

Effectiveness of Stormwater Ponds/Constructed Wetlands in the Collection of Total Mercury and Production of Methylmercury

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ABSTRACT

Mercury is a widespread problem because inorganic mercury is transported long distances in the atmosphere, deposited onto watersheds, converted to methylmercury (i.e., methylated) in aquatic systems, and then accumulated to harmful levels in fish. Methylmercury is the bioaccumulative form of mercury that leads to fish consumption advisories. Wetlands are a major site of mercury methylation in pristine watersheds; however, it is not known if this is true for storm water ponds or constructed wetlands. This study addressed the question: How do constructed stormwater wetlands compare to natural wetlands in the production of methylmercury, given the important differences in hydrologic and pollutant loads? This study collected water chemistry data from ten urban stormwater wetlands, including an intensive study of the McCarrons-Villa Park (MVP) stormwater wetland treatment system in Roseville, Minnesota, which treats most of the stormwater McCarrons Lake and consists of a primary detention basin followed by seven wetland cells. A comparison of automatic composite samplers and instantaneous grab samples demonstrated that automatic samplers can be used to collect composite samples suitable for low level mercury analysis, although grab samples can accurately collect mercury in wet weather as well as dry weather. The combined results from all sites indicate that stormwater wetlands have methylmercury concentrations similar to natural wetlands. Total mercury and methylmercury fluxes from MVP were on the low end of the range of values for natural wetlands. In MVP, 1.4% of total mercury entering the wetland was released at the outlet as MeHg. The production of methylmercury was associated with periods of anoxia in the wetlands. The MVP wetland removed 28 times more mercury than was converted to MeHg. Phosphorus and methylmercury concentrations were strongly correlated in the stormwater wetlands. In other words, if a wetland stormwater treatment system has relatively low phosphorus release, it most likely also has low methylmercury release.

ACKNOWLEDGMENTS

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I. INTRODUCTION

Mercury is a widespread problem because inorganic mercury is transported long distances in the atmosphere, deposited onto watersheds, converted to methylmercury (i.e., methylated) in aquatic systems, and then accumulated to harmful concentrations in fish. Research has shown that wetlands are a major site of mercury methylation in pristine watersheds (St. Louis *et al.* 1994; Hurley *et al.* 1995; Krabbenhoft *et al.* 1995; Branfireun *et al.* 1996), although they can also be a net sink of total mercury (St. Louis *et al.* 1994; Galloway and Branfireun 2004). All of the published research has been on relatively pristine natural wetlands in forested watersheds. With respect to methylmercury, it is not known if stormwater wetlands behave the same way as natural pristine wetlands.

Sulfate-reducing bacteria are the primary methylators of mercury (Compeau and Bartha 1985, Gilmour *et al.* 1991) and they thrive in anaerobic, carbon rich environments, such as wetlands and lake sediments. Sulfate addition to aquatic sediments and wetlands stimulates mercury methylation (Gilmour *et al.* 1992, Branfireun *et al.* 1999, Harmon *et al.* 2004, Jeremiason *et al.* 2006); however, the relationship between sulfur and mercury is not straightforward because of the complex oxidation-reduction reactions and speciation, as well as other physicochemical influences. If sulfate is sufficiently abundant and not a limiting factor for the bacteria, then presumably, residence time, organic matter load, and mercury load are the critical factors determining how much mercury is methylated in a wetland. Some of these critical factors may be very different in stormwater basins compared to natural pristine wetlands. Stormwater basins are likely to have shorter residence times and lower organic matter loading.

Stormwater wetlands are constructed primarily to provide a water quality function. They are promoted as stormwater Best Management Practices (BMPs) because they can trap nutrients and metals associated with suspended solids. Stormwater wetlands are assumed to effectively capture mercury associated with solids, but it is not known how much of the mercury is converted to methylmercury and exported. With the continued construction of stormwater wetlands as BMPs for nutrient reduction, it would be helpful to know what role these wetlands play in the fate and transport of mercury.

The goal of this project was to learn more about the behavior of mercury in stormwater wetlands and evaluate how they differ from natural wetlands in methylmercury production. Total mercury and methylmercury were measured in constructed stormwater wetlands. In addition, ancillary water chemistry analytes were measured to evaluate the correlation of mercury to other water chemistry variables. This study includes synoptic survey data on urban wetlands and intensive sample collection of two wetland-pond stormwater treatment systems. Stormwater wetlands were selected in the Minneapolis-St. Paul metropolitan area with the assistance of the MPCA staff and local government staff (e.g. watershed districts and city parks and public works). Total mercury (THg) and methylmercury (MeHg) concentrations in stormwater wetlands are compared to natural depressional wetlands, including some that receive stormwater, others receive agricultural runoff, and some are minimally-impacted (i.e., reference) wetlands.

This project also produced new information on how to sample successfully for Hg and MeHg with automatic samplers during storm events, as is done for other water chemistry in rivers and stormwater. Mercury studies have avoided automatic sampling because of the concern of sample contamination. The results for this technical evaluation are presented as quality assurance results and comparison to grab samples taken at the same time during storm events.

II. METHODS

A. Site Descriptions

Selection of stormwater wetlands was based on information from watershed districts, Metropolitan Council Environmental Services, and the MPCA. The selection criteria were: (1) exists to collect and treat stormwater and, (2) has wetland characteristics, such as emergent macrophytes. In the initial search for sites, a third criterion was a single inlet (for logistics of sampling and mass balance calculations), but this was abandoned because very few stormwater wetlands (or ponds) had only one inlet. Ten sites were selected and they are located throughout the Minneapolis-St. Paul metropolitan area (Figure 1). One site—Veritas—was a typical stormwater detention pond, rather than a wetland but was sampled even though it did not meet the second criterion.

Two intensively monitored study sites were selected where continuous flow monitoring was being done by other agencies to assess the treatment efficiency of the BMP. Three Rivers Park District was monitoring the Bass Creek Business Park system and the Capitol Region Watershed District was monitoring the McCarrons-Villa Park wetland system. Both are BMPs-in-series, consisting of ponds and wetlands. Flow data loggers were set up at the inlet and outlet of the stormwater treatment systems and automatic samplers were triggered to collect composite samples during stormwater runoff events. The other agencies were tracking nutrients and solids removal in the stormwater wetlands and ponds.

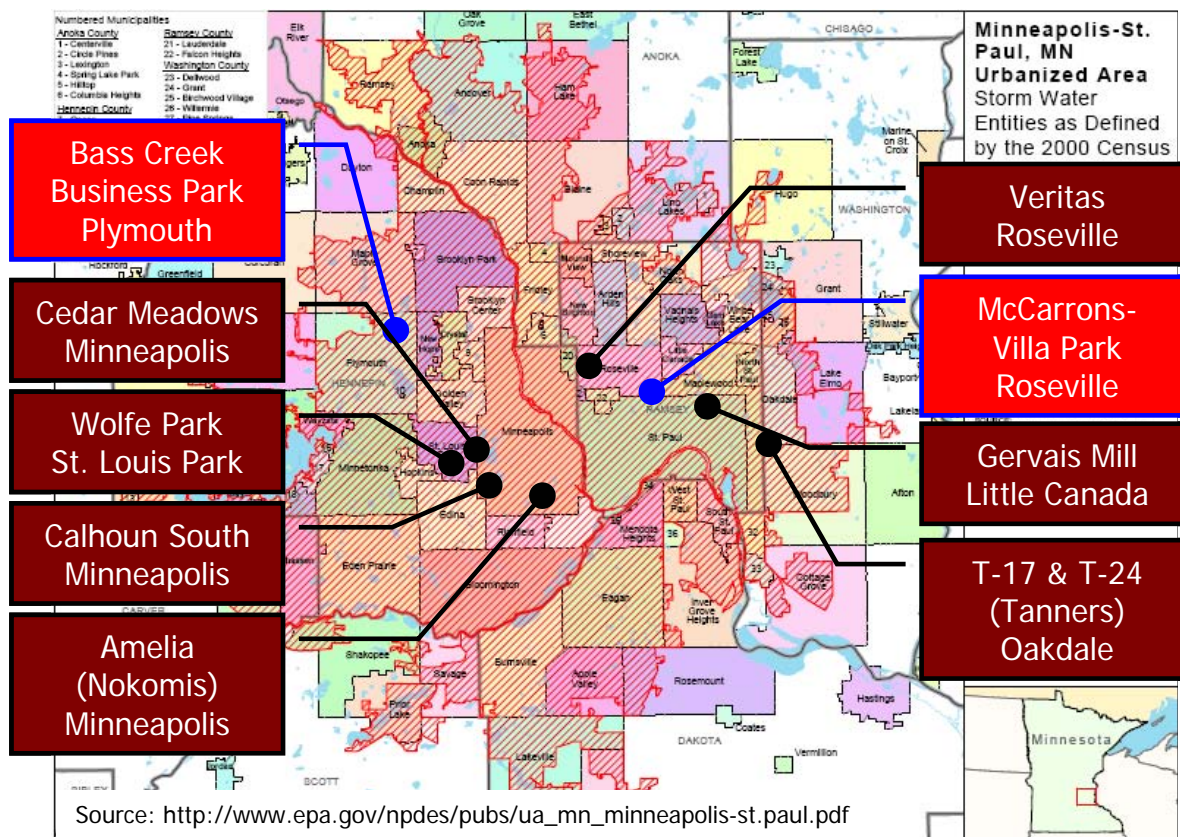


Figure 1 Sampled stormwater wetland sites in Minneapolis-St. Paul Metropolitan Area

Bass Creek Business Park

The Bass Creek Business Park stormwater treatment system (BCBP) is adjacent and immediately east of the Three River Park District's Eagle Lake Regional Park, Plymouth, Minnesota. BCBP treats stormwater from a 42 acre commercial/industrial area. The system consists of a three-cell detention pond and a 2 hectare (5 acre) cattail marsh, which discharges to Pike Lake (Figure 2a). The flow path through the ponds is about 150 meters (500 feet) and another 150 meters through the wetland. The Three Rivers Park District staff established three monitoring stations (automatic sampler/data logger) at (1) the influent pipe from the business park area to the first pond cell, (2) outlet of the third pond cell to the wetland, and (3) down stream of the wetland outlet prior to draining to Pike Lake. The three sample sites were monitored by the Park District from May through October in 2005. A tipping bucket rain gauge was also installed at this site. For the mercury study, samples were collected at the inlet and outlet stations, but not at the second station between the ponds and wetland. Additional grab samples were collected at the outlet structure of the wetland and in the first pond cell.

McCarrons – Villa Park

The McCarrons Wetland Treatment System was constructed in 1985 and completed in fall of 1986. The system was later referred to as Villa Park Ponds. For this study, it is referred to as McCarrons – Villa Park (MVP). Villa Park and the wetlands within it are owned and maintained by the City of Roseville. The Capitol Region Watershed District has assumed responsibility for monitoring the system for flow and nutrients, as well as monitoring of Lake McCarrons. The Villa Park Wetland Improvement project was completed in the spring of 2004 and included replacement of the earthen berms with wooden weirs to reduce channelization of water flow.

MVP was designed to improve the water quality of Lake McCarrons, an 81 acre lake surrounded by mostly single family homes, with a park and swimming beach on the south shore. The MVP system treats stormwater drainage from 298 hectare (736 acre) of urban residential and commercial land use (27% impervious). It consists of a 1 hectare (2.5 acre) headwater detention pond that flows via a culvert into six acres of wetlands divided into a series of five cells by wooden weirs (Figure 2b). The total flow path is about 2000 feet. Baseflow averages 0.3 cfs; runoff and snowmelt events comprise 72% of the total flow. The detention pond was dredged in January 1993 to its original configuration. An additional small detention pond also contributes inflow to the last wetland cell.

Metropolitan Council Environmental Services has conducted two studies of the treatment system. (Oberts and Osgood 1988; Oberts 1997). The first study included a Phase I study before construction, followed by Phase II, a 21 month monitoring study that began in the fall 1986. The second report—Phase III study—included six sites from March 1995 through November 1996.

T-17

T-17 is a 1.3 (3.2 acre) wetland, with direct drainage of 26.6 hectare (65.8 acre), discharges to the north side of Tanners Lake in Oakdale, Minnesota (Figure 2c). This wetland receives water from an alum settling pond as part of an alum injection stormwater treatment facility. The alum is added to decrease phosphorus loading to Tanners Lake. The Ramsey-Washington Metro Watershed District owns and operates the treatment facility and monitors the flows and water chemistry.

T-24

T-24 is a 1.5 hectare (3.7 acre) wetland, treating stormwater from a relatively small 7 hectare (17.4 acre) drainage area, before discharging to the east shore of Tanners Lake, Oakdale, Minnesota (Figure 2d). The wetland was constructed in 1997. The drainage area is 27% impervious.

Cedar Meadows

Cedar Meadows is located on the southwest side of Cedar Lake in Minneapolis (Figure 2e). It consists of a 0.6 hectare (1.5 acre) pond and 1.3 hectare (3.2 acre) wetland, which receives stormwater from a 771 hectare (1,904 acre) drainage area. The watershed area represents 85% of Cedar Lake's contributing watershed. The pond-wetland system was built in 1994 on a former open grassed field. The system has an average residence time of 10 days and has been shown to have an annual total phosphorus removal efficiency of 40%. A diversion weir upstream of Cedar Meadows allows water to discharge directly to Cedar Lake at high flows (greater than 46 cm (18 inch) depth). Water from Cedar Meadows wetland discharges to Cedar Lake.

Calhoun South

Calhoun South stormwater treatment system was built in 1998 in a former grassed open area (Figure 2f). The three pond system treats stormwater from a 363 hectare (897 acre) watershed. The system has an average residence time of 21 days and has been shown to have an annual total phosphorus removal efficiency of 66%. The pond system consists of a primary settling basin with a weir located under a pedestrian bridge separating the first pond from the elongated second pond. A tertiary elongated pond on the north side discharges to the southeast shore of Lake Calhoun.

Lake Calhoun and Cedar Lake are part of the Minneapolis Chain of Lakes, 2.4 kilometers (1.5 miles) southwest of downtown Minneapolis.

Amelia (Nokomis)

Amelia Pond is a 2.4 hectare (6 acre) wetland located on the southwest edge of Lake Nokomis in south Minneapolis (Figure 2g). Native prairie plants surround an open pond. Dredging and planting of the pond was completed in 2001 to provide stormwater treatment for a 352 hectare (870 acre) watershed, before discharging to Lake Nokomis. Aerial photos indicate the wetland was originally a saturated meadow or shrub swamp.

Gervais Mill

Gervais Mill Pond is a series of wetland ponds with a total acreage of 3.4 hectare (8.4 acre) (Figure 2h). The system treats stormwater from 31.3 hectare (77.3 acre) watershed, which is 35% impervious, and discharges to Gervais Lake in Little Canada, Minnesota. The pond system was built in 1994 by a partnership between the Ramsey-Washington Metro Watershed District and the City of Little Canada. The system consists of three connected ponds, surrounded by a wooded park with paved walking paths.

Veritas

The Veritas stormwater pond is different from all other sites in this study. It is a standard stormwater pond with an aeration system and is located within an industrial park in Roseville, Minnesota (Figure 2i). The pond was selected to provide a reference site for stormwater ponds that do not contain the typical wetland features—the pond had no emergent macrophytes and was surrounded by mowed turf grass.

