2012 STORM WATER MONITORING REPORT

Assessment of Mercury Loading Contributions from Combined Sewer Outlets at the City of Cornwall to the St. Lawrence River (Cornwall) Area of Concern Zone 1

St. Lawrence River Institute of Environmental Sciences
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Report prepared for the St. Lawrence River Restoration Council, Cornwall, ON and the Ontario Ministry of the Environment, Kingston, ON.

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EXECUTIVE SUMMARY

The purpose of the project was to determine mercury (Hg) concentrations in discharges from combined sewer and storm sewer outlets that have the potential to impact water and sediment quality along the Cornwall waterfront, and provide preliminary estimates of the loadings of Hg. A series of three duplicate samples were taken for each storm event at the Brookdale combined sewer and the Pitt St. storm sewer. Five storm events representing between 9.3 to 23.6 mm of rain were sampled between June and December, 2012. River samples sampled upstream of the discharges were also taken for comparison and for quality assurance/quality control. Samples were measured for total mercury (THg) and methyl mercury (MeHg) by the University of Ottawa mercury laboratory. Ancillary measurements for precipitation, temperature, total suspended solids, pH, turbidity, and specific conductivity were collected by the River Institute Analytical Laboratory.

The following results were obtained:

- The geometric mean of THg concentrations were 20.6 ng/L for Brookdale Avenue CSO, 5.34 ng/L for the Pitt St. Stormwater and 0.584 ng/L for the river upstream of Brookdale Avenue CSO.
- Geometric means of MeHg for the Brookdale CSO was 0.123 ng/L, the Pitt St storm sewer had a geomean of 0.10 ng/L compared with 0.034 ng/L for the river samples.
- Metered discharges from the Brookdale CSO ranged between 3000 and 5000 m^3. These events represent loadings of 0.11-0.18 g of THg, 0.0007 g of MeHg, and 233 and 341 kg of suspended solids.
- Based on an annual CSO discharge of 156,000 m^3 and using average concentrations from the measured events suggests annual discharges of 5.6 g THg, 0.02 g MeHg and 9048 kg TSS.
- A comparison of these values with modeled annual Hg inputs from advection into Zone 1 (Lessard et al. 2013) indicates that the CSO discharges are minor sources to the zone representing approximately 1% of the inflows for THg and 0.03% for MeHg. However, these estimates do not include the continuous stormwater inflows from the Brookdale sewer outlet nor from the unmetered stormwater inputs from the Pitt Street storm sewer which discharges directly into Zone 1.

Recommendations include:

- Further characterization of concurrent mercury and flow data to improve the loading estimates
- Additional measurements of stormwater from CSOs and upstream river during rain events especially in the spring which represent the major annual inflows.
- To assess the sources of the storm sewer and CSO discharges on Zone 1, a sampling strategy should incorporate sampling in the municipal sewer system upstream of the Brookdale CSO output to characterize the contribution of both sewage overflow and stormwater discharges.
- Surface water quality surveys using high resolution in situ sensors in Zone 1 during major rain events to characterize and model the inflow distribution from the Brookdale CSO into Zone 1.

Introduction

Mercury (Hg) contamination of sediments and fish are key beneficial use impairments in the St. Lawrence River (Cornwall) Area of Concern (AOC). While there have been past and ongoing studies to evaluate the atmospheric, upstream and sediment sources of Hg to the St. Lawrence River, municipal contributions from storm and combined sewer outlets along the Cornwall waterfront remain poorly characterized.

Zone 1 is one of three sediment deposition areas along the Cornwall waterfront where sediment concentrations are contaminated with mercury, largely as a result of past industrial discharges (Figure 1). A mercury trackdown project was created for Zone 1 because of unexpectantly high mercury (Hg) concentrations in biota including amphipods, spottail shiners and juvenile yellow perch collected from the zone (Ridal et al., 2010). Despite moderate levels of Hg sediment concentration relative to the other 2 contaminated zones, Zone 1 sentinel fish showed Hg concentrations that were significantly higher than similar fish from the other zones (Choy et al., 2008, Fowlie et al., 2008).

There are several possible sources that could be vectors for fugitive mercury emissions to Zone 1. These include the Cornwall canal, groundwater flow, combined sewer and storm sewer outlets that discharge into the area. Zone 1 is geographically nearest the now closed industrial sites where mercury was used in quantity, both of which are current brownfield sites (Domtar and ICI Forest Product site now closed). There has been active site deconstruction since 2008 at the former Domtar site.

