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Sent:	Saturday, October 15, 2005 12:10 AM
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Cc:	Wiegner, Harold (MPCA); Julik, Joseph (MPCA)
Subject:	RE: Oct2005recommendationstoGaryMemo.DOC
Attachments:	Fardin-CLP05-PFCproposal.doc; Fardin Notes-PFC Study.doc

Please see the attached files, describing the sampling and the preliminary results of our PFC investigation as was presented in our last PFC lateral team meeting dated September 28, 2005.

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Preliminary results of the MPCA PFC Investigation

Prepared by Fardin Oliaei, Principal Investigator

This report is intended to provide the preliminary results of our PFC investigation as was presented in our last PFC lateral team meeting dated September 28, 2005. It is important to emphasize that this study was the first phase PFC study conducted by MPCA staff and was independent of the 3M Weston PFC study. This study provided for a much more complete evaluation of the PFC compounds in the media studied, since 12 individual PFC compounds are analyzed as a part of the MPCA studies versus the 4 PFCs proposed in the 3M Weston study.

Briefly, the MPCA PFC investigation consists of sampling and subsequent analysis of perfluorocarbon compounds (PFCs) in various environmental media. This study was undertaken in order to determine the presence and extent of contamination of PFCs in the Minnesota environment, to enhance and complement other PFC characterization studies underway, and to begin to study the behavior of these compounds in various environmental media. The MPCA sampling for this investigation was conducted by the following MPCA staff: Fardin Oliaei, Joe Julik, Ingrid Verhagen, Katrina Kessler, Enrique Gentzsch, Harold Wiegner, and Don Kriens. Minnesota Department of Natural Resources staff, Jack Enblom and Mark Briggs, collected all fish for PFC analyses in this study.

A detailed sampling effort for this investigation is described in a separated report entitled "MPCA PFC Investigation: June 30, 2005" (Please see the attached file: Fardin-CLP05-PFCproposal).

A. MPCA Washington County Landfill PFC Study

PFCs sampling conducted at the Washington County Landfill included:

1. Water samples from two groundwater monitoring wells (J and V2) at the site,
2. Water samples from surface water ponded at the site,
3. Soil (sediment) samples from the surface below ponded water,
4. Soil samples from soil borings conducted, and
5. Background soil from soil borings conducted.

All samples were analyzed for the following PFC parameters: PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFBS, PFHxS, and PFOS.

A. 1. Water samples from groundwater monitoring wells:

Ground water samples (wells J and V2) were collected during fall 2004 of the monitoring system at the landfill. Duplicate samples were collected by the sampling contractor,

Interpoll Laboratories. One set was analyzed by MDH Environmental Laboratory and the other set was sent to Axys Laboratory.

The MDH reporting limits are <1.0 and <0.5 ug/L respectively but there were no estimates below these levels of PFOS or PFOA in well J. Axys Laboratories analyzed the sample from well J at the ng/mL level and detected only 0.001 of PFNA and 0.002 of PFDoA but not PFOS or PFOA.

CLIENT ID	Washington Co. Well J	Washington Co. Well V2
UNITS	ng/mL	ng/mL
PFBA	<0.110	1170
PFPeA	<0.0205	43.1
PFHxA	<0.0037	15.6
PFHpA	<0.0044	2.38
PFOA	<0.0027	41.6
PFNA	0.001	0.012
PFDA	<0.0015	0.006
PFUnA	<0.0009	<0.0039
PFDoA	0.002	<0.0032
PFTA	<0.0005	<0.0020
PFBS	<0.0201	1.31
PFHxS	<0.0257	1.77
PFOS	<0.0030	2.69
Total PFCs	**0.003**	**1278.468**

A. 2. Water samples from surface water ponded at the site:
Two surface water samples were collected from ponded water at the site. The ponded water represents water from the groundwater pump-out spray irrigation system.

CLIENT ID	Wash -CL-water#1	Wash-CL-water #2
UNITS	ng/mL	ng/mL
PFBA	371	352
PFPeA	7.98	6.89
PFHxA	3.36	3.28
PFHpA	0.582	0.659
PFOA	10.9	15.2
PFNA	0.009	0.006
PFDA	<0.0156	0.027
PFUnA	<0.0068	0.016
PFDoA	<0.0142	0.016
PFTA	<0.0202	<0.0103
PFBS	<0.333	<0.252
PFHxS	<0.422	<0.300
PFOS	1.35	1.67
Total PFCs	**395.18**	**379.76**

A. 3. Soil (sediment) samples from the surface below ponded water:
Two surface sediment or soil samples were collected at 2 areas where water had ponded as a result of the groundwater pump-out spray irrigation system. The ponded water would primarily consist of groundwater pumped out under the site. Three subsamples (3-4 cm depth) were collected from two different sites (Sediment #1 and Sediment #2).