Wolfe Park

Wolfe Park pond is in St. Louis Park, Minnesota. It receives runoff from a parking lot and streets and discharges to a Wolfe Lake (Figure 2j). The system has a relatively long flow path and discharges into a larger deep pond to the west. Cattails fill the forebay and surround the pond. Samples were collected at the outlet to Wolfe Lake; the outlet was designed to aerate the water by cascading down a boulder and pool structure.

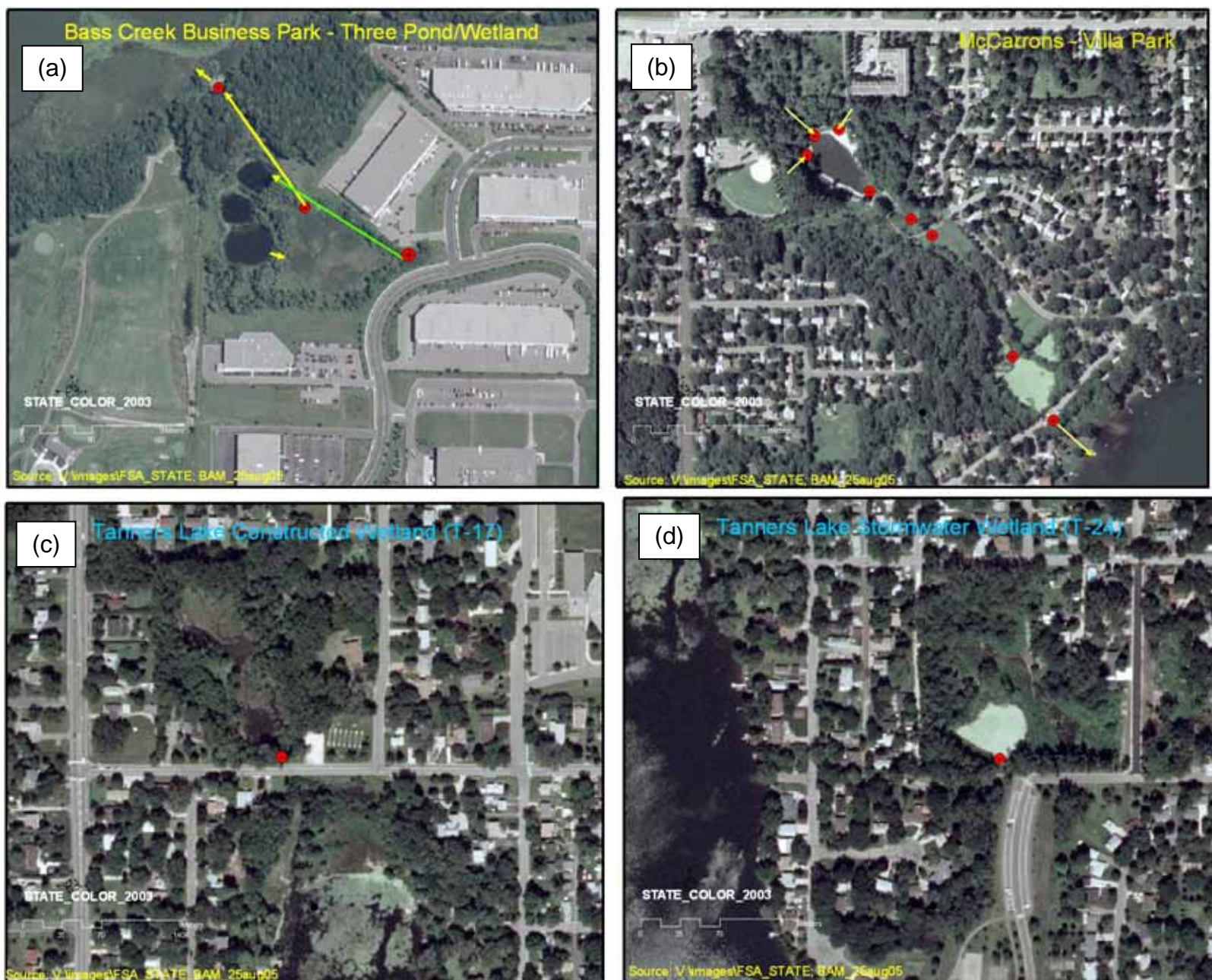


Figure 2 Aerial photographs of stormwater wetlands: (a) McCarrons -Villa Park, (b) Bass Creek Business Park, (c) Tanners T24, (d) Tanners T17; red dots are sample sites.



Figure 2 (cont'd) Aerial photographs of stormwater wetlands: (e) Cedar Meadows, (f) Calhoun South, (g) Amelia, (h) Gervais Mill; red dots are sample sites.



Figure 2 (cont'd) Aerial photographs of stormwater wetlands: (i) Veritas, and (f) Wolfe; red dots are sample sites.

B. Sample Collection

Sampling began in June 2005 and was completed in September 2006. All sample bottles and tubing were pre-cleaned by the analytical laboratories. Field duplicates were collected regularly and generally followed the rule of a duplicate for every 10 samples. Most samples were collected as grabs during storm and non-storm periods, using “clean hands-dirty hands” technique (EPA Method 1669). The aerial photos of each site (Figure 2a-j) show the sample locations. A Hydrolab MS5 multiprobe sonde and Surveyor data logger were used in the field to measure temperature, dissolved oxygen, specific conductivity, pH, and oxidation-reduction potential. Automatic sampling of storm events for all water chemistry was set up at the BCBP site in 2005 and at the MVP site in 2006. Isco 3700 automatic samplers were fitted with acid-cleaned Teflon tubing and composite sample bottle to capture samples during storm events at the inlets and outlets. Initially the composite sample bottle was a 1.5 gallon glass bottle that had contained reagent water from Frontier GeoSciences laboratory. In 2006, the sample collection was switched to Isco ProPak 2 gallon sample bags. The LDPE plastic bags were tested with laboratory reagent water and found to contain no detectable residual mercury. The samplers were connected to Hydrolab dataloggers. Three Rivers Park District managed the datalogger and an additional Isco sampler at the BCBP site; Capitol Region Watershed District did the same at the MVP site.

Precipitation data were collected from various sources. Rain gauges were located at the BCBP and the Villa Park sites; however, the University of Minnesota St. Paul Campus Climatological Observatory provided the most reliable set of precipitation data and was used as the general reference for precipitation.

C. Chemical Analyses

Frontier GeoSciences, Inc. analyzed all mercury samples (total mercury and methylmercury). In general, samples were unfiltered; however, some filtered samples were collected. Samples were filtered in the field using acid-cleaned 0.45 micron capsule filters (AquaPrep 600 Capsules). Minnesota Health Department Laboratory analyzed water samples for all ancillary water chemistry analytes (Table 1).

Table 1 Water Chemistry Analytes

Compound Name	Method	Units	Report Limit
Solids, Total [TS]	SM 2540 B	mg/L	10
Solids, Total Volatile [TVS]	EPA 160.4	mg/L	10
pH	SM 4500-H+B	Std Units	
Conductivity @ 25 deg C [SC]	SM 2510 B	µmhos/cm	0.2
Alkalinity, Total [ALK]	SM 2320 B	mg/L CaCO ₃	10
Chloride, Total [Cl]	EPA 325.2	mg/L	1
Color	EPA 110.2	CU	5
Phosphorus, Total [TP]	EPA 365.1	mg/L as P	0.003
Orthophosphate, Total [OP]	QuikChem 10-115- 01-1-A (EPA 365.1)	mg/L as P	0.005
Ammonia Nitrogen, Total [NH ₃]	EPA 350.1	mg/L as N	0.05
Kjeldahl Nitrogen, Total [TKN]	EPA 351.2	mg/L as N	0.1
Nitrate+Nitrite Nitrogen, Total [NO ₃]	EPA 353.2	mg/L as N	0.05
Total Organic Carbon [TOC]	SM 5310 C	mg/L	1
Iron [Fe]	SW 6010B	µg/L	20
Sulfate [SO ₄]	EPA 300.0	mg/L	1.00
Total Mercury [THg]	FGS-069 (CVAFS-w/BrCl oxidation)	ng/L	0.50
Methylmercury [MeHg]	FGS-070 (CVAFS-w/distillation)	ng/L	0.025

Specific Conductivity [SC]	Sonde	µmhos/cm @ 25 °C
Dissolved Oxygen [DO] & DO saturation [DO-SAT]	Sonde	mg/L
Temperature [T]	Sonde	Degrees Celsius
Oxidation-Reduction Potential [ORP]	Sonde	mV
pH	Sonde	Std Units

D. Data Analysis

Statistical analysis was performed with Microsoft Excel and SYSTAT 11. Density functions for most of the analytes were not normally distributed, based on Shapiro-Wilk normality test. A log transform brought the distributions closer to normality (discussed in Results and Discussion section). Other transformations might have improved the symmetry of some distributions; however, one transformation was used that works reasonably well for all analytes (Helsel and Hirsch, 2002).

E. Quality Assurance

Quality assurance (QA) data are summarized for the mercury analyses by Frontier GeoSciences, Inc., Seattle Washington. All other analytes were analyzed by Minnesota Health Laboratory and QA results are available upon request.

Reporting limit (RL) was 0.50 ng/L for THg and 0.025 ng/L for MeHg. Mercury QA summary (Table 2) is presented only for 2006, but 2005 results were essentially the same. QA results are excellent for blanks, certified reference material, and matrix spike recoveries. Mean duplicate relative percent difference (RPD) of 14% for MeHg is relatively high compared to only 6% for THg; however, another mercury lab used for mercury analysis on a different research project in Minnesota reported MeHg mean replicate differences of 8-16% (*GLAD progress report for Marcell Project [Dec 1, 05 – Jul 30, 06]*). Therefore, level of precision was considered appropriate for this study.

Table 2 Mercury QA Summary of laboratory accuracy and precision

	MeHg				THg			
	n	Mean	min	max	n	mean	min	max
Preparation Blanks								
Sets of 3 (ng/L)	26	0.013	0.002	0.024	28	0.12	0.08	0.20
Prep Blank Relative SD (%CV)	26	44%	6%	103%	28	17%	0%	48%
Certified Reference Material and Blank Spikes*								
CRM1 Recovery	29	100%	72%	118%	31	99%	93%	106%
CRM2 (duplicate) Recovery	29	101%	76%	118%	31	98%	88%	104%
DORM-2	16	95%	73%	108%				
Matrix Duplicates	25	0.248	0.014	0.515	31	4.34	0.73	43.62
MD – RPD	25	14%	1%	34%	31	6%	0%	29%
Matrix Spikes								
MS - % Recovered	29	103%	83%	121%	32	95%	82%	120%
MS Duplicate - % Recovered	29	103%	89%	122%	32	97%	86%	120%
MS – RPD	29	4%	0%	13%	32	3%	0%	14%

Frontier Geosciences Inc. 2006

*CRM: NIST 1641d; and blank spikes for THg and MeHg

III. RESULTS & DISCUSSION

A. All Sites

1. Water Chemistry

Water chemistry results for the stormwater wetlands are listed in Appendix A and summarized in Table 3. Based on monthly precipitation and evaporation at the St. Paul Campus Climatological Observatory, 2005 and 2006 growing seasons were very similar. For June-September, precipitation was 19.20 inches in 2005 and 18.54 inches in 2006; evaporation was 27.08 inches and 26.08 inches. Therefore, results from the two years are combined for general descriptions and comparisons. All analytes, except temperature were log-normally distributed, and this is evident in the medians less than the means.

Table 3 Summary of water chemistry for all stormwater wetland sites

	THg	MeHg	MeHg/THg	Alk	Color	TOC
N of cases	307	307	307	234	148	231
Minimum	0.55	0.013	0.007	10	10	0.5
Maximum	44.00	2.880	0.778	390	160	74.0
Median	2.43	0.344	0.147	150	40	8.9
Mean	3.96	0.479	0.191	153	41.8	9.9
Standard Dev	5.56	0.430	0.161	81	23.85	6.4

	SC	TS	TSV	Cl	SO ₄	Fe
N of cases	162	230	226	235	227	32
Minimum	62	67	29	1.0	0.5	295
Maximum	3712	1950	250	1200	87	3050
Median	555	345	93.5	69	9.1	735
Mean	641	396	104	99	12.6	924
Standard Dev	516	256.1	52.1	136	11.5	609

	T	pH_lab	pH_field	ORP	DO-Sat	DO
N of cases	162	224	162	162	162	162
Minimum	14.86	6.8	6.63	44	2.3	0.21
Maximum	29.51	9.7	11.30	454	171.6	14.12
Median	22.32	7.4	7.52	349	66.9	5.52
Mean	22.33	7.5	7.63	311	66.6	5.53
Standard Dev	2.80	0.43	0.67	94	36.0	2.93

	TP	OP	TKN	NH ₃	NO ₃ -NO ₂
N of cases	235	108	235	228	235
Minimum	0.027	0.005	0.550	0.025	0.025
Maximum	2.580	0.281	7.180	2.640	2.200
Median	0.254	0.052	1.400	0.160	0.050
Mean	0.311	0.068	1.662	0.260	0.201
Standard Dev	0.249	0.059	0.960	0.317	0.321

Refer to Table 1 for analyte abbreviations and units.

For a reference, some of these results are compared to the Nationwide Urban Runoff Program (NURP; USEPA 1983). NURP reported median concentrations of TKN, NO₃-NO₂, TP, and soluble P for four land use types: residential, mixed, commercial, and open/non-urban (Table 4). Pollutant concentrations in runoff from different urban land use categories were not significantly different; however, urban sources were significantly different from the open/non-urban land use. The median TP from the stormwater wetlands, 0.254 mg/L, is similar to the TP from NURP mixed land use—the same type of land use draining to most of this study's wetlands. The similarity also holds for TKN and soluble P (i.e., OP). The only analyte that is considerably different is NO₃-NO₂. In NURP runoff, it was reported as a median of

about 0.5 mg/L, whereas in the stormwater ponds the median $\text{NO}_3\text{-NO}_2$ was 0.050 mg/L, which was the detection limit for that analyte. While TKN, TP and soluble P do not show a substantial decrease relative to the runoff concentrations, $\text{NO}_3\text{-NO}_2$ was the exception and was often undetectable in the wetlands, thus demonstrating that stormwater wetlands are very effective at denitrification.

Table 4 Median nutrient chemistry from the NURP program and this stormwater wetlands study

Land Use/Cover	TKN	$\text{NO}_2\text{-NO}_3$	TP	Soluble P
Residential	1.900	0.736	0.383	0.143
Mixed	1.288	0.448	0.263	0.056
Commercial	1.179	0.572	0.201	0.080
Open/non-urban	0.965	0.543	0.121	0.026
Stormwater (SW)				
Wetlands	1.400	0.050	0.254	0.052
SW Inlets	0.85 - 2.74	0.31 - 0.80	0.145 - 0.289	0.055 - 0.172

2. Mercury & Methylmercury

Combining data from all sites, THg and MeHg closely approximated a normal distribution after a log-transform (Figure 3). Histograms on the left are linear (un-transformed data) and histograms on the right are the same data log-transformed. Distributional statistics are evident when the THg and MeHg concentrations are presented as a quantile plot (Figure 4). The 50th percentile (median) is 0.34 ng/L for MeHg and 2.5 ng/L for THg. The 10th -90th percentile ranges are 0.1 – 1 ng/L for MeHg and 1 – 7 ng/L for THg.

