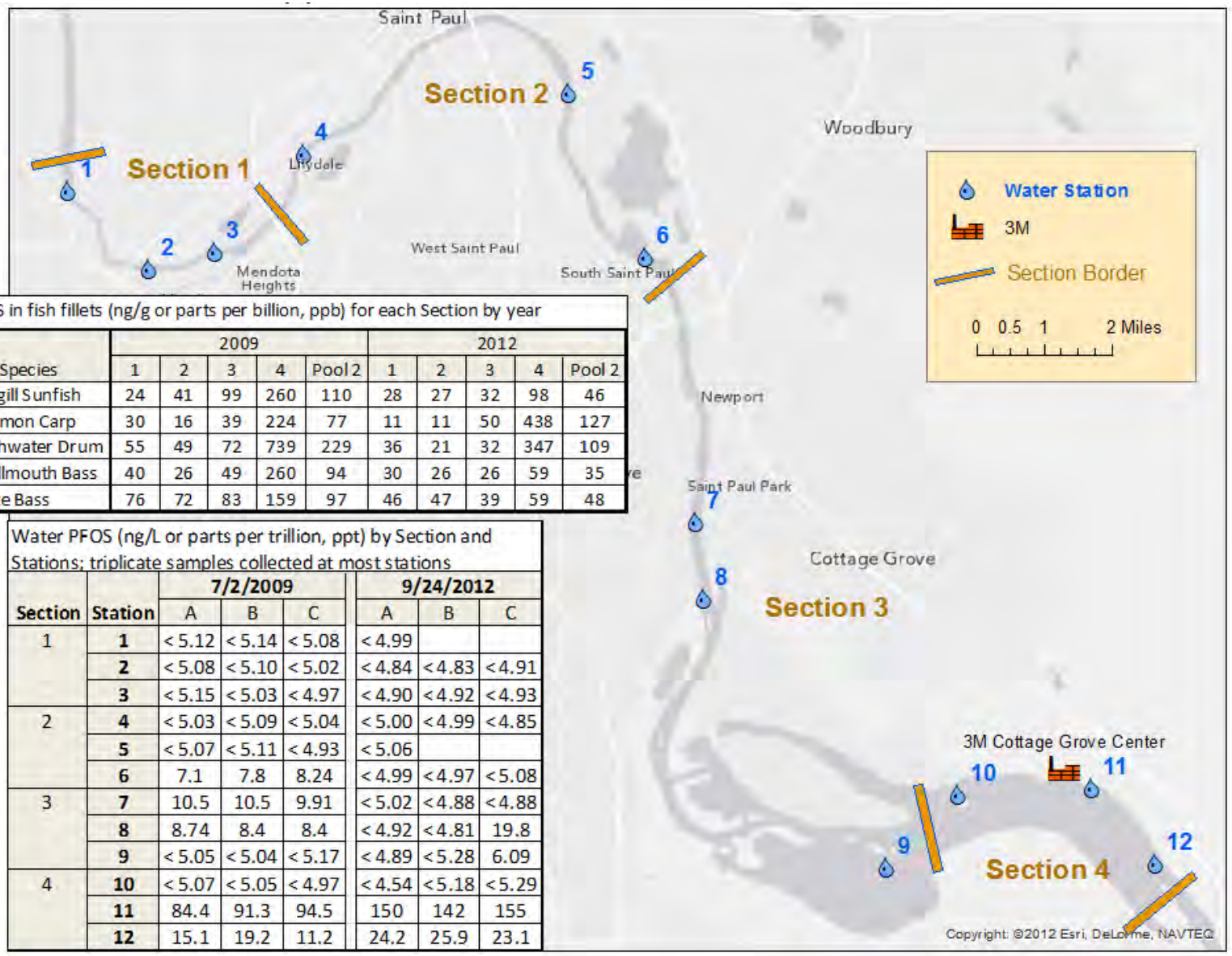
Perfluorochemicals in Mississippi River Pool 2: 2012 Update

Fish, benthic invertebrates, water, and sediment were tested for PFCs in 2012. Results are summarized and compared to previous results from Pool 2.