CLIENT ID	**Wash-CL-sediment #1**	**Wash-CL-sediment #2**
UNITS	ng/g (dry weight basis)	ng/g (dry weight basis)
PFBA	13.5	22.9
PFPeA	1.27	2.64
PFHxA	2.54	3.66
PFHpA	0.669	0.858
PFOA	22.3	31.1
PFNA	<0.331	<0.350
PFDA	0.4	0.545
PFUnA	<0.317	<0.335
PFDoA	<0.315	<0.333
PFBS	<0.314	<0.332
PFHxS	0.355	<0.333
PFOS	10	14.6
PFOSA	<0.309	<0.327
Total PFCs	**51.034**	**76.303**

A. 4. Soil samples from soil borings conducted:
A soil boring was completed at a location right at the edge of the landfill treatment area (TA-1) where the groundwater monitoring determined contamination of PFCs at this location. The soil boring was completed to collect soil samples at specific depth increments. Analysis of PFCs was done at 15 increments to determine the extent of PFC soil contamination at various depths.

CLIENT ID	#1 (0-1ft)	#2 (1-2ft)	#3 (4.5ft)	#4 (5.5ft)	#4 (5.5ft) (DUP)	#6 (7.5ft)	#8 (9.5ft)	#10 (12.5ft)
% MOISTURE	12.5	8.6	12.1	7.69	8.33	12.3	9.31	8.6
UNITS	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g
PFBA	5.49	2.68	3.67	3.33	3.25	3.01	1.45	3.06
PFPeA	0.471	<0.209	0.328	0.375	<0.205	<0.233	0.226	0.299
PFHxA	0.702	0.375	0.405	0.465	0.424	0.58	0.416	0.495
PFHpA	0.223	<0.206	<0.223	<0.203	<0.201	0.247	<0.207	0.293
PFOA	10.5	3.59	2.66	8.51	8.89	5.42	4.28	21.6
PFNA	<0.230	<0.220	<0.238	<0.217	<0.215	<0.245	<0.221	<0.222
PFDA	0.24	<0.212	<0.230	<0.209	<0.208	<0.237	<0.214	<0.214
PFUnA	<0.220	<0.210	<0.227	<0.207	<0.206	<0.234	<0.212	<0.212
PFDoA	<0.218	<0.209	<0.226	<0.206	<0.204	<0.233	<0.211	<0.211
PFBS	<0.218	<0.208	<0.225	<0.205	<0.204	<0.232	<0.210	<0.210
PFHxS	<0.218	<0.209	<0.226	<0.206	<0.204	<0.233	<0.211	<0.211
PFOS	7.83	2.43	0.719	4.19	4.49	3.41	3.59	8.41
PFOSA	<0.214	<0.205	<0.222	<0.202	<0.200	<0.228	<0.207	<0.207
Total PFCs	**25.456**	**9.075**	**7.782**	**16.87**	**17.054**	**12.667**	**9.962**	**34.157**

CLIENT ID	#11 (13.5ft)	#12 (16ft)	#14 (18ft)	#16 (20ft)	#18 (22ft)	#20 (24ft)	#22 (26ft)
% MOISTURE	7.57	6.92	13.8	3.07	3.42	3.54	5.99
UNITS	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g
PFBA	2.38	2.9	3.87	0.874	1.01	1.63	2.64
PFPeA	<0.219	0.291	0.427	<0.216	<0.208	<0.209	<0.209
PFHxA	0.426	0.296	0.526	<0.209	<0.202	0.233	0.387
PFHpA	0.239	<0.207	0.245	<0.212	<0.204	<0.205	<0.206
PFOA	21.7	1.89	7.94	<0.208	1.43	1.24	9.58
PFNA	<0.230	<0.221	<0.245	<0.226	<0.218	<0.219	<0.220
PFDA	<0.222	<0.214	<0.237	<0.219	<0.211	<0.211	<0.212
PFUnA	<0.220	<0.212	<0.234	<0.216	<0.209	<0.209	<0.210
PFDoA	<0.219	<0.210	<0.233	<0.215	<0.207	<0.208	<0.209
PFBS	<0.218	<0.209	<0.232	<0.214	<0.207	<0.207	<0.208
PFHxS	<0.219	<0.210	<0.233	<0.215	<0.207	<0.208	<0.209
PFOS	6.1	1.51	1.54	<0.218	<0.210	<0.211	1.48
PFOSA	<0.215	<0.206	<0.228	<0.211	<0.203	<0.204	<0.205
Total PFCs	**30.845**	**6.887**	**14.548**	**0.874**	**2.44**	**3.103**	**14.087**

A. 5. Background soil from soil borings conducted:
A background soil boring was completed in an area outside of the influence of the landfill site contamination. Soil samples were also collected at 4 specific depth increments for the background soil boring.