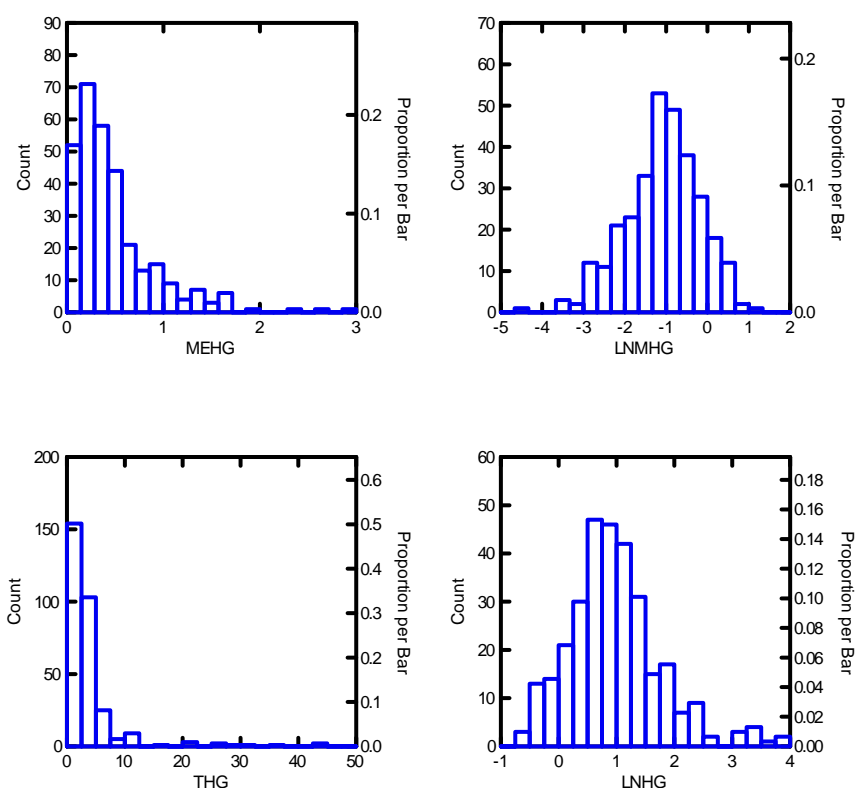


Figure 3 Histograms of linear and log-transformed MeHg and THg

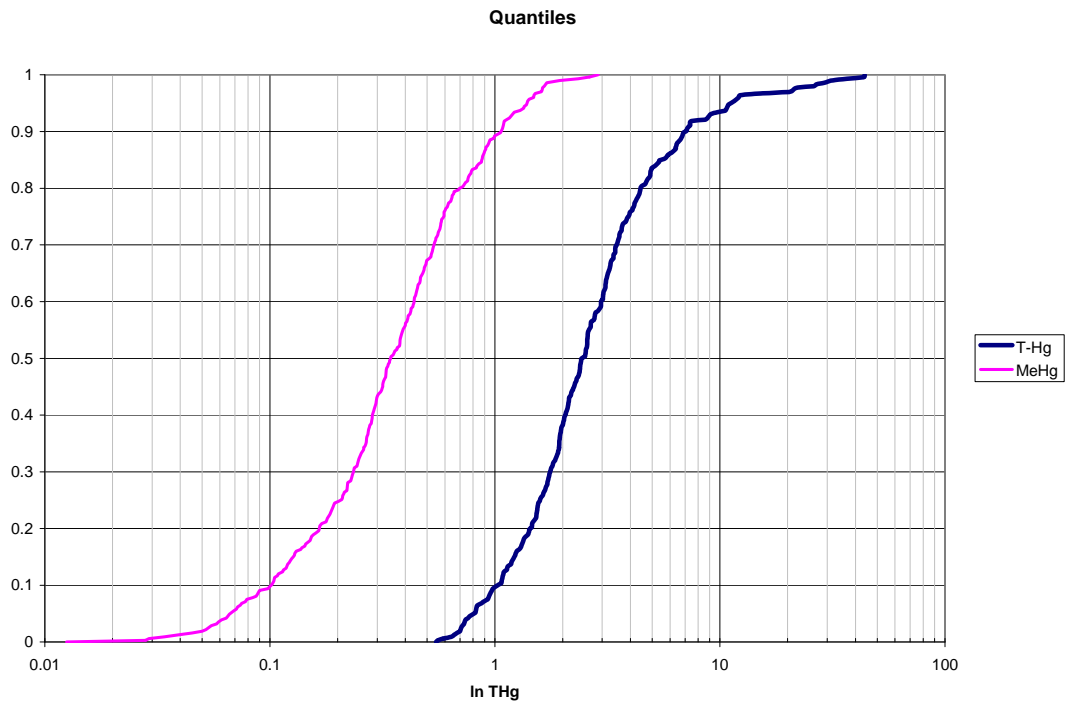


Figure 4 Quantile plot for all THg and MeHg concentrations

Methylation efficiency is typically presented as the ratio of MeHg:THg or percentage (%MeHg). Lakes and rivers generally have %MeHg less than 10%. The median value from the sampled wetlands is 15% and the 10th – 90th percentile range is 3% - 43% (Figure 5).

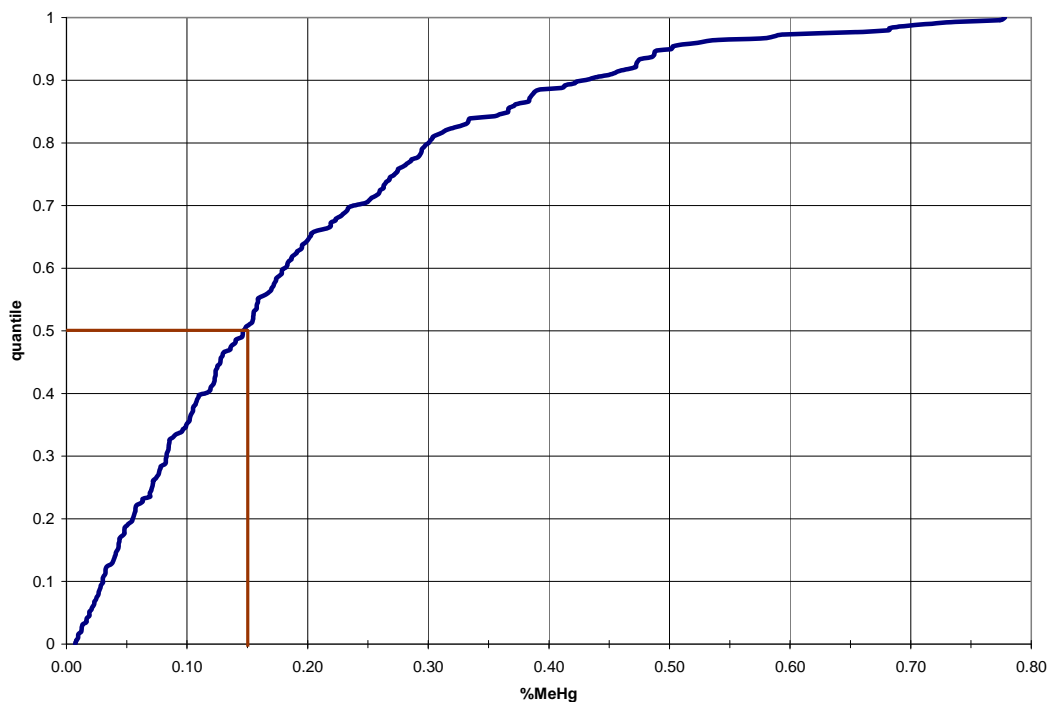


Figure 5 Quantile plot for methylation efficiency (%MeHg)

Methylation efficiency varies from site to site and MeHg concentrations cannot be predicted from THg concentrations. That is, there is no relationship between THg and MeHg (Figure 6). This is generally true for all surface waters, not just stormwater wetlands.

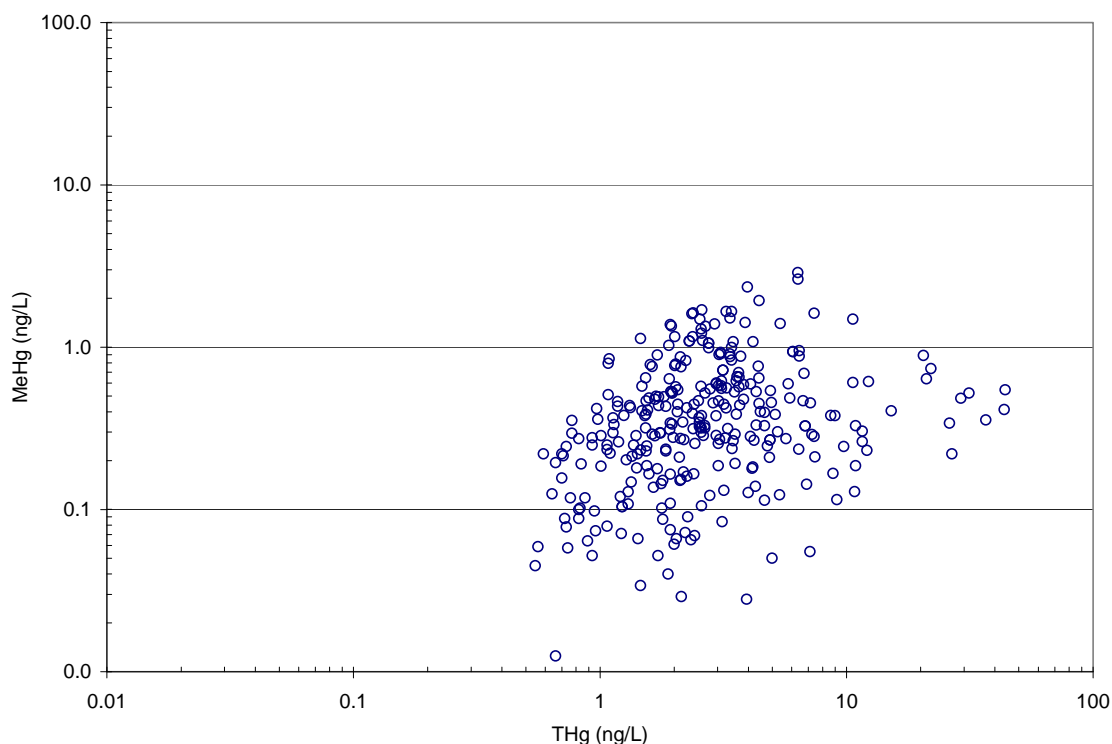


Figure 6 Log-log scatterplot of THg and MeHg

To provide a reference to natural wetlands, the mean THg, MeHg, and %MeHg at the stormwater wetlands are compared to MPCA Biomonitoring Wetlands (Table 5), which include wetlands in agricultural areas (Ag), minimally impacted reference wetlands (Ref), and urban stormwater impacted wetlands (Urb). The biomonitoring wetlands are natural wetlands that are not designed for stormwater treatment. Most wetlands were sampled one to six times. BCBP sites were sampled up to 14 times and McCarron-Villa Park sites were sampled up to 39 times. THg concentrations ranged from 0.82 ng/L to 4.45 ng/L – more than a five-fold range; and MeHg concentration ranged from 0.03 ng/L to 1.54 ng/L – about a 53-fold range. Upper THg concentrations are high compared to lakes, but rivers with high suspended solids load can easily exceed the maximum THg seen in these wetlands. Upper MeHg concentrations are higher than is typically seen in either lakes or rivers.

Distributions of the results by site type are summarized in

Table 6. The stormwater wetlands have a median MeHg concentration that is 56% higher than the biomonitoring wetlands; however, the interquartile ranges (25th to 75th percentiles) were similar for the two wetland groups. Particularly noteworthy is %MeHg, with a range of 9-26% for biomonitoring wetlands and 10-24% for the stormwater wetlands, indicating a similarity in their typical methylation efficiencies. The highest MeHg concentration and highest %MeHg were in stormwater wetland T-24. As described above, it is a small stormwater wetland, with a small watershed, that discharges to the west side of Tanners Lake. T-24 does not appear to have any significant net groundwater inflow, only discharging during storm events through the raised outlet structure. The small watershed and lack of groundwater input result in a long residence time for this wetland, thereby encouraging anaerobic conditions, sulfate reduction, and mercury methylation. The other discharge to Tanners Lake, T-17, drains a wetland but receives nearly continuous flow during non-storm periods and, most importantly, an alum treatment

system is immediately upstream to remove particulates and phosphate from the stream before entering Tanners Lake. Consequently, T-17 has the lowest THg concentrations among all wetlands, including the biomonitoring wetlands, and the second lowest MeHg concentration. The differences between T-17 and T-24 regarding phosphorus and MeHg are discussed in the next section.

Table 5 Data summary for biomonitoring and stormwater wetland sites

Type	SiteName	n	THg	MeHg	%MeHg	FlowPath	County
Ag	06Meek001	1	1.54	0.386	25.1%	throughflow	Meeker
Ag	06Todd001	2	2.77	0.413	15.2%	outflow	Todd
Ag	Breen	2	4.45	0.753	19.8%	isolated	LeSueur
Ag	Frikken	2	0.92	0.233	26.8%	inflow	Grant
Ag	JohnLake	2	3.65	1.540	42.6%	throughflow	Pope
Ag	New Prairie	1	1.75	0.297	17.0%	isolated	Pope
Ag	QuistFr	1	3.37	0.874	26.0%	isolated	Todd
Ag	Sethre	2	2.00	0.549	27.4%	outflow	Ottertail
Ag	Tyrone	2	1.07	0.077	8.4%	throughflow	Meeker
Ref	CrowRef	3	2.30	0.311	13.3%	isolated	Hennepin
Ref	Glacial	1	1.77	0.144	8.1%	isolated	Pope
Ref	Prairie	3	0.89	0.040	1.9%	isolated	Hennepin
Ref	RenoRef	1	2.14	0.029	1.4%	isolated	Pope
Urb	LakeJo	2	2.23	0.235	10.2%	isolated	Ramsey
Urb	Legion	3	2.57	0.849	32.6%	isolated	Hennepin
Urb	Oasis	3	2.32	0.238	18.7%	throughflow	Ramsey
Urb	RoseHS	3	2.12	0.246	11.3%	isolated	Ramsey
Urb	SpringBrk	2	1.23	0.257	21.7%	throughflow	Anoka
Urb	Wood	3	1.53	0.099	7.1%	isolated	Hennepin
SW	Amelia	5	1.62	0.222	13.7%	throughflow	Hennepin
SW	BCBP	14	3.54	1.086	34.8%	throughflow	Ramsey
SW	Calhoun S	5	3.94	0.484	12.3%	throughflow	Hennepin
SW	Cedar Meadows	7	2.95	0.540	17.6%	throughflow	Hennepin
SW	Gervais Mill	2	2.26	0.159	7.0%	throughflow	Ramsey
SW	MVP	39	2.39	0.504	26.4%	throughflow	Ramsey
SW	T-17	3	0.82	0.070	8.6%	throughflow	Washington
SW	T-24	3	2.19	1.269	57.9%	throughflow	Washington
SW	Veritas	1	2.56	0.320	12.5%	throughflow	Hennepin
SW	Wolfe	8	2.97	0.102	3.4%	throughflow	Hennepin

Ag: agricultural; Ref: Reference; Urb: Urban (stormwater influenced); SW: stormwater wetland

Table 6 Descriptive statistics for wetland site types

Type	THg				MeHg				%MeHg			
	AG	REF	URB	SW	AG	REF	URB	SW	AG	REF	URB	SW
Minimum	0.92	0.89	1.23	0.82	0.077	0.029	0.099	0.07	8%	1%	7%	3%
25%tl	1.423	1.33	1.53	2.19	0.281	0.035	0.235	0.159	17%	2%	10%	9%
Median	2.00	1.955	2.175	2.475	0.413	0.092	0.242	0.402	25%	5%	15%	13%
75%tl	3.44	2.22	2.32	2.97	0.783	0.227	0.257	0.540	27%	11%	22%	26%
Maximum	4.45	2.3	2.57	3.94	1.540	0.311	0.849	1.269	43%	13%	33%	58%
Mean	2.391	1.775	2.00	2.524	0.569	0.131	0.321	0.476	23%	6%	17%	19%
Std Dev	1.231	0.63	0.512	0.903	0.441	0.131	0.265	0.408	10%	6%	9%	16%
N	9	4	6	10	9	4	6	10	9	4	6	10

3. Correlations

The Pearson correlation matrix for chemical analytes shows many significant correlations, as indicated by the many Bonferroni probabilities (p) of 0.000 (Table 7). A log-transform improved the symmetry of the distributions and the variance and brought them all closer to normality. All values, except temperature, were log-transformed before applying a correlation test. The variable pairs with a correlation coefficient (r) greater than 0.5 are in bold text. The strong correlations are consistent with an expectation of anaerobic conditions in the wetlands. Nitrate (NO₃) is strongly correlated with THg because both are relatively high concentrations in the runoff influent to wetlands but are removed within the wetland.