Minnesota Pollution Control Agency

May 2013



PFOS in fish fillets (ng/g or parts per billion, ppb) for each Section by year

	2009					2012				
Fish Species	1	2	3	4	Pool 2	1	2	3	4	Pool 2
Bluegill Sunfish	24	41	99	260	110	28	27	32	98	46
Common Carp	30	16	39	224	77	11	11	50	438	127
Freshwater Drum	55	49	72	739	229	36	21	32	347	109
Smallmouth Bass	40	26	49	260	94	30	26	26	59	35
White Bass	76	72	83	159	97	46	47	39	59	48

Water PFOS (ng/L or parts per trillion, ppt) by Section and Stations; triplicate samples collected at most stations

		7/2/2009			9/24/2012		
Section	Station	A	B	C	A	B	C
1	1	< 5.12	< 5.14	< 5.08	< 4.99		
	2	< 5.08	< 5.10	< 5.02	< 4.84	< 4.83	< 4.91
	3	< 5.15	< 5.03	< 4.97	< 4.90	< 4.92	< 4.93
2	4	< 5.03	< 5.09	< 5.04	< 5.00	< 4.99	< 4.85
	5	< 5.07	< 5.11	< 4.93	< 5.06		
	6	7.1	7.8	8.24	< 4.99	< 4.97	< 5.08
3	7	10.5	10.5	9.91	< 5.02	< 4.88	< 4.88
	8	8.74	8.4	8.4	< 4.92	< 4.81	19.8
	9	< 5.05	< 5.04	< 5.17	< 4.89	< 5.28	6.09
4	10	< 5.07	< 5.05	< 4.97	< 4.54	< 5.18	< 5.29
	11	84.4	91.3	94.5	150	142	155
	12	15.1	19.2	11.2	24.2	25.9	23.1

Figure ES-1. Locations of Sections and Stations and summary tables of mean PFOS concentrations in fish and water