Sampling of combined sewer overflow (CSO) and storm sewer (SS) discharges in the vicinity of Zone 1 was carried out in 2007 and 2008. The results showed variable levels of mercury in the stormwater. In their review of the Mercury Trackdown Project, Golder Associates (2010) concluded:

While none of the sources appeared to be a significant or overwhelming source of mercury, the storm sewer sampling has indicated that not only is mercury present in the discharges at higher concentrations than in the upstream river water during rainfall events, but that there are also spikes in mercury concentrations that appear to coincide with the more intense rainfall events and during snow melt conditions.

The authors also noted that these inputs would attenuate the reduction in sediment concentrations within the zone as expected with the cessation of industrial inputs.

The purpose of the current study is to characterize the mercury contents of the CSO and SS discharges into Zone to compare with the previous measurements in 2007 and 2008, and where possible estimate the loading of these sources to Zone 1.

Methods

Three sites were sampled: the Brookdale CSO, the Pitt Street SS, and a nearshore river sample taken upstream of the Brookdale CSO (Figure 1). Samples were taken on 5 separate occasions through the year in June 12, July 23, Sept 18, Oct 19 and Dec 5 representing a range of runoff conditions. Because of construction of the new Brookdale bridge, land access to the Brookdale CSO was coordinated with the site supervisor and was limited to 8a.m.- 4 p.m. on weekdays. Therefore collections at this site depended on the timing of the storm. As a result, Brookdale CSO samples were not taken in July and December.

Stormwater and river water samples were taken by grab sample or by pole sampler from the effluent stream at its point of entry to the river. It is important to recognize that the Brookdale CS outlet is partially submerged and the possibility of dilution of the CSO event with surface river water is possible and will vary with the intensity of the discharge. Sampling of the Brookdale CSO was undertaken with the pole sampler at the point of greatest specific conductivity representing the greatest concentration of stormwater.

Brookdale CSO and Pitt St SS samples were taken in duplicate into 1-L pre-cleaned HDPE bottles at three different times separated by a time interval of 30-45 minutes using a "clean hands – dirty hands" technique for total mercury (THg) and methyl mercury (MeHg). The river samples were taken in triplicate as a single sampling event. Filled sample bottles were labeled, bagged immediately and stored on ice during transport to the laboratory. Additional 1-L samples were taken for total suspended solids (TSS). Site characteristics were recorded and chain of custody forms filled. Specific conductivity and temperature was done on site using a YSI model 30 conductivity meter. The conductivity meter was calibrated against a standard NaCl solution (Standard Methods, 2005). The temperature indicator from the meter was also calibrated against a NIST traceable thermometer. pH was also taken using a calibrated pHTester©. Before each use the meters were rinsed with RO water.

Samples for mercury analysis were shipped overnight to the University of Ottawa for detailed processing and analysis using state of the art methods described elsewhere (Ridal et al 2010). THg samples were preserved with BrCl and MeHg samples with HCl in a clean room facility upon receipt. Suspended solids were filtered onto pre-cleaned and pre-weighed 1.5-µm pore-sized borosilicate glass fiber filters (ProWeigh®, Delta Scientific) and dried to constant weight. Statistical comparisons were calculated using MiniTab v.10 software on log transformed data to normalize the data and reduce heteroscedasticity.

Results and Discussion

Precipitation and Discharge Events

Overall, 2012 was a slightly drier year (888 mm total precipitation) than the long term 1971-2000 average of 989 mm of total precipitation based on values measured at the St. Anicet monitoring station (Environment Canada, 2013). Stormwater sampling events coincided with days that had 9.3 – 23.6 mm of precipitation in a 24 hr period (Figure 2). Only three of the larger events (July 23, Sept 18, and Oct 19) were recorded as CSO events with 24-hr precipitation values ranging 19.7-23.6 mm of rain. CSO events resulted in overflow discharges of 3000-5000 m^3 at Brookdale (Figure 2). The City of Cornwall does not meter the Pitt St. outfall.

General Water Quality Characteristics

Because of the strong unidirectional flow in the vicinity of the Brookdale CSO, sampling upstream of the Brookdale CSO is representative of the background St. Lawrence River water quality. Specific conductivity in river samples ranged 272–311 µS/cm, TSS values ranged <3 – 3.18 mg/L and pH values of ranged 7.2-8.7 (Table 1). As expected, the Brookdale CSO samples fluctuated much more widely with specific conductivity values between 184-528 µS/cm, TSS ranged 15-274 mg/L, and pH values 7.3-8.5. The Pitt St SS values for specific conductivity had the greatest variation (49.5-752 µS/cm), while TSS values ranged <3-45 mg/L, and the pH was similar to Brookdale CSO and river samples (7.2-8.7). Water temperatures during sampling ranged from 6.0 to 21.4˚C (Table 1).