Table 7 Pearson correlation matrix for all water chemistry analytes

	THg			MeHg			% MeHg (MeHg/Hg)			Chloride			TKN		
	R	p	n	r	p	N	R	p	n	R	p	n	r	P	n
MeHg	0.242	0.002	307												
%MeHg	-0.602	0.000	307	0.629	0.000	307									
Cl	-0.587	0.000	233	-0.267	0.004	233	0.271	0.003	233						
TKN	0.355	0.000	233	0.502	0.000	233	0.104	1.000	233	-0.155	1.000	232			
NH ₃	0.417	0.000	228	0.277	0.002	228	-0.126	1.000	228	-0.452	0.000	227	0.232	0.043	228
NO ₃	0.543	0.000	233	-0.246	0.016	233	-0.639	0.000	233	-0.373	0.000	232	-0.010	1.000	233
pH	-0.178	0.774	225	-0.534	0.000	225	-0.274	0.003	225	0.327	0.000	225	-0.202	0.241	225
TP	0.143	1.000	233	0.695	0.000	233	0.430	0.000	233	-0.214	0.107	232	0.683	0.000	233
TS	-0.383	0.000	227	-0.274	0.003	227	0.099	1.000	227	0.818	0.000	227	-0.096	1.000	226
TSV	-0.306	0.000	223	0.174	0.969	223	0.389	0.000	223	0.374	0.000	223	0.216	0.125	222
SO ₄	-0.217	0.100	229	-0.228	0.053	229	-0.002	1.000	229	0.437	0.000	229	-0.015	1.000	229
TOC	0.359	0.000	231	0.305	0.000	231	-0.057	1.000	231	-0.133	1.000	231	0.454	0.000	230
Fe	-0.215	1.000	42	0.222	1.000	42	0.373	1.000	42	0.197	1.000	42	0.048	1.000	42
OP	0.416	0.001	107	0.460	0.000	107	-0.061	1.000	107	-0.440	0.000	107	0.306	0.144	107

	NH ₃			NO ₃			pH			TP			TS		
	r	p	n	R	p	n	r	p	n	r	p	n	r	P	n
NO ₃	0.423	0.000	228												
pH	-0.497	0.000	220	-0.051	1.000	225									
TP	0.415	0.000	228	-0.145	1.000	233	-0.485	0.000	225						
TS	-0.313	0.000	221	-0.056	1.000	226	0.267	0.005	225	-0.134	1.000	226			
TSV	0.021	1.000	217	0.038	1.000	222	-0.140	1.000	221	0.351	0.000	222	0.617	0.000	223
SO ₄	-0.035	1.000	224	0.216	0.104	229	0.141	1.000	222	-0.087	1.000	229	0.522	0.000	223
TOC	0.295	0.001	225	0.246	0.017	230	-0.197	0.334	223	0.379	0.000	230	0.023	1.000	225
Fe	0.673	0.000	42	-0.132	1.000	42	-0.417	0.632	42	0.687	0.000	42	0.128	1.000	42
OP	0.753	0.000	107	0.409	0.001	107	-0.455	0.000	106	0.689	0.000	107	-0.115	1.000	107

	TSV			SO ₄			TOC			Fe		
	r	p	n	r	p	n	r	p	n	r	p	n
SO ₄	0.518	0.000	219									
TOC	0.311	0.000	221	0.122	1.000	227						
Fe	0.308	1.000	42	0.049	1.000	42	0.083	1.000	42			
OP	0.256	0.807	107	-0.157	1.000	104	0.483	0.000	107	0.759	0.000	42

*All variables log-transformed, except temperature
r - correlation coefficient
p - Bonferroni probability
n - sample size
Notably strong Correlations in bold.*

Under anaerobic conditions, orthophosphate-P (OP) and iron (Fe) are released from the sediments and NO_3^- is reduced to ammonia (NH_3). This is supported by the strong positive correlations between NH_3 , OP, and Fe. MeHg is strongly correlated to total phosphorus (TP) (Figure 7; $R^2 = 0.45$) but less so to OP; however, the sample size for OP-MeHg is less than half the sample size for TP and MeHg. Much of the TP in the wetlands is most likely OP, as indicated by the strong positive correlation between TP and OP ($r = 0.689$). Thus anaerobic conditions in the wetlands are effective in removing nitrogen (NH_3 either evades as a gas or is reduced further to nitrogen gas), while increasing MeHg and phosphorus concentrations in the water. The positive TP-MeHg relationship implies that effectively captures phosphorus will also happen to minimize MeHg release. A comparison of T-17 and T-24 illustrates this relationship: in the former, alum treatment removes phosphorus and also has a low MeHg concentration, whereas in the latter there is higher TP and higher MeHg (boxes in Figure 7).

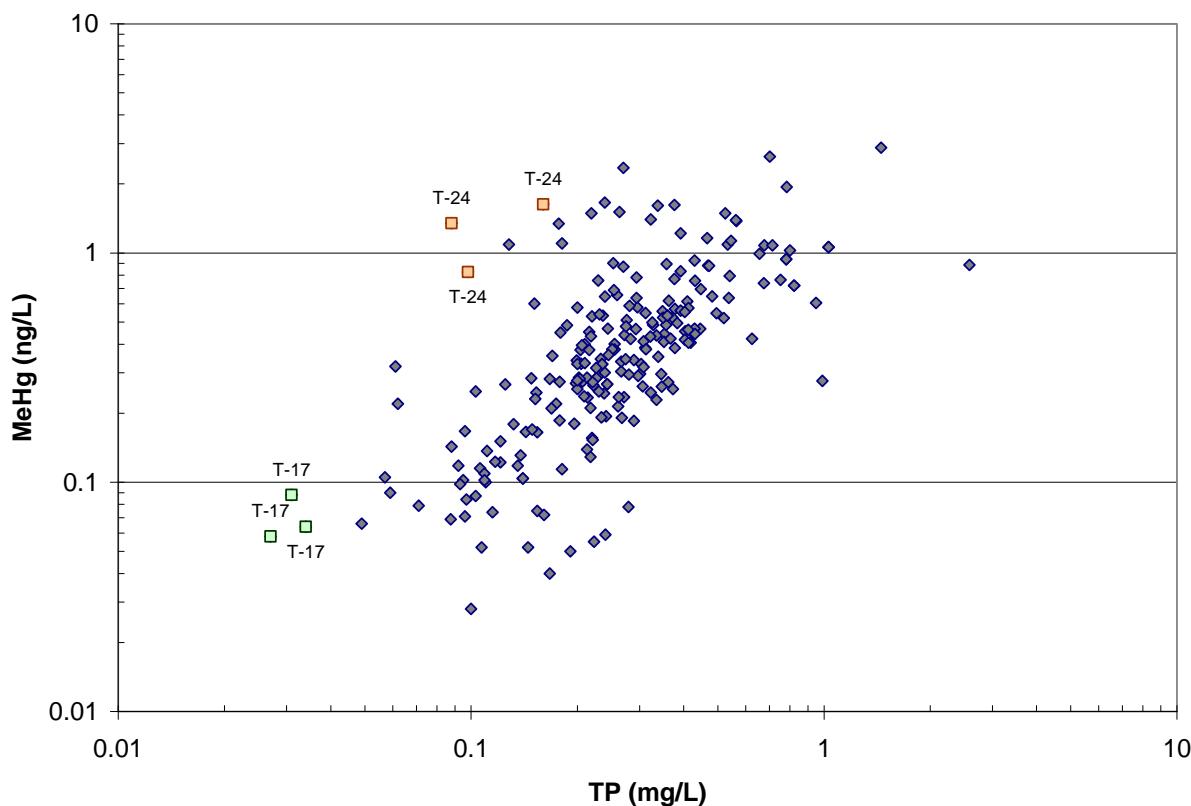


Figure 7 Log-log scatterplot of MeHg and TP from all stormwater wetlands

McCarrons-Villa Park (MVP) outlet has much more data than any other site. A linear regression of MeHg and TP at the outlet has a coefficient of determination (R^2) of 0.74, indicating a very strong relationship between the two variables (Figure 8). For every 0.1 mg/L increase in TP, MeHg increased about 0.2 ng/L. MeHg and OP also have a strong linear relationship, but there are fewer OP data to pair with MeHg. The relationship between TP, OP, and MeHg is evident in the time series at MVP outlet (Figure 9), with high concentrations occurring in late-July and early August when temperatures are high and dissolved oxygen concentrations are low. The MeHg-TP-DO relationship is discussed more in the next section on MVP intensive monitoring results.

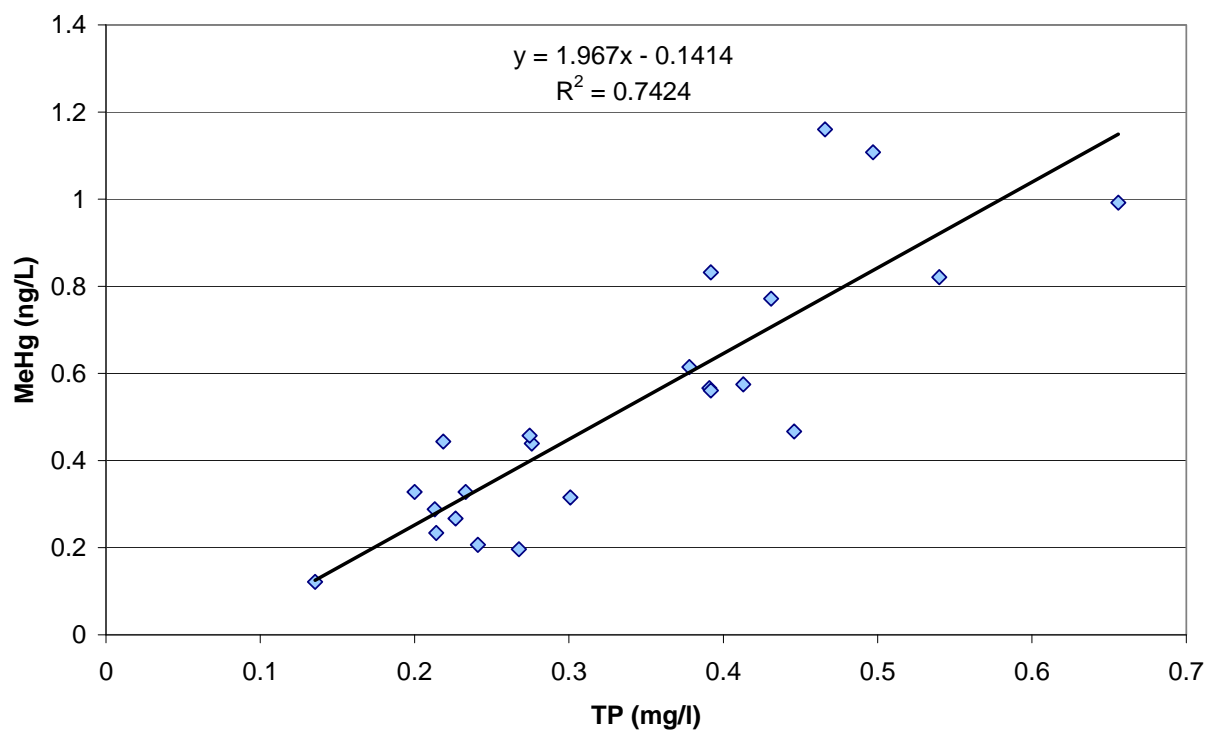


Figure 8 Linear relationship between MeHg and TP at McCarrons-Villa Park outlet

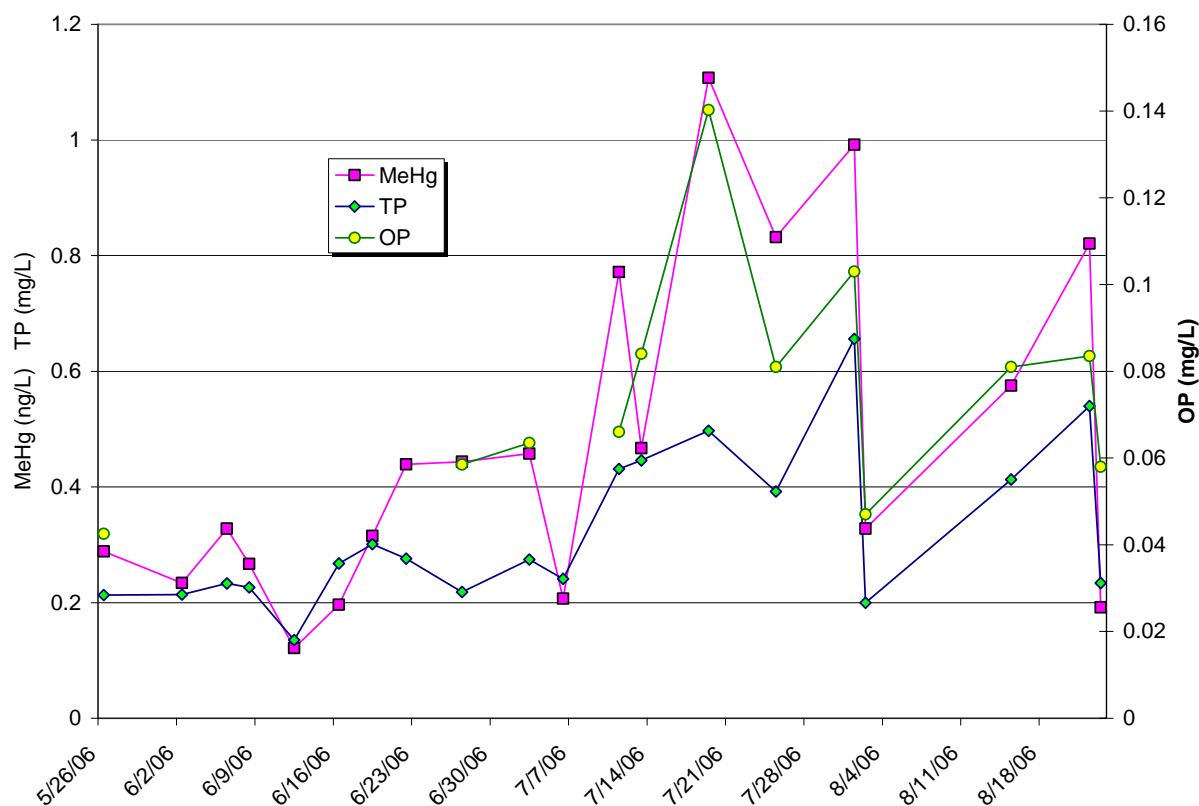


Figure 9 Time series of MeHg, TP, and OP at McCarrons-Villa Park outlet

As discussed in the Introduction, sulfate-reducing bacteria are known to methylate mercury and additional sulfate in sulfate-limited wetlands can stimulate their activity and mercury methylation (e.g. Jeremiason 2006). It is hypothesized that at very high sulfate concentrations (e.g., greater than 100 mg/L) high sulfide concentrations inhibit rather than simulate methylation because the excess sulfide binds with Hg, making it unavailable for methylation. There is no relationship between sulfate and MeHg in the stormwater wetlands (Figure 10). Nor is there any correlation between sulfate and THg or %MeHg (see Table 7). Because methylation is most likely occurring in the wetland sediments and releasing MeHg into the water, a negative relationship between sulfate and MeHg is more likely observable in the wetland sediments. No sediment samples were collected for this study.