CLIENT ID	Background soil surface	Background soil surface (DUP)	Background Soil -4ft	Background Soil-6ft	Background Soil-8ft
% MOISTURE	12.2	12.3	4.96	19.7	4.53
UNITS	ng/g (dry weight basis)	ng/g (dry weight basis)	ng/g (dry weight basis)	ng/g (dry weight basis)	ng/g (dry weight basis)
PFBA	0.6	0.388	<0.217	<0.243	<0.202
PFPeA	<0.233	<0.219	<0.214	<0.239	<0.200
PFHxA	<0.226	<0.213	<0.208	<0.232	<0.194
PFHpA	<0.229	<0.215	<0.210	<0.235	<0.196
PFOA	1.28	1.23	4.25	2.52	4.87
PFNA	<0.244	<0.230	<0.224	<0.251	<0.209
PFDA	<0.236	<0.222	<0.217	<0.243	<0.202
PFUnA	<0.234	<0.220	<0.215	<0.240	<0.200
PFDoA	<0.232	<0.219	<0.213	<0.239	<0.199
PFBS	<0.231	<0.218	<0.213	<0.238	<0.198
PFHxS	<0.232	<0.219	<0.213	<0.239	<0.199
PFOS	1.66	1.46	0.309	<0.242	<0.202
PFOSA	<0.228	<0.215	<0.209	<0.234	<0.195
Total	**3.54**	**3.078**	**4.559**	**2.52**	**4.87**

B. MPCA 3M Cottage Grove Plant PFC Study

PFC sampling was conducted at the 3M Cottage Grove plant on June 27, 2005. Samples were collected from the treated process wastewater discharge SD001, the cooling water discharge SD002, the wastewater treatment plant influent (Phase 1 and 2), and the influent and effluent of the Phase 1 and 2 granular activated carbon treatment system. PFC sampling was conducted at the plant at these locations as a normal part of the NPDES program, to more fully characterize the PFC compounds discharged by analyzing 12 PFCs versus the 5 PFCs typically analyzed, to determine the performance of the wastewater treatment plant and the Phase 1 and 2 activated carbon treatment system on the day of sampling, and to determine the extent of PFC compounds in the SD002 cooling water on the day of sampling. All samples for PFC analysis were collected on June 27, 2005.

B. 1. 3M Cottage Grove WWTP PFC Study Results

- PFBS, the PFC base compound now used for 3M PFC production, was found at a concentration of 104 ppb in the SD001 discharge. PFBS was found in the cooling water at 3.9 ppb. The discharge to the river would be about 107.9 ppb.

- PFBA, resulting from current 3M C-4 PFBS based production, was found at a concentration of SD001 at 80.6 ppb, cooling water at 6.7 ppb, with a discharge to the river at 87.3 ppb.
- PFOA was found in SD001 at 62.4 ppb, cooling water at 4 ppb, with a discharge to the river at 64.4 ppb.
- PFOS was found at 19.2 ppb at SD001, cooling water at 1.7 ppb, with a discharge to the river at 20.9 ppb.
- PFHxS was found at an unexpected concentration in the cooling water at 11.3 ppb. The 3M cooling water consists of Woodbury groundwater pumpout water with some 3M Cottage Grove plant production well water.
- PFNA, PFDA, PFUnA, and PFDoA were not detected at SD001 or the cooling water with low ppt detect limits (<1.0 ppt).
- PFPeA, PFHxA, and PFHpA were found in SD001 at concentrations ranging from 2.3 to 9.96 ppb, and at relatively low ppt concentrations in the cooling water.
- With the exception of PFBS, PFC concentrations for all compounds showed an increase at SD001 versus the GAC (granular activated carbon) effluent. The GAC effluent is directed to a final SD001 channel for chlorination and pH adjustment. SD001 sample was taken just prior to the confluence with the cooling water. Differences in concentrations of GAC effluent and SD001 are likely due to the influences of the final effluent channel (retention time and possible retention of PFCs on channel sediment substrates).
- Greater concentrations of some relatively low level PFC compounds in GAC influent versus GAC effluent is most likely due to the relative retention times of the GAC system supply pond and the retention time of the activated carbon system. In other words the samples for influent and effluent GAC, although taken at approximately the same time, will not necessarily represent the same "point in time" flow due to the retention time of the activated carbon system and the retention and configuration of the GAC supply pond.
- The effluent concentrations found for the 5 PFCs monitored by 3M pursuant to the NPDES permit are comparable to those found in this study.
- The incinerator was down for maintenance during our sampling. Therefore, any contributions resulting from the incinerator blowdown stream, and the phase 3 incinerator GAC system effluent, was not included in the SD001 sampling.
- The concentration of total PFC in the discharge to the river found in this study was 321.7 ppb (SD001 plus cooling water).