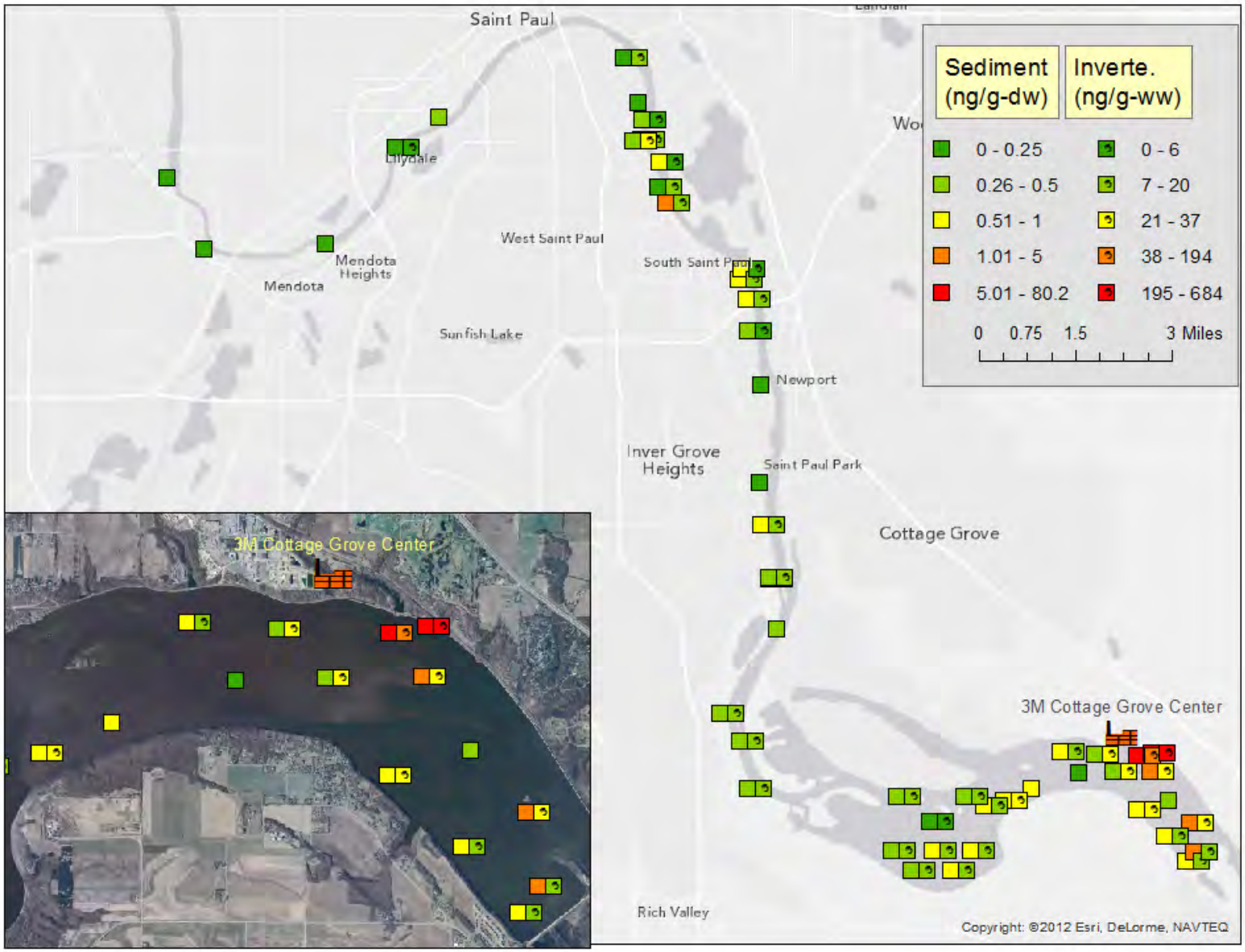


Figure ES-2. PFOS concentrations in sediment and benthic invertebrates in Pool 2 from 2011-2012

Why this study?

The MPCA is the state agency responsible for assessing and listing impaired waters for Minnesota, subject to federal U.S. Environmental Protection Agency (EPA) approval. MPCA rules specify that the MPCA shall list waters as impaired if the fish consumption advisory for a lake or river is more restrictive than a meal per week (Minn. R. 7050.0150, subp. 7). Pool 2 had been listed as impaired for mercury and PCBs in fish. Impairment caused by PFOS in fish was added in 2008, based on a one meal per month advisory for bluegill sunfish in 2007. Freshwater drum, first sampled in 2009, also had PFOS levels that warranted a meal per month advisory.

The 2012 sample collection was a follow-up to the 2009 intensive study by the MPCA and the 2011 study by Cardno-Entrix for 3M. The MPCA and the Minnesota Department of Natural Resources (MDNR), with participation of the Minnesota Department of Health (MDH), have analyzed fish and river water for PFCs from Pool 2 since 2004. The 2009 study—which was designed together by 3M, MPCA, MDNR, and MDH—was the first year when the entire 32.5 mile reach of Pool 2 was sampled for PFCs in fish and water. Earlier collections focused on the lower five miles of Pool 2. Of the 367 fish analyzed from 2004 to 2009, 297 (81 percent) were collected in 2009.

To characterize the spatial distribution of PFCs in 2009, Pool 2 was divided into four sections, with Section 1 at the most upstream end and Section 4 above the Hastings Dam (Figure 1). That same monitoring plan was followed in 2012.

The 2011 study conducted by 3M was similar to the 2009 study design except that Pool 2 was divided into ten reaches (instead of four), three water samples were collected in each reach but not at the same location. Carp were not collected in 2011, but the other four species tested in 2009 were collected. Ten fish of each species were collected in each reach, for a total of 400 fish. Compared to the 2009 study, the 2011 sampling design collected 100 of each species instead of 60 of each species and reduced the percentage of fish collected in the lower reach (Section 4) from 25 percent (15/60 per species) to 18 percent (18/100 per species). The report by Cardno-Entrix and a second report by Exponent in November 2011 comparing the 2009 and 2011 results showed PFOS concentrations had declined from 2009 in the four tested fish species. Because of lower PFOS concentrations in 2011, the average PFOS concentration for the combined years dropped below the meal per month advisory threshold to an advisory level of one meal per week.

MPCA did not delist Pool 2 as impaired for PFOS in fish based on the 2011 study because it was not sufficient to indicate a permanent downward trend in the PFOS concentrations and the sampling design in 2011 differed from the 2009 sampling design. Consequently, MPCA conducted the 2012 study, following the same sample design as 2009, to determine if the PFOS concentrations had indeed dropped to lower levels throughout Pool 2.