THg Concentrations

When all sampling events are considered, THg concentrations at the Brookdale CSO ranged from 7.68 ng/L to 161 ng/L with a geometric mean of 20.6 ng/L (Table 1, Figure 3). However, when only confirmed CSO events (Sept 18 and Oct 19th based on the City of Cornwall records) are assessed, the THg values ranged between 9.65 ng/L and 161 ng/L with a geometric mean of 35.5 ng/L. For non-confirmed CSO events, the geomean of the THg concentrations was 6.65 ng/L. When the two means are compared, there is a significant difference between confirmed CSO event measurements and the other sampling events at the Brookdale CSO (one-way ANOVA, F=17.3, p=0.001). However, both means are higher that the background THg values in the nearshore river water which ranged from a low of 0.35 ng/L to 1.46 ng/L with a geometric mean of 0.59 ng/L. These observations indicate that some stormwater flow occurs in the Brookdale CSO even in the absence of a combined sewer overflow event. The variations at the Pitt St. Stormwater were lower than those at the Brookdale CSO with values as low as 2.33 ng/L to a high of 10.0 ng/L while the geometric mean for this sampling area was 5.34 ng/L (Table 1, Figure 3).

Stormwater THg values are much lower than the Provincial Water Quality of Objective of 200 ng/L. However, in certain instances and in particular Brookdale CSO exceeded the Canadian Water Quality Guideline for the Protection of Aquatic Life of 26 ng/L. The authors of the Guideline acknowledge that the 26 ng/L aquatic life criterion, while protecting the health of the fish themselves, may not prevent the unacceptable bioaccumulation of Hg in fish tissue, which would adversely affect the health of humans consuming the fish (Environment Canada 2003).

MeHg Concentrations

Upstream from the Brookdale CSO values of the samples taken were as low as 0.01 ng/L up to 0.06 ng/L with a geographic mean of 0.034 ng/L. Brookdale CSO varied with results as low as 0.11 ng/L to 0.16 ng/L well above upstream results and having a geometric mean of 0.123 ng/L. There was no significant difference for MeHg between overflow and non-overflow events at the Brookdale site. The Pitt St SS had a much higher variation. On the low side the results were 0.04 ng/L while on the high side the results were 0.18 ng/L (Figure 3). The geometric mean for the Pitt St. sampling set was 0.10 ng/L.

Percent MeHg

The %MeHg to THg is considered an indication of the net MeHg production within a site. The %MeHg variation ranged from 1.8%-14% for upstream river samples (Figure 4). Brookdale CSO

had a %MeHg as low as 0.4% to a high of 1.6%. On the other hand the Pitt St. Stormwater had values between 0.9% to 2.9%. River samples showed a slightly higher than the typical value of MeHg which normally represents less than 10% of the total Hg in surface waters while higher values (10-30%) are reported for perturbed systems such as newly-formed reservoirs (CCME 2003).

Table 1. Summary of water quality characteristics measured during the study period. Shown are number of observations (N), median values, and range.

Measure	Site	N	Geo Mean	Minimum	Maximum
Temperature (˚C)	Upstream	11	13.0	6.0	20.8
	Brookdale CSO	18	18.0	14.7	20.6
	Pitt St. Stormwater	27	17.1	9.2	21.4
Specific conductivity (uS/cm)	Upstream	11	296.8	272.0	311.1
	Brookdale CSO	18	303.8	183.8	528
	Pitt St. Stormwater	27	162.3	49.5	752
TSS (mg/L)	Upstream	14	1	0.00	3.
	Brookdale CSO	12	88	15	274
	Pitt St. Stormwater	18	14	<1	45
Turbidity (NTU)	Upstream	13	1.1	0.5	3.4
	Brookdale CSO	12	78.9	16..8	305
	Pitt St. Stormwater	18	17.9	4.4	41.4
pH	Upstream	9	7.8	7.2	8.7
	Brookdale CSO	6	7.8	7.3	8.5
	Pitt St. Stormwater	9	7.7	7.2	8.7
THg (ng/L)	Upstream	14	0.58	0.34	2.6
	Brookdale CSO	18	20.6	3.46	107
	Pitt St. Stormwater	27	5.34	2.29	11.5
MeHg (ng/L)	Upstream	11	0.034	0.011	0.062
	Brookdale CSO	16	0.123	0.071	0.294
	Pitt St. Stormwater	22	0.096	0.027	0.318

Relationship between Suspended Solids and Total Mercury

Previous studies on urban stormwater have found strong relationships between THg and TSS indicating that the particulate-bound mercury was the main source of mercury (Eckleya and Branfireuna, 2009). However, the relationship between TSS and THg was only weakly statistically significant (r^2=0.19, p=0.034, Figure 5) for the Pitt St. stormwater and not significantly related for the Brookdale CSO of the river samples. A greater number of samples

would be required to confirm this lack of relationship, however the results suggest that mercury in the Cornwall stormwater samples are mainly in the dissolved form and potentially available for uptake. Previous work on St. Lawrence River samples have found that approximately 80% of the THg is dissolved (Ridal et al., 2010).