B.2. 3M Granulated Activated Carbon Treatment System Efficiency

- PFOS is being removed at a relatively high efficiency at about 94%. The average PFOS (Jan 2004 through April 2005-3M data) is 6.6 ppb in the discharge.
- PFOA is not being removed very efficiently in the GAC system with a 46% removal. PFOA averaged about 45 ppb (Jan 2004 through April 2005-3M data) in the discharge.
- PFBS and PFHS are being removed at relatively acceptable rates of about 74%, although PFBS remains relatively high in the discharge at 193 ppb (Jan 2004 through April 2005-3M data).
- PFBA, found at relatively high concentration in our study, should be required as a PFC parameter for 3M NPDES monitoring. PFBA may not be removed very efficiently.
- The GAC system is apparently less effective in removal of acidic PFCs.
- The separate contribution of PFCs from the phase 3 incinerator blowdown and phase 3 activated carbon system should be measured to determine the relative contributions from the phase 1 and 2 and the phase 3 GAC systems.
- The influence of the final chlorination channel should probably be examined as a potential past reservoir for PFCs, since all PFCs in our study except for PFBS increased at SD001 from the GAC effluent.
- Further study would be required to understand PFC removal behavior through the wastewater treatment system and the activated carbon system.

CLIENT ID	WWTP-inf	WWTP-inf (DUP)	GAC-inf	GAC-efflu	SD001	SD002
UNITS	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L
PFBA	165000	178000	100000	58100	80600	6740
PFPeA	1340	1920	2350	3130	9960	1110
PFHxA	1620	1720	2100	3760	9270	1320
PFHpA	<1220	<1240	<1240	1090	2350	437
PFOA	3370	3740	7760	1670	62400	4010
PFNA	<1300	<1330	<1330	<884	<882	<53.6
PFDA	<1260	<1280	<1280	<855	<852	<51.8
PFUnA	<1250	<1270	<1270	<847	<844	<51.3
PFDoA	<1240	<1260	<1260	<842	<839	<51.0
PFBS	3530	3300	26100	169000	104000	3870
PFHxS	9090	11000	10000	1160	3480	11300
PFOS	2310	3170	24800	1330	19200	1670
PFOSA	<1210	<1240	<1240	<825	<822	<50.0
Total PFCs	**186260**	**202850**	**173110**	**239240**	**291260**	**30457**

C. MPCA MCES Metro Wastewater Treatment Plant PFC Study

PFC sampling was conducted at the Metropolitan Council of Environmental Services (MCES) main metro wastewater treatment plant (WWTP) in St. Paul on April 25, 2005. Samples were collected at the following locations:

1. Influent wastewater after the primary screens,
2. Final treated effluent prior to disinfection chlorination,
3. Primary sludge solids,
4. Secondary sludge solids, and
5. Dewatered sludge prior to incineration.

The metro WWTP is one of the largest wastewater treatment plants in the U.S. and treats an average of 215 million gallons per day (MGD) of wastewater from approximately 62 communities and 800 industries. The metro WWTP treats about 75% of the wastewater generated in the metro region. The facility utilizes an activated-sludge process for treating wastewater to an advanced secondary treatment level prior to discharge to the Mississippi River.

Sludge generated is processed by thickening, chemical and/or thermal conditioning and high pressure or centrifugal dewatering prior to incineration. Ash from incineration is transferred off-site.

PFC sampling at the metro WWTP was done to ascertain levels of PFCs at a municipal WWTP where, although specific PFC production processes are not discharged to the system, PFCs contained in some products or wastes from domestic and industrial sources may be introduced into the sewer system. This study helped us to determine the concentration of PFCs in sludges generated from treatment of these wastewaters, and determined the levels of PFCs in the discharge.

C.1. Preliminary Metro Plant Results in Influent and Effluent:
Wastewater samples were obtained from the influent and effluent. The influent sample was collected from the east channel of the primary clarifier by the sampler. The final effluent sample was collected by obtaining one-half of the sample from the west final clarifier (train) and one-half of the sample from the east final clarifier (train). Final effluent was collected prior to final disinfection/chlorination.