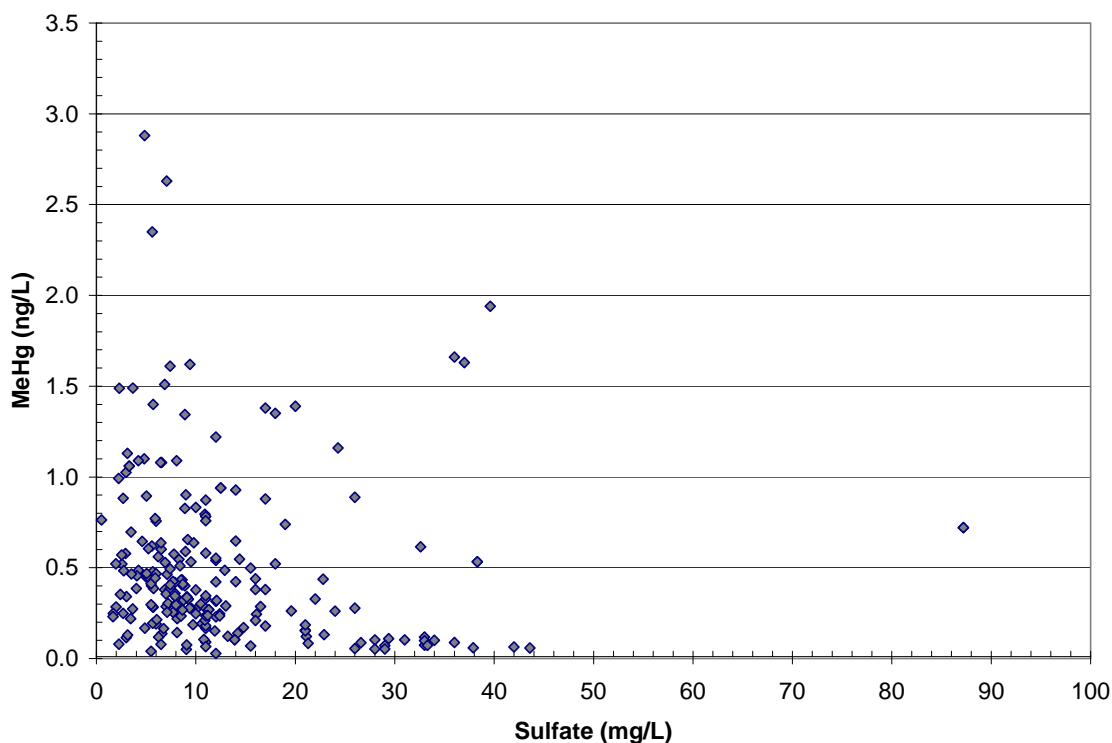


Figure 10 Scatterplot of MeHg and sulfate from all stormwater wetlands

4. Dissolved and Particulate Fractions

Most samples were collected as unfiltered grabs or automatic composites; however, in 2005 some samples were collected with a peristaltic pump fitted with acid-cleaned Teflon tubing and 0.45 micron capsule filters to collect both total (i.e., particulate and dissolved) and filtered (i.e., dissolved) samples. All filtered and unfiltered samples were analyzed for all analytes. The dissolved fraction—filtered/unfiltered—is summarized for all analytes in Table 8. As expected, alkalinity, ammonia, and chloride are completely in the dissolved fraction. Sulfate had a mean dissolved fraction less than 100% despite all sulfate samples being filtered before analysis; however, the upper 95% confidence limit is 99% and, therefore, can be considered essentially all dissolved. Other analytes show a range of partitioning between dissolved and particulate phases. Total organic carbon, total volatile solids, and total solids are almost all dissolved. Most of the total solids are dissolved solids, such as sulfate, chloride, and bicarbonates, rather than suspended solids. For total organic carbon, the results indicate that TOC must closely match dissolved organic carbon. The analytes that are more unpredictable and had a range of partitioning are total Kjeldahl nitrogen (TKN), total phosphorus (TP), THg and MeHg. On average, 68% of TKN and 38% of TP were in the dissolved phase, whereas about half the THg and MeHg were in the dissolved phase.

Table 8 Dissolved fraction of analytes

Analyte	N	mean	Stdev	CV%	95% UCL
Alkalinity, Total	16	0.98	0.04	4%	1.00
Ammonia	5	1.00	0.00	0%	1.00
Chloride	10	1.00	0.06	6%	1.04
Kjeldahl Nitrogen, Total	16	0.62	0.21	34%	0.73
Phosphorus, Total	16	0.38	0.20	53%	0.49
Solids, Total	16	0.96	0.05	5%	0.98
Solids, Total Volatile	16	0.90	0.10	11%	0.95
Sulfate	16	0.95	0.08	8%	0.99
Total Organic Carbon	15	0.94	0.04	4%	0.96
THg	15	0.51	0.23	45%	0.63
MeHg	15	0.52	0.36	68%	0.72

nitrate-nitrate not included because most results were < 0.05 mg/L (DL)

Looking in more detail at the THg and MeHg partitioning provides some insights into the behavior of mercury. Table 9 lists unfiltered, filtered, and dissolved fraction (filtered/unfiltered) for the specific samples. For BCBP, the dissolved fraction of THg increased somewhat from the inlet to the outlet, but MeHg dissolved fraction increased from 9% to 62%—a seven-fold increase in the dissolved fraction. Two samples were collected in mid-August and early September at Gervais Mill, MVP S1 and MVP S5. They show that THg dissolved phase was consistent at a given site, even with very different THg concentrations, such as at S1. Comparing S1 and S5, partitioning changed from 65% on solids at the inlet, S1, to 45% on solids near the outlet, S5. Recall that S1 is after the primary detention pond at MVP; therefore, THg in the inflows to the detention pond were probably close to 100% on solids. MeHg at S1 is about 75-80% on solids, but at S5 the MeHg concentration was up to ten-fold higher than at the inlet and nearly all of it in the dissolved phase. In the Tanners Lake wetlands, nearly all THg in T-17 was dissolved after particulates had been removed by the alum treatment, yet T-24, with THg concentration 2.5 to 3 times higher than T-17, also had most of the THg in the dissolved phase. MeHg in both T-17 and T-24 is all in the dissolved phase. Considering all the partitioning data for THg and MeHg, at high THg concentrations 60% or more is in the particulate phase, whereas it is the opposite for MeHg: at high MeHg, more than 60% is in the dissolved phase.

Table 9 THg and MeHg partitioning among dissolved and particulate phases

Sample	Date	THg			MeHg		
		Unfiltered	Filtered	Diss.frac.	Unfiltered	Filtered	Diss.frac.
BCBP In	8/17/05	6.89	1.65	0.24	0.143	0.0125	0.09 *
BCBP Out	8/17/05	8.38	2.68	0.32	1.344	0.837	0.62
Amelia	8/25/05	1.03	0.84	0.82	0.077	0.048	0.62
Amelia Dup	8/25/05	1.11	0.80	0.72	0.081	0.05	0.62
Calhoun South	8/18/05	3.11	0.98	0.32	0.619	0.081	0.13
Gervais Mill	8/19/05	2.40	0.91	0.38	0.166	0.145	0.87
Gervais Mill	9/2/05	2.05	0.7	0.34	0.153	0.031	0.20
MVP S1	8/19/05	4.90	1.72	0.35	0.268	0.063	0.24
MVP S1	9/1/05	1.23	0.43	0.35	0.104	0.0125	0.12 *
MVP S5	8/19/05	1.94	1.06	0.55	0.533	0.389	0.73
MVP S5	9/1/05	2.76	1.52	0.55	1.06	1.09	1.03
T-17	8/23/05	0.74	0.72	0.97	0.058	0.062	1.07
T-24	8/23/05	2.23	1.76	0.79	0.827	0.825	1.00
Veritas	8/23/05	2.56	0.73	0.29	0.32	0.075	0.23
Wolfe	8/18/05	2.27	1.45	0.64	0.09	0.026	0.29
mean		2.91	1.20	0.51	0.39	0.25	0.52
stdev		2.19	0.59	0.23	0.40	0.36	0.36
median		2.27	0.98	0.38	0.17	0.06	0.62
min		0.74	0.43	0.24	0.06	0.01	0.09
max		8.38	2.68	0.97	1.34	1.09	1.07

* Used 0.5 DL ($0.5 \times 0.025 = 0.0125$)

B. McCarrons – Villa Park

1. Watershed Description

McCarrons – Villa Park stormwater treatment system (MVP) receives most of the runoff from the Lake McCarrons watershed and discharges to the northwest side of the lake (Figure 11). MVP was occasionally sampled in 2005 and intensively sampled in 2006. In 2005, the outflow was monitored for flow and nutrient chemistry by Terry Noonan, Ramsey County Public Works. Responsibility for monitoring was transferred to Capitol Region Watershed District (CRWD) in 2006. The CRWD staff used the same setup at the outlet and added an inlet station at the outlet of the primary detention pond (S1). Although this inlet site was downstream of the primary detention pond it served as inlet for the remaining wetland treatment system. Grab sample results (see below) indicated the detention pond did collect solids, including mercury.

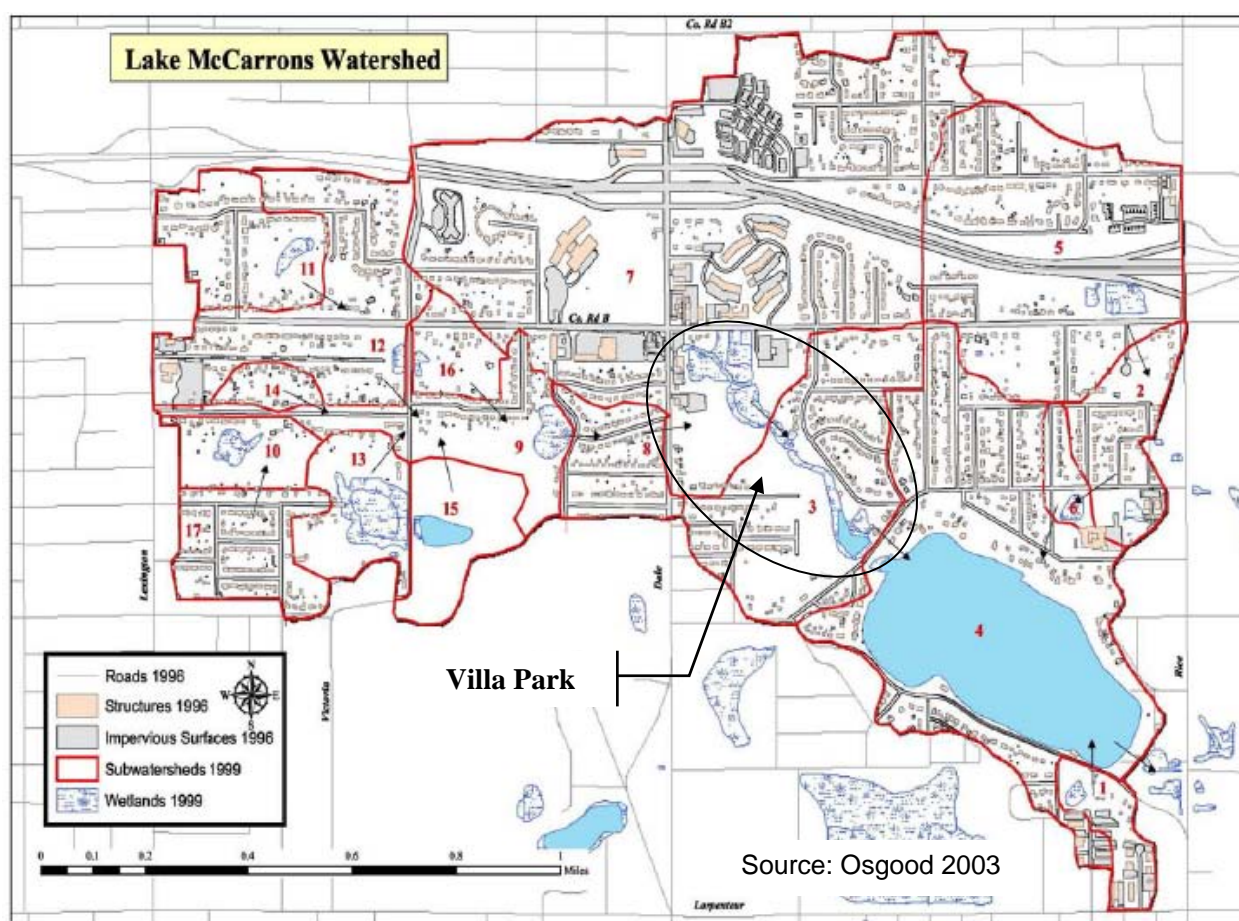


Figure 11 Lake McCarrons watershed and location of Villa Park

Flows at S1 inlet and the outlet are very similar (Figure 12), thus indicating there are no other significant inflows. The correlation coefficient for inflow and outflow (pairwise comparison) is 0.86. In a mass balance, inflow mass load ($Q_{in}C_{in}$) equals outflow mass load ($Q_{out}C_{out}$) plus change in storage (ΔS). Given the similarity of the inlet and outlet flows ($Q_{in} \cong Q_{out}$), and no apparent change in storage, changes in concentration are proportional to changes in load. In other words, differences in inflow and outflow concentrations over the same time period indicate equivalent changes in load.