In addition to collection of fish and water in 2012, the MPCA collected sediments and benthic macroinvertebrates in 2011 and 2012 to better understand the extent of the PFC contamination in Pool 2 and the possible direct source of PFOS in the fish. Unlike fish and water, sediments and insect nymphs living in the sediments are stationary and better represent the specific locations within the river. Freshwater drum and common carp, which had the highest PFOS concentrations in 2009, feed on sediments and benthic invertebrates more so than the other tested fish species.

Conclusions

Compared to 2009 PFOS concentrations in the targeted fish species declined in the last two years (2011 and 2012) of monitoring in Pool 2. PFOS concentrations in water from the Lower Pool 2 did not decline. Consequently, the calculated bioaccumulation factors were lower, which led to a higher site-specific water quality criterion for PFOS: from 7 ng/L calculated from 2009 results to 14 ng/L calculated from 2012 results.

Despite the average decline for all of Pool 2, PFOS concentrations in all tested media—fish, benthic macroinvertebrates, sediment, and water—remain high in the Lower Pool 2, downstream of the 3M Cottage Grove Center.

References

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Tables

Table 1. PFOS concentrations (ng/L) in water samples collected at the same twelve stations in 2009 and 2012; A, B, and C refer to consecutive grab samples collected at each station; in 2012 two samples from Stations 1 and 5 were used for laboratory matrix spikes.

	2 July 2009				24 September 2012			
Station	A	B	C	Mean	A	B	C	Mean
1	< 5.12	< 5.14	< 5.08	< DL	< 4.99			< DL
2	< 5.08	< 5.10	< 5.02	< DL	< 4.84	< 4.83	< 4.91	< DL
3	< 5.15	< 5.03	< 4.97	< DL	< 4.90	< 4.92	< 4.93	< DL
4	< 5.03	< 5.09	< 5.04	< DL	< 5.00	< 4.99	< 4.85	< DL
5	< 5.07	< 5.11	< 4.93	< DL	< 5.06			< DL
6	7.1	7.8	8.24	7.7	< 4.99	< 4.97	< 5.08	< DL
7	10.5	10.5	9.91	10.3	< 5.02	< 4.88	< 4.88	< DL
8	8.74	8.4	8.4	8.5	< 4.92	< 4.81	19.8	< DL?
9	< 5.05	< 5.04	< 5.17	< DL	< 4.89	< 5.28	6.09	< DL?
10	< 5.07	< 5.05	< 4.97	< DL	< 4.54	< 5.18	< 5.29	< DL
11	84.4	91.3	94.5	90.1	150	142	155	149
12	15.1	19.2	11.2	15.2	24.2	25.9	23.1	24.4

Table 2. Descriptive statistics for PFOS (ng/g -ww) in the five target fish species; combined results for 2004-2012

	Statistic					
Species	N	Minimum	Maximum	Arithmetic Mean	Geometric Mean	Median
Bluegill Sunfish (BGS)	230	3.57	2097	83.0	31.4	28.6
Common Carp (C)	125	0.995	6160	107.0	21.2	23.6
Freshwater Drum (FWD)	220	3.17	3580	113.1	36.9	34.1
Smallmouth Bass (SMB)	246	2.37	5150	99.7	40.4	32.8
White Bass (WHB)	219	13.0	1860	80.9	62.5	59.7

Table 3. PFOS concentrations (ng/g -ww) for each fish species and year from all of Pool 2 (left) and only Lower Pool 2—Section 4 (right); the top row of each species is for all years; results from the study in 2011 used lower Reach 9 and Reach 10 to represent the Lower Pool 2; in 2004-2008 all fish were collected in the Lower Pool 2.