CLIENT ID	Metro Eff	Metro Inf	Metro Inf (dup)
UNITS	ng/mL	ng/mL	ng/mL
PFPeA	0.014	0.012	0.006
PFHxA	0.022	0.01	0.015
PFHpA	0.007	<0.0043	<0.0046
PFOA	0.078	0.046	0.04
PFNA	<0.0042	<0.0043	<0.0047
PFDA	<0.0040	<0.0041	<0.0045
PFUnA	<0.0042	<0.0042	<0.0046
PFDoA	<0.0039	<0.0040	<0.0044
PFBS	<0.0023	<0.0024	<0.0026
PFHxS	<0.0044	<0.0044	0.007
PFOS	0.081	0.053	0.051
Total PFCs	**0.202**	**0.121**	**0.119**

- Effluent PFOS was found at 81 ppt and PFOA at 78 ppt with other PFCs at lower levels to non-detect
- Influent PFOS was found at 53 ppt and PFOA at 46 ppt with other PFCs at lower levels to non-detect.
- Higher influent PFC concentrations versus effluent PFC concentrations may in part ~~beare likely~~ due to the retention time through the system and the recycle of waste activated sludge. Although sampled at nearly the same time, the influent and effluent samples would not represent the same point in time for flow given the long hydraulic retention time through the system. In addition, recycle of waste activated sludge complicates any comparison.
- Higher effluent versus influent PFOS may be due in part to PFC precursors degrading to PFOS via microbial activity in the system. PFOS has not been shown to degrade.
- Higher effluent versus influent PFOA may be due in part to microbial degradation of fluorotelomer alcohols to PFOA in the system. PFOA has not been shown to degrade.

C.2. Preliminary Metro plant results in Primary sludge, secondary sludge, and dewatered sludge prior to incineration

Primary and secondary sludge samples were collected at the sludge processing building. Primary sludge contained about 5-6% solids. Secondary sludge contained about 3-4% solids. The biosolids (sludge cake) sample was collected from the incinerator building. The biosolids sample contained about 35% solids.

CLIENT ID	Primary Sludge	2ndary Sludge	Biosolid	Biosolid (dup)
% Moisture	94.3	96.1	73.6	75.2
UNITS	ng/g	ng/g	ng/g	ng/g
PFHxA	2.37	4.09	2.18	3.65
PFHpA	<0.863	2.21	0.604	<0.492
PFOA	3.79	21.5	10	11.1
PFNA	1.92	10.4	3.42	5.63
PFDA	3.34	39.5	15.1	17
PFHxS	<0.876	10.3	4.3	6.35
PFOS	25.9	309	65.9	79.7
Total PFCs	**131.62**	**493.1**	**175.104**	**198.63**

- PFOS was found at 25.9 ppb and PFOA at 3.79 ppb, with other PFCs at low ppb to non-detect levels in the primary sludge.
- Much higher concentrations of PFCs were found in the secondary sludge (waste activated sludge) with PFOS at 309 ppb, PFOA at 21.5 ppb, PFDA at 39.5 ppb, PFUnA at 22.3 ppb, PFDoA at 25.8 ppb, PFHxS at 10.3 ppb, PFNA at 10.4 ppb, with other PFCs at lower ppb levels to non-detect.
- Biosolids were found to contain PFCs with PFOS at 79.7 ppb, PFOA at 11.1 ppb, PFDA at 17 ppb, PFBS at 8.41, PFHxS at 6.35 ppb, PFNA at 5.63 ppb with other PFCs at lower levels (less than 5 ppb).
- The removal of individual PFCs is expected to vary according to the individual PFC compound chemistry.
- At a discharge flow rate of about 200 million gallons per day the Metro plant discharges about 0.132 lbs/day of PFOS and 0.127 lbs/day of PFOA, with annual discharges estimated at 48 lbs/year PFOS and 46 lbs/year PFOA, based on this effluent sampling.
- Mass balance calculations will be performed where applicable. The mass loading of PFCs to sludges and biosolids will be completed.

D. MPCA Pine Bend Landfill PFC Study

Pine Bend Landfill receives wastewater sludges containing PFCs from the 3M Cottage Grove plant, since 1975. The extent of PFC concentrations in the 3M sludges deposited at the Pine Bend Landfill is unknown since 3M does not monitor PFCs in its sludges.

The Pine Bend Landfill and is the largest open landfill in Minnesota and has both unlined and lined portions. Leachate is stored in 2 tanks, the east and west storage tanks. Leachate is transported for treatment at MCES wastewater treatment system. The landfill has an active gas collection system which produces a condensate that is transported and treated at the MCES wastewater treatment system.