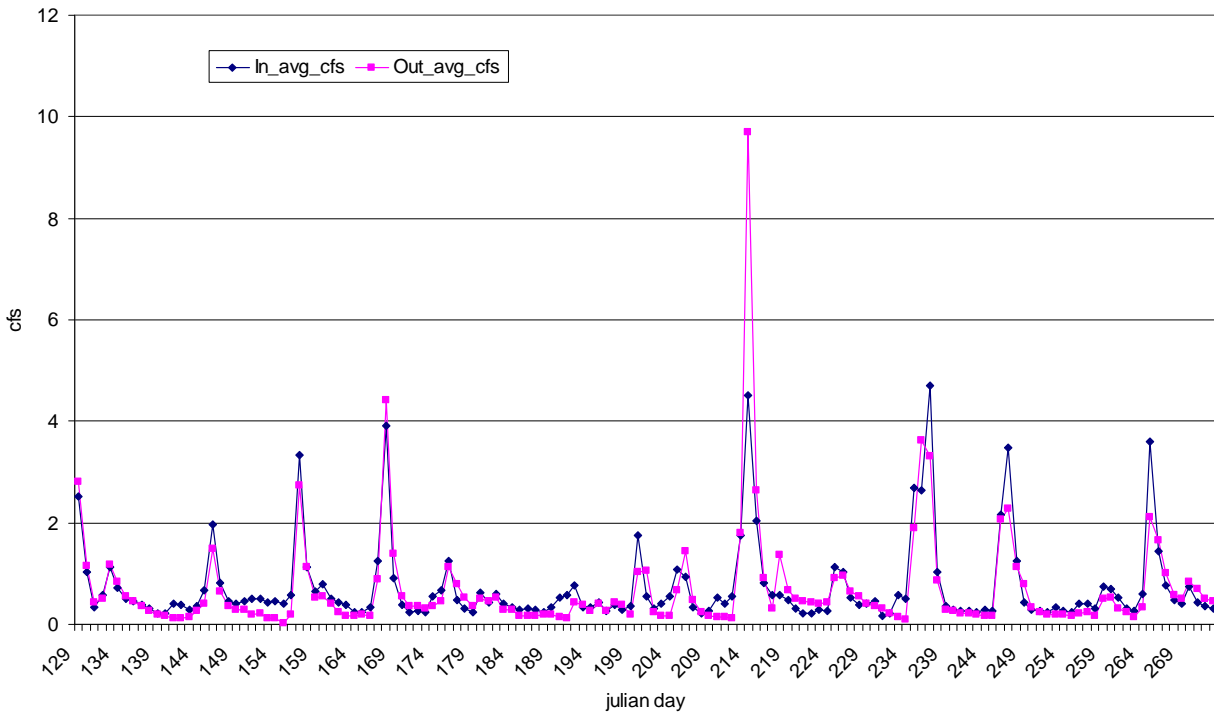


Figure 12 MWTs 2006 average daily flows at S1 (inlet) and Outlet

A time series of paired inlet and outlet THg and MeHg concentrations show THg at the inlet (S1) was nearly always greater than or equal to the outlet (Figure 13). In contrast, MeHg concentration at the outlet was considerably higher than the inlet by mid July, although by mid-August they are similar again. This apparent reduction in THg and increase MeHg concentration is consistent with mercury methylation occurring in the wetlands during mid-summer.

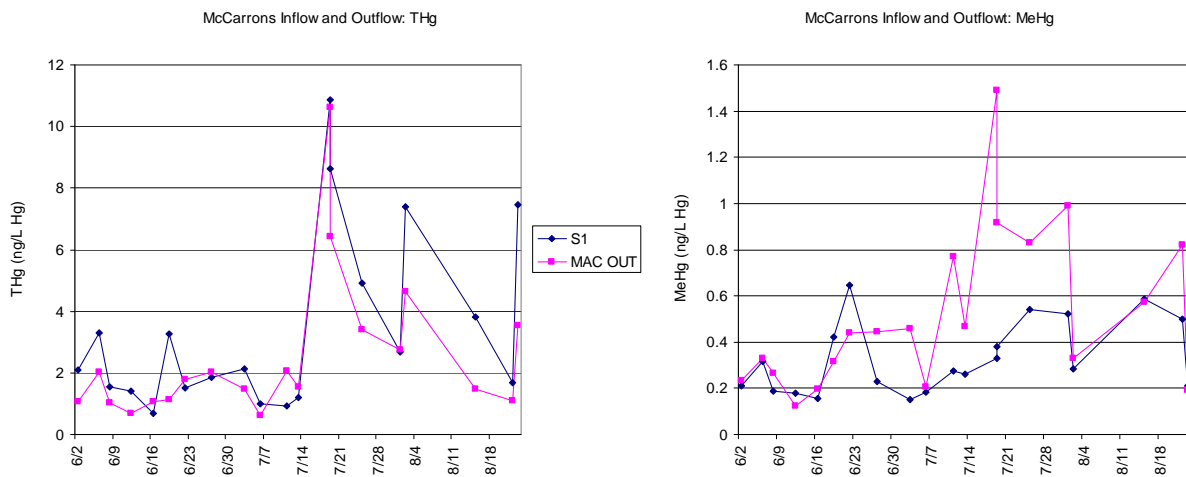


Figure 13 MVP Inflow and Outflow: (a) THg and (b) MeHg through Summer of 2006

2. Comparison of Automated and Grab Sample Results

A question addressed by this study at MVP was what is the difference between composite automatic samples and grab samples? Automatic samplers have not been used for mercury sampling—even for storm event monitoring—because of the concern about contamination. This is apparently the first study that attempts to use automatic samplers for low level mercury sampling in surface waters. Automatic samplers have been used for wastewater influent sample collection, but there is less of concern about contamination since mercury concentrations are at least ten-fold higher than typical surface water concentrations. Blanks of deionized water collected through an Isco (automated composite) sample train following surface water collection indicated no carryover contamination following double flushing of the Teflon lines between samples.

Grab samples were collected during dry and wet weather, while composite samples were only collected during storm events. Resulting mercury concentrations at S1 and the outlet are shown in Figure 14 and Figure 15, along with flows at the inlet and outlet.

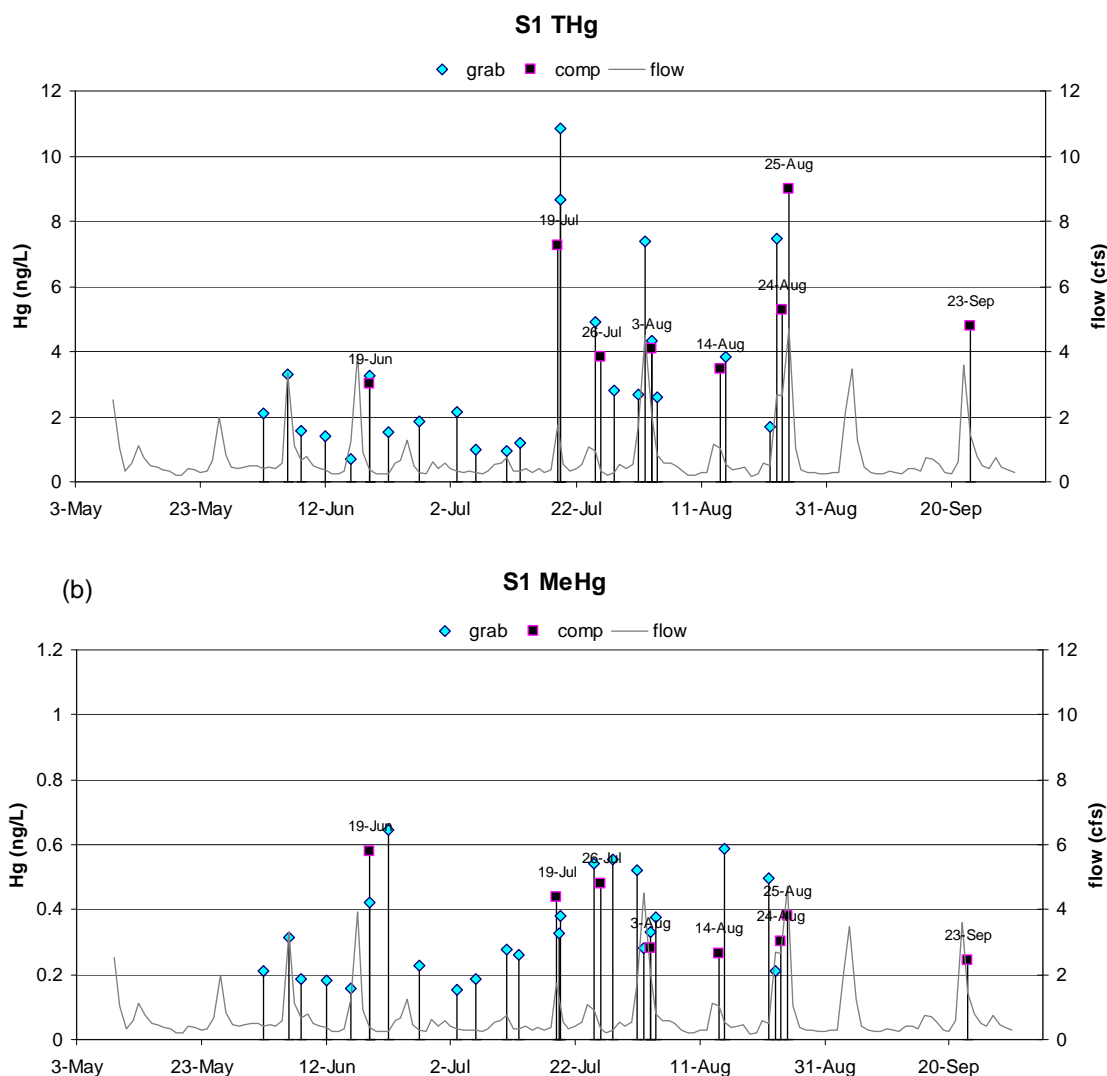


Figure 14 S1 flow and (a) THg and (b) MeHg concentrations (grabs and composite samples)

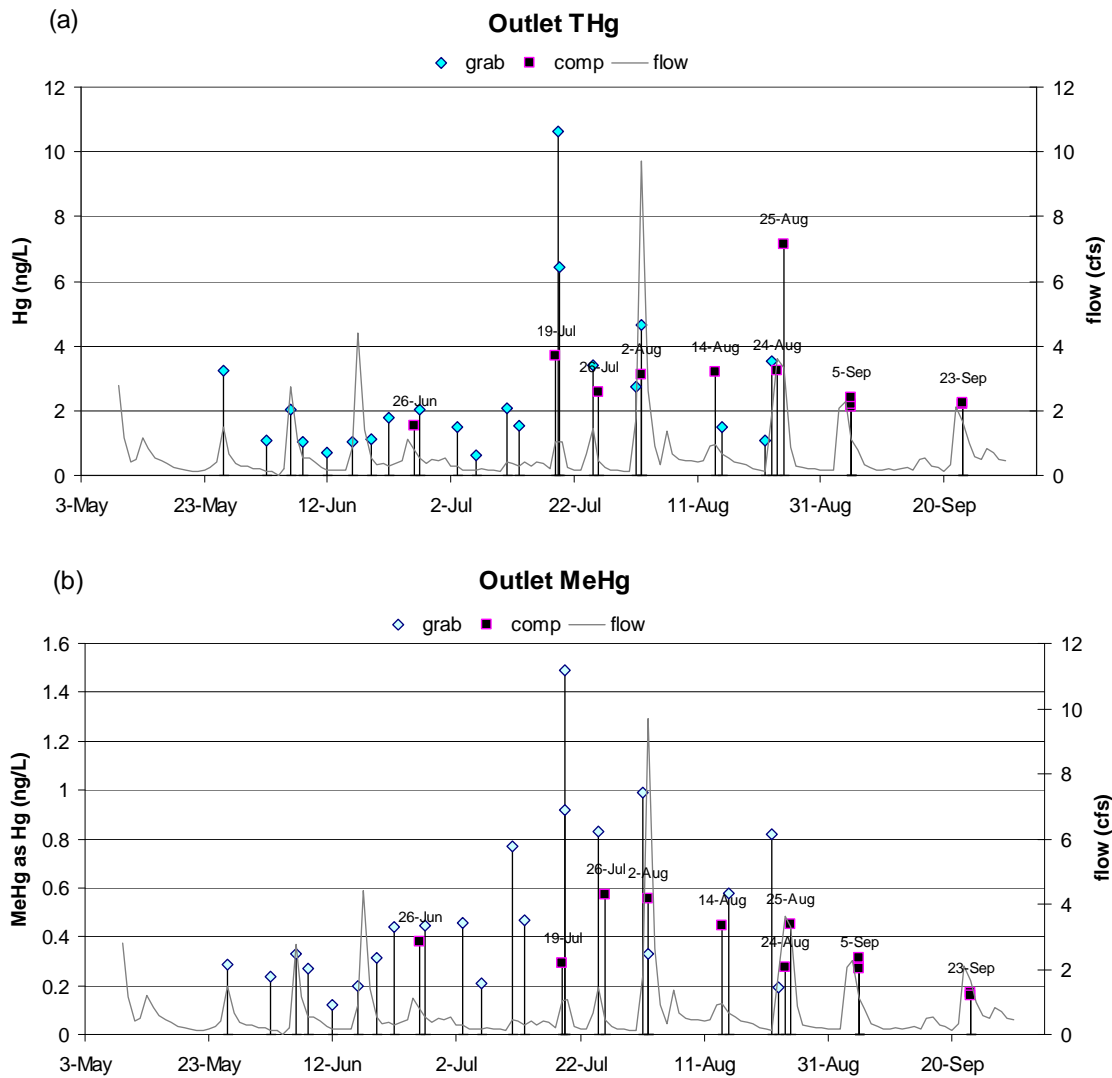


Figure 15 MVP outlet flow and (a) THg and (b) MeHg concentrations (grabs and composite samples)

The paired differences between grabs and automatic composite samples indicate grab samples from the same location and overlapping time have slightly higher THg concentrations and very similar MeHg concentrations (Table 10). A notable exception was at the outlet on 19-July when THg and MeHg in the grab samples were much higher than the composite sample. Two grab samples collected two hours apart on that sample date were dissimilar, but both were above the composite sample concentrations. At this storm event, the composite sample was delayed because of a dead battery; therefore, the composite sample did not include the first flush. The first grab samples had the higher concentrations and did include the first flush. Although the THg concentration of 3.7 ng/L in the outlet composite sample on 19-July is similar to other sample dates, the grab sample THg concentration of 6.4 ng/L is similar to the relatively high concentrations measured at the inlet on the same day. This comparison suggests the grab sample was a more accurate representation of concentrations on that date.

Table 10 Comparison between grab samples and automatic composite samples at the inlet and outlet

Date	S1	ISCO 1	Diff	OUT	ISCO 2	Diff
THg						
6/19/06	3.25	3.03	0.22	1.14	3.06	(1.92)
6/27/06	---	---	---	2.03	1.52	0.51
7/19/06	8.64	7.24	1.40	6.43	3.69	2.74
7/25/06	4.92	3.82	1.10	3.42	2.57	0.85
8/2/06	---	---	---	4.65	3.11	1.54
8/3/06	4.31	4.08	0.23	---	---	---
8/15/06	3.82	3.47	0.35	1.48	3.18	(1.70)
Means	4.99	4.33	0.66	3.19	2.85	0.34
MeHg						
6/19/06	0.422	0.580	(0.16)	0.316	0.270	0.05
6/26/06	---	---	---	0.444	0.378	0.07
7/19/06	0.380	0.439	(0.06)	0.917	0.290	0.63
7/26/06	0.540	0.478	0.06	0.832	0.574	0.26
8/3/06	0.282	0.282	0.00	0.328	0.557	(0.23)
8/14/06	0.589	0.265	0.32	0.575	0.444	0.13
8/24/06	0.211	0.301	(0.09)	0.192	0.275	(0.08)
Means	0.40	0.39	0.01	0.51	0.40	0.12

The mean THg and MeHg concentrations are higher in the grab samples than in the composite samples; however, based on a paired t-test ($\alpha = 0.05$), the differences between grabs and composite samples were not significant even when inlet and outlet grab-composite pairs were combined to give a larger sample size (Table 11). Thus, these results indicate that grab samples can adequately represent the composite concentrations from a storm event.

Comparing only grab samples at the inlet and outlet, there was a significant decrease in THg and a significant increase in MeHg (bottom of Table 11). Going from inlet to outlet, the mean concentrations from 20 sample dates were 26% lower for THg and 58% higher for MeHg. The fraction MeHg (MeHg/THg), consequently, shows a significant ($p=0.0008$) increase from the inlet (15%) to the outlet (26%).