	Mississippi Pool 2 (all reaches)					Lower Pool 2 (Section 4)				
Species-Year	N	Min	Max	Arith. Mean	Median	N	Min	Max	Arith. Mean	Median
BGS	230	3.6	2097	83	29	61	4.5	2097	204	46
2006	6	30	709	249	195	6	30	709	249	195
2007	2	2001	2097	2049	2049	2	2001	2097	2049	2049
2008	5	102	317	173	157	5	102	317	173	157
2009	57	8.3	1350	110	45	15	32	1350	260	53
2011	100	3.6	392	36	18	18	4.5	305	63	26
2012	60	6.8	1020	46	26	15	11	1020	98	28
C	125	1.00	6160	107	24	35	6.0	6160	315	56
2005	5	66	420	216	175	5	66	420	216	175
2009	60	4.7	1340	77	28	15	8.7	1340	224	87
2012	60	1.00	6160	127	11	15	6.0	6160	438	15
FWD	220	3.2	3580	113	34	48	4.8	3580	356	33
2009	60	4.8	3580	229	63	15	24	3580	739	401
2011	100	3.2	607	46	30	18	4.8	607	81	22
2012	60	3.9	1580	109	25	15	6.0	1580	347	23
SMB	246	2.4	5150	100	33	69	7.3	5150	252	83
2004	4	92	985	528	517	4	92	985	528	517
2005	6	122	336	201	163	6	122	336	201	163
2006	11	19	5150	793	178	11	19	5150	793	178
2008	5	49	380	162	120	5	49	380	162	120
2009	60	13	612	94	41	15	42	612	260	210
2011	100	4.9	757	39	30	13	9.5	757	109	44
2012	60	2.4	192	35	28	15	8.1	192	59	47
WHB	219	13	1860	81	60	50	27	1860	144	78
2004	2	137	139	138	138	2	137	139	138	138
2005	5	84	1860	559	240	5	84	1860	559	240
2009	60	38	764	97	75	15	44	764	159	88
2011	96	13	394	64	58	15	41	394	92	71
2012	56	20	153	48	42	13	27	153	59	46

Table 4. Summary statistics for sediment and invertebrate measurements

	Statistic					
Measurement	N	Minimum	Maximum	Arithmetic Mean	Geometric Mean	Median
Percent Moisture	58	20.8	61.9	38.95	37.57	37.5
Fraction Organic Carbon, f_{OC} (%)	58	0.10	12.8	1.30	0.90	1.00
Sediment PFOS dry wt. (ng/g)	58	<0.188	80.2	3.405	0.548	0.497
Sediment PFOS wet wt. (ng/g)*	50	0.072	32.6	1.848	0.423	0.310
Sediment PFOS per OC. (ng/g)*	50	2.3	2,823	235.3	66.5	56.1
Invertebrate PFOS wet wt. (ng/g)	39	1.65	684	35.71	13.41	11.9

*Eight dry weight sediment PFOS concentrations were less than the reporting limit, precluding calculation of wet weight concentrations for those eight.

Table 5. Replicates of sediment PFOS concentrations with matching invertebrate PFOS concentrations and BSAF

Date	Sample ID_Sed	Sed_PFOS_ ng/g_dw	sed_% Moisture	Sed_PFOS ng/g_ww	foc	Sed_PFOS ng/g _OC
11/23/11 15:00	517 SED1	80.2	59.3	32.64	2.84%	2,824
11/23/11 15:10	517 SED2	33.3	51.1	16.28	1.75%	1,903
11/23/11 15:18	517 SED3	41.1	52.9	19.36	1.62%	2,537
	RSD	48.8	7.9	38.2	32.4	19.5
10/16/12 15:06	K SED	8.58	45.8	4.65	0.98%	874.2
10/16/12 15:10	K SED FD	6.38	43.5	3.60	0.70%	916.7
	RSD	20.8	3.6	17.9	24.1	3.4
10/16/12 11:20	G SED	0.601	40.6	0.357	0.95%	63.0
10/16/12 11:25	G SED FD	0.860	45.9	0.465	1.13%	76.1
	RSD	25.1	8.7	18.6	11.9	13.4
10/16/12 13:55	M SED	0.203	25.9	0.150	0.36%	56.2
10/16/12 13:58	M SED FD	0.366	28.6	0.261	0.66%	55.8
	RSD	40.5	7.0	38.1	41.1	0.6
05/22/12 14:00	MC_1_SED	0.905	44.6	0.501	2.17%	41.8
05/22/12 14:05	MC_2_SED	0.672	32.2	0.456	1.67%	40.2
05/22/12 14:15	MC_3_SED	0.581	26.8	0.425	0.59%	98.6
	RSD	23.2	26.4	8.3	54.6	55.2
05/23/12 13:55	P2_525_SED	0.525	61.9	0.200	2.03%	25.9
11/30/11 13:10	525 SED	0.330	39.2	0.198	1.17%	27.9
	RSD	33.1	31.8	0.6	37.8	5.1