Because of the active disposal of 3M sludges at the landfill containing PFCs this study was done to determine the extent of PFC concentrations in following samples:

1. Leachate from east and west leachate storage tanks.
2. Leachate from the duel landfill gas and leachate extraction wells. Samples were taken from the #15 unlined and #219 lined areas.
3. The gas condensate sample was collected from the landfill gas collection system site in order to provide an insight into the potential levels of PFCs contained in the recovered gas and potentially discharged to the atmosphere.
4. Water samples were obtained from groundwater monitoring wells at the site. Wells 11A and 26 were sampled. Well 11A is an upgradient well at the site that has not demonstrated contamination of previously analyzed parameters. Well 26 is a downgradient well that demonstrates contamination by previously analyzed parameters.

D.1. Leachate and gas condensate samples:

CLIENT ID	West tank	East tank	#15 Unlined	# 219 Lined	Gas Cond	Gas Cond (dup)
UNITS	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL
PFBA	1.62	2.2	1.4	1.6	4.28	4.57
PFPeA	7.71	5.02	9.23	2.71	4.51	5.48
PFHxA	21.6	28.9	16.9	13.1	35.9	37.9
PFHpA	7.5	14.7	4.27	3.99	17.5	15.1
PFOA	41.5	81.8	29.8	14.2	75.3	83.8
PFNA	0.381	0.884	0.235	0.243	0.785	0.788
PFDA	0.109	0.335	0.07	<0.0420	0.17	0.214
PFUnA	<0.0483	0.053	<0.0475	<0.0433	0.044	0.056
PFDoA	<0.0459	<0.0455	0.278	<0.0411	0.092	0.125
PFBS	2.57	4.78	1.89	1.82	5.89	6.3
PFHxS	4.28	7.44	2.18	4.39	12.1	9.48
PFOS	8.18	31.4	4.04	3.14	26.4	29.9
Total PFCs	**95.45**	**177.512**	**70.293**	**45.193**	**182.971**	**193.713**

D.2. Water samples from groundwater monitoring wells

CLIENT ID	Pine Bend Well 11A	Pine Bend Well 26	Pine Bend Well 26 (DUP)
UNITS	ng/mL	ng/mL	ng/mL
PFBA	0.006	5.08	4.97
PFPeA	<0.0041	1.04	1.39
PFHxA	<0.0041	0.913	1.18
PFHpA	<0.0042	0.251	0.317
PFOA	0.008	1.59	1.6
PFNA	<0.0042	<0.0036	<0.0043
PFDA	<0.0040	<0.0034	<0.0041
PFUnA	<0.0042	<0.0035	<0.0042
PFDoA	<0.0040	<0.0034	<0.0040
PFBS	<0.0023	0.044	0.069
PFHxS	<0.0044	0.048	0.051
PFOS	<0.0043	0.082	0.114
Total PFCs	**0.014**	**9.048**	**9.691**

E. MPCA Mississippi River PFC Study

Sampling was conducted on the Mississippi River in pool 2 above, below, and proximate to the 3M Cottage Grove facility. 3M discharges its treated wastewater into a ravine where it combines with an intermittently flowing natural stream. The ravine widens into a relatively quiescent "cove" area prior to discharge to the Mississippi River. Water and sediment samples were taken upstream (above) and downstream (below) of the 3M discharge point (cove area) in the Mississippi River, and within the cove. Water and sediment samples were taken at 5 separate locations including: a water and sediment sample just upstream of the 3M discharge (cove) and the MCES Eagle Point WWTP discharge, water and sediment samples for 3 separate downstream locations (number # 1, # 2, and # 3 downstream), and water and sediment samples of the cove area. See the attached map and description, including GIS coordinates, for samples taken in the Mississippi River and in the cove. All sampling for this project occurred between about 11AM and 8PM on May 20, 2005.

E.1. Preliminary results – water and sediment

River water and composite sediment cores were sampled upstream and downstream of the 3M discharge, and at the cove area receiving the 3M discharge. 12 PFCs were analyzed. The 10 cm sediment cores would represent only relatively recent (last 2-4 years) river sediment deposition. Relatively high ppb PFC contamination levels ranging from about 10 ppb to 99 ppb were found in river cove sediments. PFC contamination at ppb levels (PFOS up to 28 ppb, PFOA up to 7 ppb) was found in downstream river sediments. A relatively low level of PFOS at 1.6 ppb (part per billion) was found in the upstream sample sediment. Higher ppb concentrations of several PFC compounds were found in the river cove water (ranging from about 2 ppb to 85 ppb), consistent with PFC discharge concentrations shown in monitoring reports by 3M. PFOS was found in downstream river water at 14.4 ppt, diminishing to 6 ppt further downstream. PFOA was found in downstream river water at 35.3 ppt and non-detect at further downstream locations. PFOS was also found in upstream river water at 5.1 ppt, with other PFCs non-detect in upstream river water

- Upstream PFOS was found at 5.14 ppt in the water (water samples were taken at 2 ft below surface). Other PFCS, including PFOA, were non-detect in upstream river water at the 2 ft depth.
- PFOA was found at 35.3 ppt in the water at downstream location #1, just downstream of the 3M discharge point. PFOA was non-detect at downstream locations #2 and 3.
- PFOS was found at a concentration of 14.5 ppt at downstream location #2, 6 ppt at downstream location #2, and non-detect (D.L limit 5.11 ppt) at downstream location #3.