Table 11 Statistical (t-test) results comparing grab samples and automatic composite samples

		THg			MeHg		
		Mean	N	p	Mean	N	P
Inlet	Grabs	4.99	5	0.055	0.404	6	0.856
	Composites	4.33			0.391		
Outlet	Grabs	3.19	6	0.671	0.515	7	0.303
	Composites	2.85			0.398		
Inlet & Outlet	Grabs	4.01	11	0.262	0.464	13	0.299
	Composites	3.52			0.395		
Grabs	Inlet	3.42	20	0.005	0.329	20	0.012
	Outlet	2.53			0.520		

3. Mercury Mass Loading

The wetland system removes Hg, yet methylates a fraction of the Hg. Is the MeHg load from the wetland system a significant contribution to Lake McCarrons? To answer this question, the concentration is multiplied by flow to get the mass load out of the system. THg and MeHg loads were calculated for MVP in 2006 using the FLUX model (Walker 1996). In 2005, flows were available only for the outlet and the sampling was not as intensive as in 2006.

The total flow volume during the 2006 sample period (145 days) was essentially the same at the inlet (S1) and outlet: about 250,000 m³ or 0.25 hm³ (Table 12a). At both the inlet and outlet, the mean *sampled* flows were higher than the total mean flow rate, which is expected given sampling was most intensive around storm events, although this study included considerable baseflow samples.

The FLUX model generates load estimates using six methods. The method with the lowest coefficient of variation (CV) is generally the preferred method, unless the mass load estimate is considerably divergent from other estimates. The lowest CVs for THg load estimates were two regression methods (Methods 4 and 5), which is expected given the positive relationship between flow and THg concentration (Table 12b). Method 2 was used for MeHg, which uses a weighted average concentration rather than a flow-concentration regression to estimate load. Method 2 is most appropriate when there is no relationship between flow and concentration.

Table 12 Summary of FLUX model results for MVP 2006

(a) Flow Summary	S1	OUTLET
Flow Date Range	5/9/06 - 9/30/06	5/9/06 - 9/30/06
Sample Date Range	6/2/06 - 9/23/06	5/26/06 - 9/23/06
Flow Duration (days):	145	145
Number of sample days	27	27
Total Flow mean rate (hm ³ /y)	0.643	0.606
Total Flow Volume (hm ³)	0.26	0.24
Sampled Flow mean rate (hm ³ /y)	1.145	1.226

(b) Load Summary	THg		MeHg	
	S1	OUT	S1	OUT
Method	5	4	2	2
Coefficient of Variation (CV)*	0.082	0.094	0.065	0.136
C/Q slope	0.481	0.425	-0.019	0.003
Probability of C/Q slope	0.001	<0.0001	0.836	0.973
Mass (mg)	1093	649	82.9	98.6
Weighted Mean Conc. (ng/L)	4.28	2.70	0.325	0.410
Load (mg/y)	2754	1635	209	248
Drainage Area (ha)	248	298	248	298
Flux (µg m ⁻² yr ⁻¹)	1.11	0.55	0.08	0.08

* Out - MeHg had highest CV; methods 2, 3, 4, and 5 gave very similar estimates for mass and CV; Method 4 had lowest CV (0.131) and gave a mass of 98.4 mg.

THg concentration was positively related to flow at the inlet and outlet, as shown by the significantly positive C/Q slope; whereas MeHg concentrations were not correlated to flow (i.e., C/Q slope around zero and p>0.05). Much of the inorganic Hg, which makes up most of the THg, is bound to particulates. Consequently, THg mass and annual load decreased from the S1 to the outlet by 41% (1-649/1093), most

likely because particulates settled out in the wetland. In contrast, MeHg mass and annual load increased by 19% (1-98.6/82.9) between the inlet and outlet. Actual change in mass during the 145 days of summer flows was -444 mg of THg (649 – 1093) and +16 mg of MeHg (98.6 – 82.9). If the mass is extrapolated to the entire year, 1120 mg of THg are removed in the system and 40 mg of MeHg are produced. Of the 1093 mg THg entering the system (during 145 days), only a net 1.4% (16 mg) was converted to MeHg that was discharged out of the system to McCarrons Lake.

Flux calculations are the annual load divided by the drainage area. THg flux was $1.1 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$ at the inlet and $0.55 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$ at the outlet. The 51% decrease; is greater than seen in annual load because the area (divisor) increases between the inlet and outlet. Surprisingly, MeHg flux is the same at the inlet and outlet: $0.08 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$. MeHg flux is also the same for the difference between loads and areas (40 mg/50 ha). Thus, these results indicate the addition of the wetland does not increase the flux (or yield) of MeHg from the watershed. The 50 ha difference between the inlet and outlet includes about 22 ha of upland area that drains directly to the last wetland cell; as indicated above, the flow rate at S1 and the outlet were nearly identical, thereby ruling other significant inflows. Therefore, if the upland flow directly into the last wetland cell is assumed negligible, MeHg is divided by only the wetland area (28.2 ha) to give a MeHg flux of $0.14 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$.

For comparison, sulfate and phosphorus fluxes were estimated. Sulfate input was $9,105 \text{ kg y}^{-1}$ at S1 and atmospheric deposition directly to MVP was 250 kg y^{-1} ; outflow sulfate load was $5,611 \text{ kg y}^{-1}$, giving a net 40% removal of sulfate. Flow weighted sulfate concentration was 14 mg/L at the inlet and 9 mg/L at the outlet. Total phosphorus load increased from 182 kg y^{-1} at the inlet to 206 kg y^{-1} at the outlet – a 13% increase. TP flux was about $70 \text{ mg m}^{-2} \text{ y}^{-1}$, which is very close to a flux of $63 \text{ mg m}^{-2} \text{ y}^{-1}$ reported as the loading to another urban wetland (Reinelt and Horner 1995). Flow-weighted TP concentration increased from 0.279 mg/L at the inlet to 0.325 mg/L at the outlet. These results show that a substantial mass of sulfate is removed in the wetland, but the concentration remains at a similar level. In contrast, phosphorus is not removed in the wetland and instead increases slightly, which supports the other information about TP concentrations throughout the MVP wetland chambers (see Continuous Monitoring Study below).

The MeHg flux—including the higher MeHg flux estimate—is on the low end of estimates from other wetlands (Table 13). The THg flux from MVP is lower than even the low estimates from other wetlands, but within the range for Ontario uplands. MVP is the only urban residential/commercial watershed among the wetlands listed in Table 13. For example, the New York site is a deciduous forested beaver pond in the Adirondacks, the Ontario upland and wetland are in boreal forests, and the Southern Ontario wetland is a forested swamp consisting of cedar and deciduous species. MVP's THg flux may be lower because of more Hg associated with solids in the urban runoff and consequently greater removal efficiency. Relatively low MeHg flux is consistent with the understanding that urban runoff probably has a greater hydrologic load to the wetland but much lower organic matter to support the anaerobic microbial community. Based on these MVP's flux rates, the MVP wetland removes about 28 times more Hg than is produced as MeHg.

Galloway and Branfireun (2004) reported a net MeHg production internal to the wetland of $0.1 \mu\text{g m}^{-2} \text{ y}^{-1}$, which is midway between the two estimates (0.08-0.14) for MVP wetlands. This comparison suggests the MVP wetland produces MeHg at the same rate as a natural wetland; yet the overall MeHg flux from MVP is generally below other MeHg flux rates from non-urban wetlands. One interpretation of this difference is that the MeHg load to the non-urban wetlands is higher than the MeHg load from the urban runoff and it is this upland load that accounts some of the difference.

Table 13 Comparison of THg and MeHg flux ($\mu\text{g m}^{-2} \text{yr}^{-1}$) from wetlands

Location	THg Flux	MeHg Flux	Reference
Sweden	0.8-5.9	---	Johannson et al., 1991
Southern Sweden	2.3-3.5	0.12	Lee and Hultberg, 1990
Northern Sweden	1.2-1.8	0.08-0.16	Lee et al., 1995
Wisconsin	0.8	0.06-0.15	Krabbenhoft et al., 1995
Ontario	0.6-2.1	---	Mierle and Ingram, 1991
Ontario Upland	0.3-2.3	0.007-0.098	St. Louis et al., 1994
Ontario Wetland	---	0.18-0.55	St. Louis et al., 1994
New York	2.2	0.17	Driscoll et al., 1998
Southern Ontario	2.1	0.18	Galloway and Branfireun, 2004
McCarrons–Villa Park	0.55	0.08	This Study

Most of this table based on Table 1 in Driscoll et al. 1998

How does the MeHg load from the watershed compare to the MeHg deposited on the watershed by rain, snow, and dry deposition? Multiplying the atmospheric deposition of MeHg and drainage area to S1 would give an estimate of atmospheric deposition. Our best estimate of annual atmospheric deposition of mercury (inorganic and MeHg) is 125 mg per hectare (Swain *et al.* 1992). MeHg concentration in rain and snow is estimated at 0.5% to 2.5% of THg concentration (Lindberg *et al.* 2007); therefore, the MeHg load estimate would range from 155 $\text{mg}\cdot\text{y}^{-1}$ to 774 $\text{mg}\cdot\text{y}^{-1}$. The MeHg load estimate reported here is 209 $\text{mg}\cdot\text{y}^{-1}$. Thus, it appears reasonable that all MeHg entering the wetland from the watershed could be from atmospheric deposition. One might expect direct MeHg export from rain and snowmelt given the abundant impervious surface cover in the urban watershed.

What does the MeHg load of 40 $\text{mg}\cdot\text{y}^{-1}$ represent to MeHg mass balance of Lake McCarrons? Other sources of MeHg are direct atmospheric deposition, delivery from other watershed drainage, and in-lake methylation. There is no estimate of in-lake methylation, but the other two sources can be estimated. Using the atmospheric deposition described above, direct MeHg load would be 21-103 $\text{mg}\cdot\text{y}^{-1}$. Multiplying the watershed MeHg flux (0.08 $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$) by the total watershed area (332 ha) gives a watershed MeHg load of 280 mg. The total MeHg load to Lake McCarrons—assuming in-lake methylation is negligible—is 301-383 $\text{mg}\cdot\text{y}^{-1}$. Therefore, the annual load of 40 mg from MVP wetlands represents 10-13% of the total load. While this is a significant contribution to the total MeHg load to the lake, the similarity of the upland and wetland MeHg fluxes imply that 40 mg would be released from the same area if it were a surrounding land cover other than a wetland. The only way to remove the 40 mg MeHg from the lake's mass balance would be to eliminate drainage from the area or somehow decrease the methylation efficiency of the wetland.

To understand what affect the 40 mg MeHg has to the biomass of the lake, a bioaccumulation model, such as the Mercury Cycling Model, needs to be calibrated for the lake and the mercury inputs. The model also requires an estimate of phytoplankton, zooplankton, and fish biomass, as well as a hydrologic balance. The modeling exercise is beyond the scope of this report. Simply looking at the MeHg concentration or mass in the water column is not sufficient to understand the relative contribution from the wetland. Three samples were collected from the lake during the summer 2005. The lake's MeHg concentration in all three samples was less than the detection limit ($<0.025 \text{ ng/L}$); mean THg concentration was 0.65 ng/L ($\text{CV} = 9.5\%$, $n=3$). Using limnological data compiled by Myrbo and Shapley (2006), the estimated epilimnetic volume is 840,235 m^3 . The product of this volume and a MeHg concentration one-half the detection limit (0.0125 ng/L) is 10.5 mg; well below the estimated annual load of MeHg to the lake.

4. Continuous Monitoring Study

Beginning in mid-June, five recording YSI sondes were deployed along the flow path of MVP at sample sites S1-S5 (Figure 16). Each sonde recorded temperature, dissolved oxygen, pH, and specific conductivity at 15 minute intervals. The sondes were deployed twice between July 28 and August 4, 2006. The largest storm of the 2006 growing season was on August 2nd. In general, the results confirmed that some areas, in particular the outlet wetland, go anoxic during the summer. All the results of that study are presented in Appendix B. Only the results at three sites during the week of the largest storm event are discussed here.

Results for sites S1, S3, and S5 are summarized in Figure 17. The St. Paul Climatological Observatory reported a total of 5.1 inches of rain on 8/1/06 and 8/2/06. Two other precipitation stations in St. Paul confirmed that at least 3.0 inches of rain fell on 8/2/06. Before the August 2nd storm, S1 showed clear diurnal fluctuations in dissolved oxygen; temperature and conductivity rose slightly, and pH remained steady. In contrast, S3 and S5 were anoxic before the storm. On August 2nd, all three sites exhibit a sharp decrease in conductivity. Dissolved oxygen was initially low at S1 and then all three sites had a marked rise in dissolved oxygen as the stormwater flushed through the system.

After the storm event, dissolved oxygen dropped to anaerobic conditions at S1, but continued to fluctuate diurnally at S3 and S5. Corresponding to the changes during the storm event, THg and MeHg showed a sharp change as well (Figure 18). THg increased and MeHg decreased at all sites during the storm event. After the storm, THg concentrations returned to pre-storm level, whereas MeHg concentrations remained low at sites S1 and S3, but increased to pre-storm levels at S5. Total phosphorus (TP) and ortho-phosphate phosphorus (OP) showed patterns similar to MeHg (Figure 19). The combined results clearly show that MeHg and TP are an inverse function of dissolved oxygen concentrations in the wetland system.