Figures

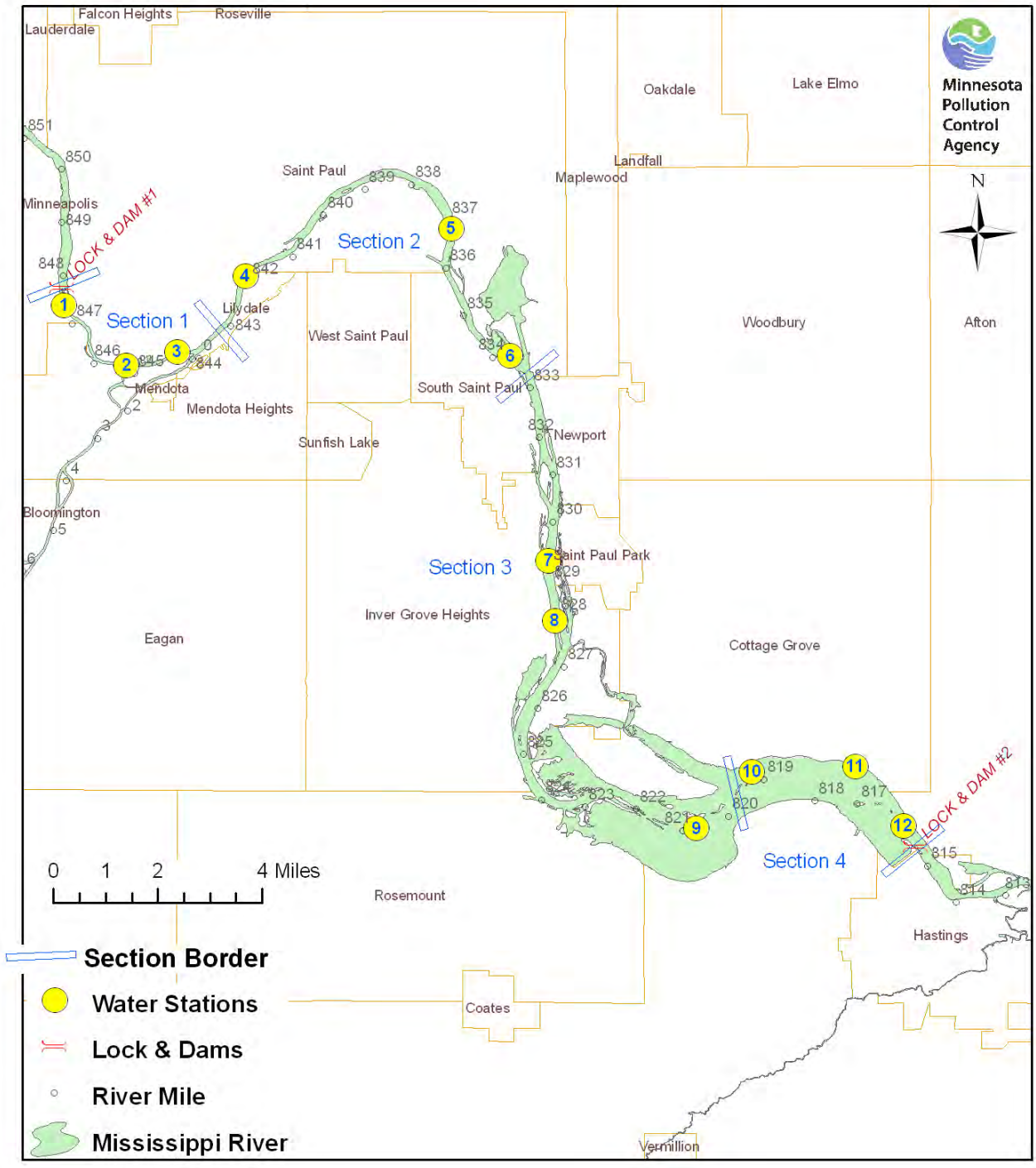

Figure 1. Pool 2 showing river miles between Lock & Dam No. 1 at river mile 847.6 to Lock & Dam No. 2 at river mile 815.6 (~32.5 miles); shows four sections and PFC water stations for 2009 and 2012