- The remaining PFC compounds were not detected in the upstream and downstream river water samples (detection limit generally in the 5 ppt range).
- Water samples taken at the cove (3m discharges to the cove) area discharging to the river contained PFOS at 10.8 ppb, PFBS at 84.8 ppb, PFOA at 3.25 ppb, PFHS at 8.23 ppb, PFBA at 5 ppb, PFPeA at 1.32 ppb, and PFHxA at 1.78 ppb.
- PFBS was not detected in downstream river water samples even though it was found at relatively high levels in the cove water (84.8 ppb and 89.8 ppb) and may be due in part to its greater vapor pressure and a likely predominant concentration of PFCs within the very top surface water layer.
- Water samples taken closer to the top surface of the cove water showed a much higher concentration of PFOS at 18.2 ppb. Slightly increased concentrations of PFHxS and PFBS were also noted in samples taken closer to the top surface of the cove water.
- Higher concentration of PFCs on the surface layer of the water column is consistent with PFC physical chemistry and behavior.
- Water samples were taken at downstream locations #1 and 2 in areas that would likely be within the zone of influence of the 3M discharge. Water sample at location # 3 is likely in an area outside of the 3M discharge "zone of influence".
- Composite sediment cores were taken at the surface to 10 cm depth and each sample was a composite of 4 separate locations.
- PFOS was detected at 1.57 ppb in the upstream river sediment sample. Other PFCs, including PFOA, were non-detect in the upstream sediment.
- PFC levels in the cove sediment found PFOS at 99.4 ppb, PFBS at 49.8 ppb, PFOA at 18 ppb, PFHxS at 9.24 ppb, with other PFCs at lower ppb levels.
- River sediment in downstream location #1 showed PFOS at 27.9 ppb and PFOA at 6.62 ppb, with other PFCs also present but at the 1.0 ppb or less range.
- River sediment at downstream location #2 found diminishing PFC concentrations with PFOS at 8.26 ppb, PFOA at 1.31 ppb, PFDA at .49 ppb, PFDoA at .365 ppb, with other PFCs at non-detect.
- River sediment at downstream location # 3, sampled in a quiescent area likely outside of the 3M discharge "zone of influence", found PFOS at 1.69 ppb with all other PFCs non-detect.

CLIENT ID	Sed-Miss-up	Sed-Cove	Sed-Miss-down #1	Sed-Miss-down #2	Sed-Miss-down #3
UNITS	ng/g (dry wt)	ng/g (dry wt)	ng/g (dry wt)	ng/g (dry wt)	ng/g (dry wt)
PFPeA	<0.308	1.21	0.966	<0.320	<0.312
PFHxA	<0.299	2.28	0.755	<0.311	<0.302
PFHpA	<0.302	0.758	0.262	<0.315	<0.306
PFOA	<0.298	18	6.62	1.31	<0.301
PFNA	<0.323	0.671	0.333	<0.336	<0.327
PFDA	<0.312	2.93	1.13	0.49	<0.316
PFUnA	<0.309	1.73	0.437	<0.322	<0.313
PFDoA	<0.307	2.47	0.281	0.365	<0.311

PFBS	<0.306	49.8	1.74	<0.318	<0.310
PFHxS	<0.307	9.24	1.54	<0.320	<0.311
PFOS	1.57	99.4	27.9	8.26	1.69
Total PFC	**1.57**	**188.489**	**41.964**	**10.425**	**1.69**

E.2. Considerations for Further Study and Actions/Sediments and River Water:

- PFCs in solids in the 3M discharge have deposited within the river cove area and in river sediments proximate to the discharge, with levels diminishing at distal locations.
- It is likely that portions, perhaps a majority, of 3M discharge solids are transported downstream, and are more fully mixed with the river downstream of lack and dam #2.
- Future sediment samples in the river should use cores at deep depths corresponding to past years/decades of 3M PFC discharge, and where possible be dated accordingly. Calculations based on past PFC concentrations in the 3M discharge indicate that a potential 50,000 lbs/year of PFCs were discharged.
- Cove sediments are more highly contaminated with PFCs. Further sampling of cove sediment should be completed to determine the PFC contaminant load within the cove sediment. Remediation/dredging of the cove sediment for removal of PFC contaminated sediment should be evaluated.
- Future sediment cores should also be taken at Lake Pepin since Lake Pepin is a repository for Mississippi River suspended solids.
- Future water samples should focus on the water column top surface layer. Chemistry indicates that PFCs may reside primarily in the surface water layer. Other studies, including open ocean work, demonstrate that most PFCs reside in the surface water layer, although PFCs have been detected at considerable ocean depths.
- Fish analyzed should include focus on species which feed predominantly from the surface.

E.3. MPCA PFC Fish Sampling in Mississippi River

Fish were collected by the MDNR from the Mississippi River in the vicinity of the 3M Cottage Grove Center discharge. 12 PFCs were analyzed. Relatively high ppb levels of PFOS were found in fish livers with one small mouth bass liver containing an extremely high PFOS level of 53,000 ppb, the highest level we are aware of reported in fish liver in the world to date. Composites of whole fish species showed PFOS contaminant levels from about 300 to 1100 ppb

The fish data will be used to associate any trends from other sampling media (water and sediment), and will help us to construct a model of PFC bioaccumulation. This model will serve to assess potential human and wildlife exposures from consuming PFC contaminated fish. Fish sampling was performed along the Mississippi River miles 818-828, upstream of the 3M Cottage Grove Plant. Target species for the fish sampling effort were included Common carp (*Cyprinus carpio*), Walleye (*Stizostedion vitreum*), White bass (*Morone chrysops*), and Smallmouth bass (*Micropterus dolomieui*).

CLIENT ID	SMB #2	SMB#3,#4	SMB#5	SMB #1	WB#2,#3,#4,#5	WB #1
sex/age	1F&3M/2y	2F/3y	1F/4 y	1F/8 y	3F & 1M/6y	1F/7y
UNITS	ng/g (wet)	ng/g (wet)	ng/g (wet)	ng/g (wet)	ng/g (wet)	ng/g (wet)
PFBA	<3.76	<3.76	<3.88	<3.70	<3.88	<3.92
PFHxA	<0.360	20.2	<0.371	10.4	<0.371	<0.376
PFHpA	<0.365	<0.365	4.17	1.49	1.1	6.32
PFOA	0.551	<0.359	<0.370	0.489	1.27	<0.374
PFNA	<0.390	<0.390	<0.401	0.635	4.26	3.17
PFDA	13.1	25.5	18.1	63	19.4	11.2
PFUnA	26.1	34.5	21.2	31.2	6.95	5.03
PFDoA	25.9	21.9	21.4	84.7	4.15	4.6
PFTA	14	4.32	5.1	44.6	6.67	0.828
PFHxS	<0.371	<0.371	<0.382	<0.364	<0.382	3.16
PFOS	1030	597	717	52500	1120	305
PFOSA	<0.363	<0.363	<0.374	481	<0.374	<0.379
Total PFCs	**1109.651**	**703.42**	**786.97**	**53217.514**	**1163.8**	**339.308**

CLIENT ID	Carp #2,#4,#5	Carp #3	Carp #1	Carp #1(dup)	WE #2	WE #1
sex/age	2F&1M/6y	1F/7y	1F/8 y	1F/8 y	1M/4y	1F/9 y
UNITS	ng/g (wet)	ng/g (wet)	ng/g (wet)	ng/g (wet)	ng/g (wet)	ng/g (wet)
PFBA	<3.70	<3.83	<3.62	<3.74	<3.81	<3.74
PFHxA	<0.354	2.91	<0.346	<0.358	<0.365	<0.358
PFHpA	0.969	<0.371	<0.351	<0.363	<0.369	3.17
PFOA	0.662	<0.365	<0.345	<0.357	0.651	<0.357
PFNA	1.5	0.89	0.817	<0.387	<0.394	2.91
PFDA	6.54	4.99	2.86	5.33	13.6	8.41
PFUnA	1.66	3.21	3.18	2.52	5.5	3.17
PFDoA	1.73	1.82	1.14	1.44	2.29	<0.368
PFTA	5.39	0.455	0.408	0.563	3.31	2.17
PFHxS	<0.364	<0.377	0.88	1.39	<0.375	<0.368
PFOS	309	130	202	199	371	184
PFOSA	<0.357	<0.370	<0.349	<0.361	<0.368	<0.361
Total PFCs	**327.451**	**144.275**	**211.285**	**210.243**	**396.351**	**203.83**