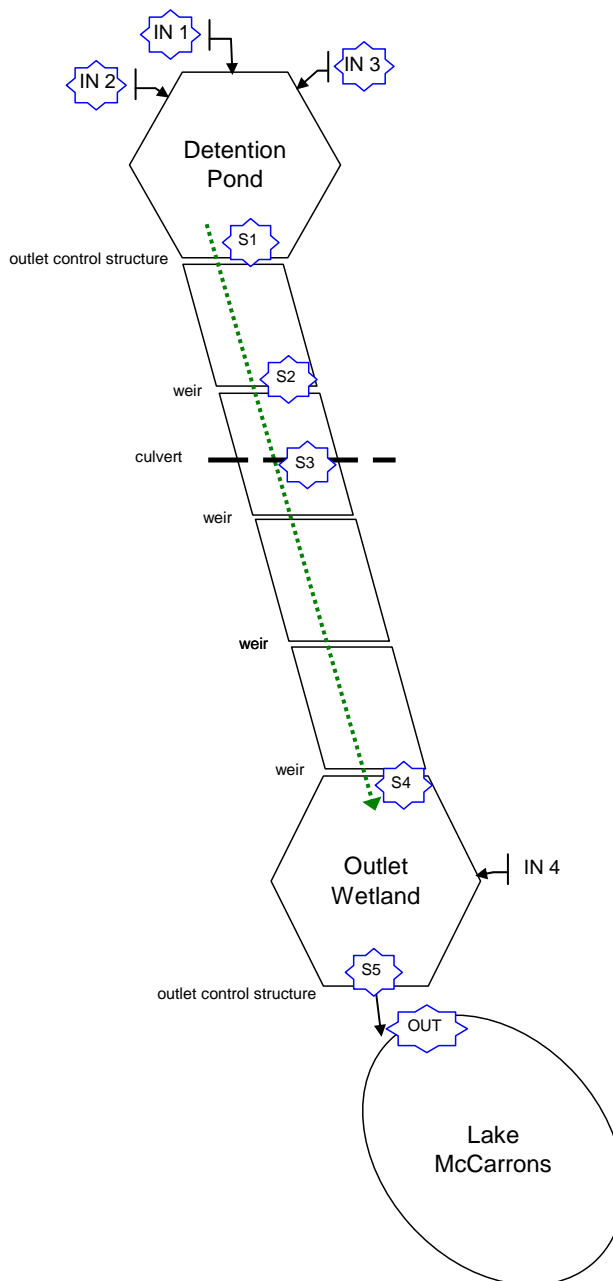


Figure 16 Schematic of MVP showing sample sites

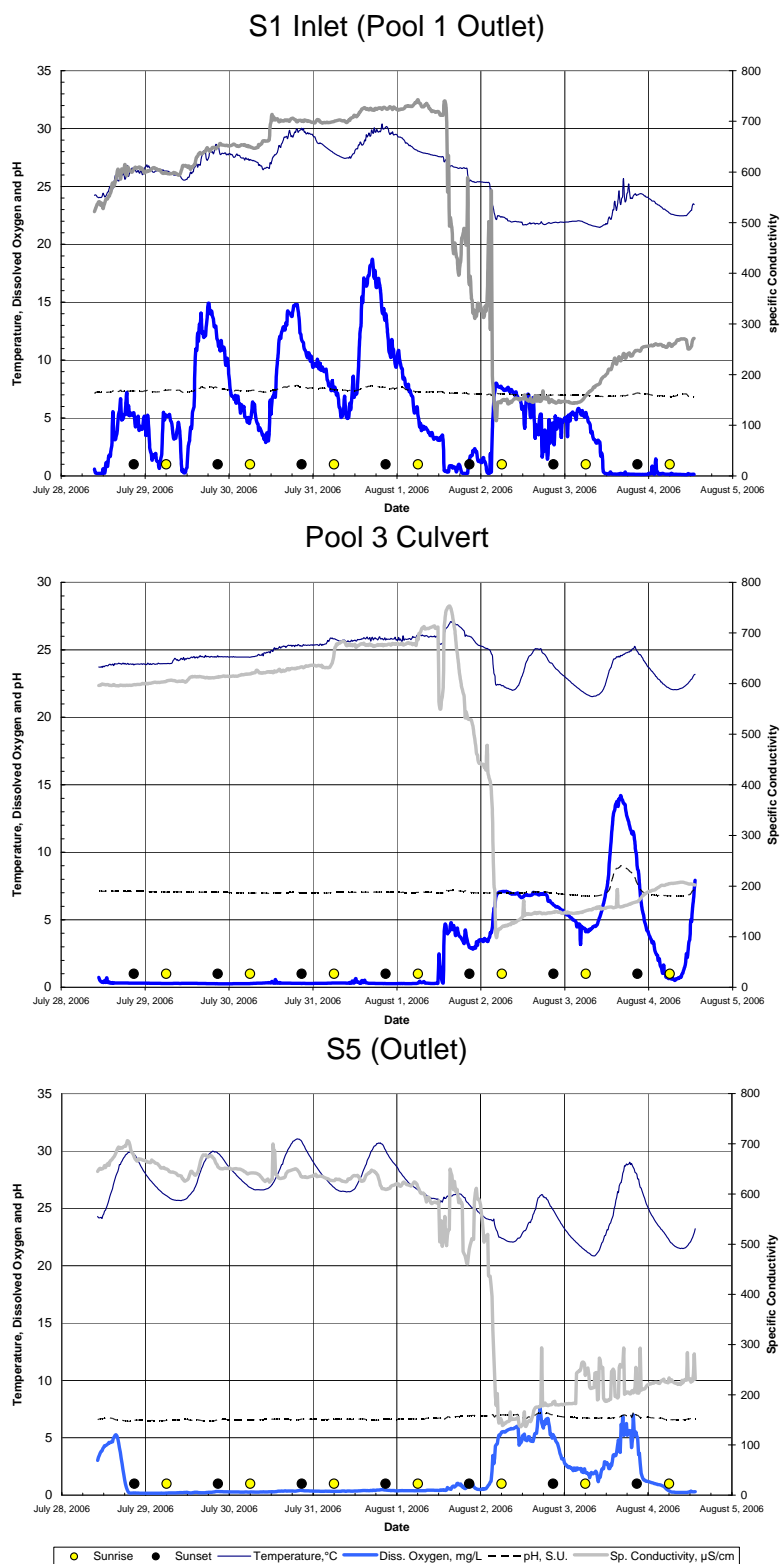


Figure 17 Continuous recording during the week of July 28 – August 4, 2006 at Sites S1, S3, and S5

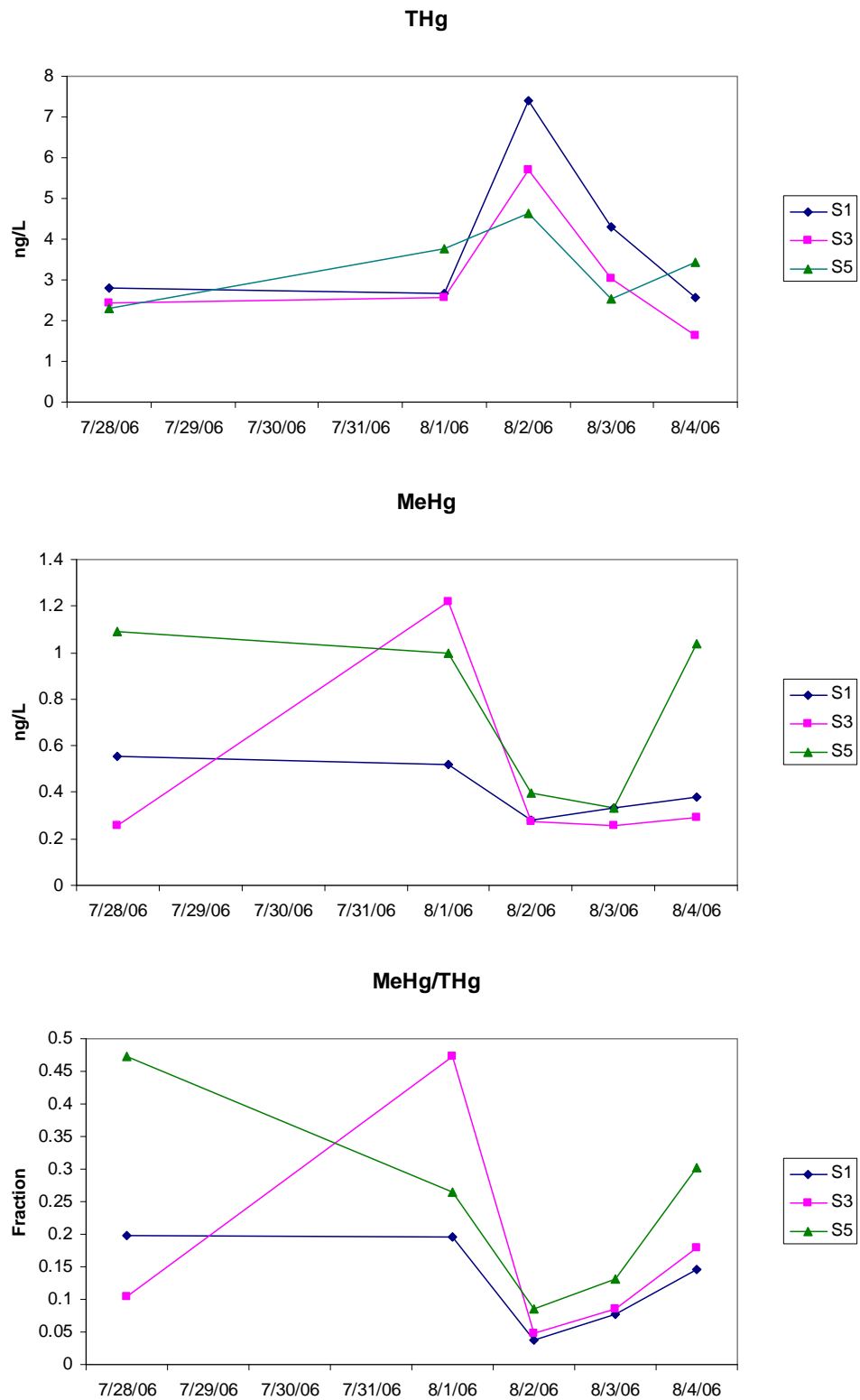


Figure 18 THg, MeHg, and MeHg/THg during the week of July 28 – August 4, 2006

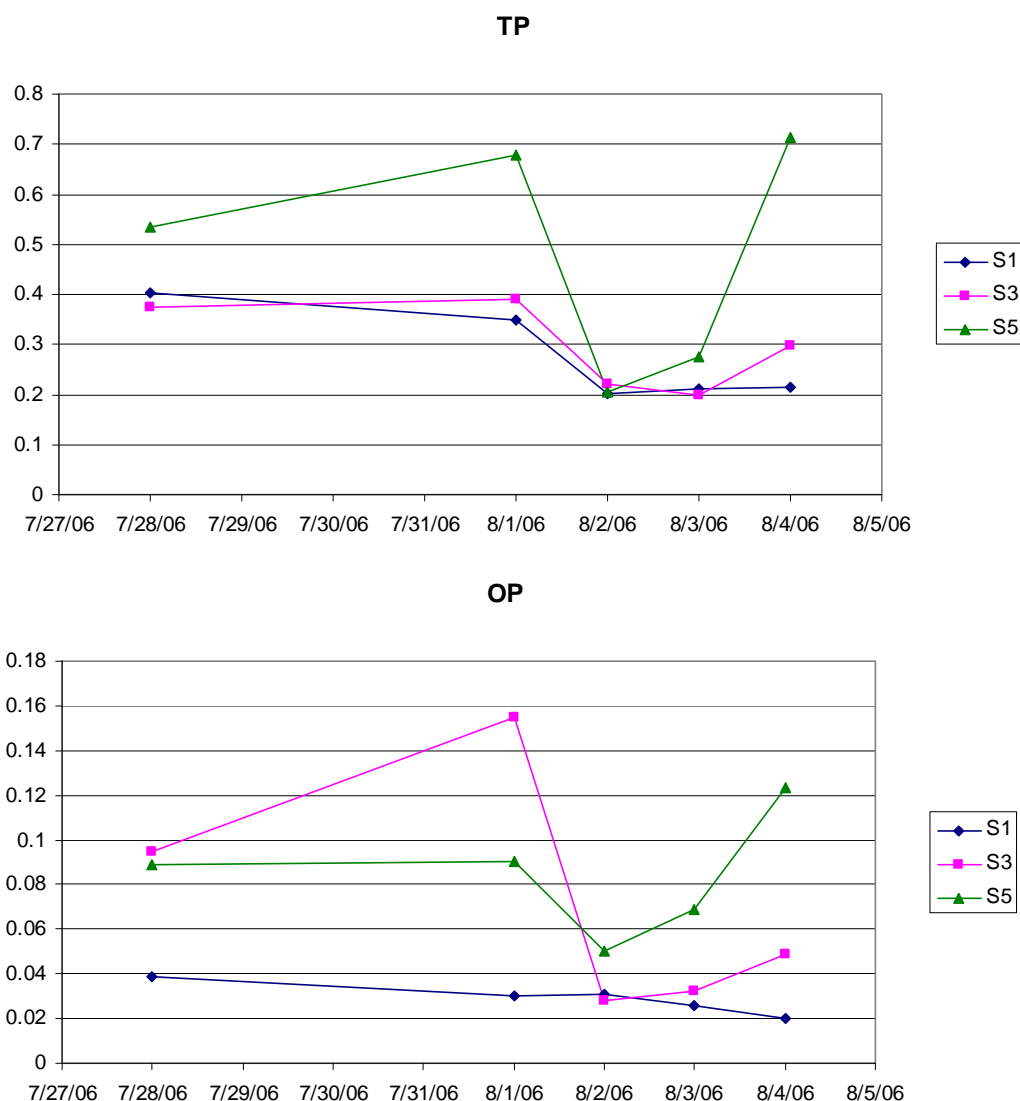


Figure 19 Total P and Ortho-P showing same pattern as MeHg

C. Bass Creek Business Park

The Bass Creek Business Park monitoring in 2005 included inlet and outlet automatic composite sampling as well as grab samples collected throughout the season. The data from BCBP were included in the All Sites analysis (Section III.A.). Mass loading was not calculated as intended because of malfunctioning data loggers. In addition, there was outflow when no surface inflow was observed, indicating substantial groundwater inflow to the system. Despite the groundwater input, concentrations of THg and MeHg at the inlet and outlet indicated BCBP behaved similar to MVP.

V. CONCLUSIONS

The observations from this study have shown that stormwater wetlands behave similar to natural wetlands receiving stormwater and to natural wetlands receiving agricultural runoff. The sulfate-reducing bacteria in these urban stormwater wetlands apparently are not sulfate limited, because MeHg concentration was not correlated to sulfate concentration. MeHg concentration was strongly correlated to phosphorus concentration, which indicates that if a wetland system is effective at net removal of phosphorus it may be ineffective at mercury methylation.

This study demonstrated that automatic composite samples can effectively collect storm event samples of THg and MeHg. Furthermore, grab samples are reliable at representing the concentrations during wet weather as well as dry weather, based on the similarity of THg and MeHg concentrations in grabs and composite samples collected during storm events.

How can we ameliorate the natural process of methylation in these wetlands? The first step is to reduce the input of Hg and sulfate to the wetland; however, sulfate-reducing bacteria are not likely sulfate-limited in the urban stormwater wetlands, as indicated above. Suppressing anaerobic conditions is not necessarily the best answer since the anaerobic bacteria are providing other beneficial water quality functions, such as denitrification, and removing sulfate through sulfate reduction. Another approach is to consider the loss mechanisms of MeHg other than outflow, such as photodegradation.

Canadian researchers have shown photodegradation is an important loss mechanism of MeHg in lakes, accounting for as much as 50% of the MeHg removal (Sellers *et al.* 1996 and 2001). Photodegradation can begin with demethylation and continue with photoreduction of the Hg(II) to Hg(0), which is a gaseous form of Hg that evades from the water. Photodegradation is a function of MeHg concentration, light intensity and light attenuation in the water. Light attenuation depends on water color and turbidity. Photodegradation drops off exponentially with depth as light is attenuated; therefore, it is only significant in the upper few feet (or less) in the water column. To enhance photodegradation in a wetland, water clarity must be improved and shading minimized. Perhaps an outlet structure could be designed to create sheet flow of only several inches depth that would maximize exposure to the sun and encourage a biofilm that would further demethylate and reduce the mercury.

A policy-relevant outcome of this study is that wetlands may not be appropriate BMPs for removal of mercury and phosphorus from stormwater. Considerable removal of THg was achieved in the MVP wetland, but this was most likely due to solids removal, which is effectively accomplished in detention ponds. Wetlands are not good for phosphorus or mercury reduction because both pollutants are released as bioavailable forms from anaerobic processes inherent in wetlands. Wetlands do, of course, provide other valuable aesthetic and wildlife habitat functions. Because they are also very effective at sulfate reduction and nitrate reduction, they are probably beneficial as agricultural BMPs where nitrate concentration can be very high in runoff.

A next step after this study is modeling of the stormwater wetland systems and their relative impact on downstream lakes. Given the large hydrologic load to urban lakes, the MeHg from stormwater wetlands may not be consequential to the fish in the lake, especially when compared to the Hg removed and buried in sediments before entering a lake. If modeling indicates the stormwater wetlands are indeed a substantial source of MeHg to a lake, the modeling can also be used to analyze means of reducing conditions that favor methylation.

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