Comparison with Previous Measurements

Values from the 2012 sampling events for both THg and MeHg are similar to measurements taken in 2007/8. The CSO events at Brookdale had geometric THg mean values in 2007/8 and 2012 of 26.0 and 35.7 ng/L, respectively (Figure 6). A one-way ANOVA of the data found no significant difference between the two data sets (p=0.562). MeHg values during CSO events at Brookdale were also not significantly different (p = 0.119).

Very similar results were also observed at the Pitt St and River sites in 2007/8 and 2012 sampling. These results suggest that concentrations of MeHg and THg from CSO and stormwater events into Zone 1 are similar over time and loadings into Zone 1 from these sources will vary mainly on the amount of precipitation in the given year.

THg Loadings

Loadings of THg and TSS to the St. Lawrence River from the Brookdale CSO can be estimated based the City of Cornwall measurements of the overflow volume. Loadings are calculated based on the formula:

Loading (g) = volume discharged (m^3) x concentration (ng/L) x 1000 L/m^3 x 10^{-9} g/ng (1)

The loadings of THg from the Brookdale CSO on these particular events ranged from 0.11 to 0.18g, loadings of MeHg loadings averaged 0.0007 g, while TSS loadings were 233 to 341 kg (Table 2).

Table 2. Loadings of THg and TSS to the St. Lawrence River from the Brookdale CSO.

Date	**Mean THg (ng/L)**	**Discharge (m^3)**	**Loading (g)**
Sept 18, 2012	35.6	5000	0.18
Oct 19, 2012	35.9	3000	0.11
Date	**Mean MeHg (ng/L)**	**Discharge (m^3)**	**Loading (g)**
Sept 18, 2012	0.141	5000	0.0007
Oct 19, 2012	0.109	3000	0.0007
Date	**Mean TSS (mg/L)**	**Discharge (m^3)**	**Loading (g)**
Sept 18, 2012	68	5000	341,000
Oct 19, 2012	47	4000	233,000

In 2012, the City of Cornwalll recorded 11 overflow events at the Brookdale CSO totaling 156,000 m^3 (Figure 6). Assuming the measured CSO concentrations are representative of the annual events (mean values of 36 ng THg/L, 0.125 ng MeHg/L and 58 mg TSS/L), the volume of discharge would result in annual loading estimates of 5.6 g THg, 0.02 g MeHg and 9048 kg TSS. Lessard et al. (2013) have established a steady state mass balance model to assess the relative contributions of different sources and sinks of mercury into Zone 1. The model indicates that advective inputs from upstream river inflows represent 960 g of THg and 64 g of MeHg per year. Therefore, the CSO inputs are an additional 1% and 0.03% contribution to the THg and MeHg

inputs to Zone 1, respectively.These results suggest that the Brookdale CSO is a weak source of Hg to the St. Lawrence River and a more significant source of TSS.

Conclusions and Recommendations

The results of the 2012 sampling suggest little variation over the past 5 years in the concentrations of THg and MeHg from the two main municipal discharges into the St. Lawrence River at Zone 1. The similarity of the Hg results indicates that these levels may represent long term concentrations of fugitive sources of mercury to Zone 1. However, despite the current efforts overall numbers of CSO samples are relatively small and further characterization of concurrent mercury and CSO flow data to improve the loading estimates is recommended. To assess the sources of the storm sewer and CSO discharges on Zone 1, a sampling strategy should incorporate sampling in the municipal sewer system upstream of the Brookdale CSO output to characterize the contribution of both sewage overflow and stormwater discharges.

It is difficult to attribute the elevated concentrations of THg in the Brookdale CSO stormwater to industrial sources alone because of the presence of municipal sewage in the discharge which may contain elevated levels of Hg from a variety of sources including dental discharges, compact fluorescent bulbs and human excretions. Sampling surface water runoff directly from former industrial sites would provide a more direct measure of the importance of these sites for mercury. To assess the sources of the storm sewer and CSO discharges on Zone 1, a sampling strategy should incorporate sampling in the municipal sewer system upstream of the Brookdale CSO output to characterize the contribution of both sewage overflow and stormwater discharges.

Acknowledgements

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Figure 1. South shore of the St. Lawrence River North of Cornwall depicting the map of the sampling areas; 1) River, 2) Brookdale CSO, 3) Pitt St. Stormwater.

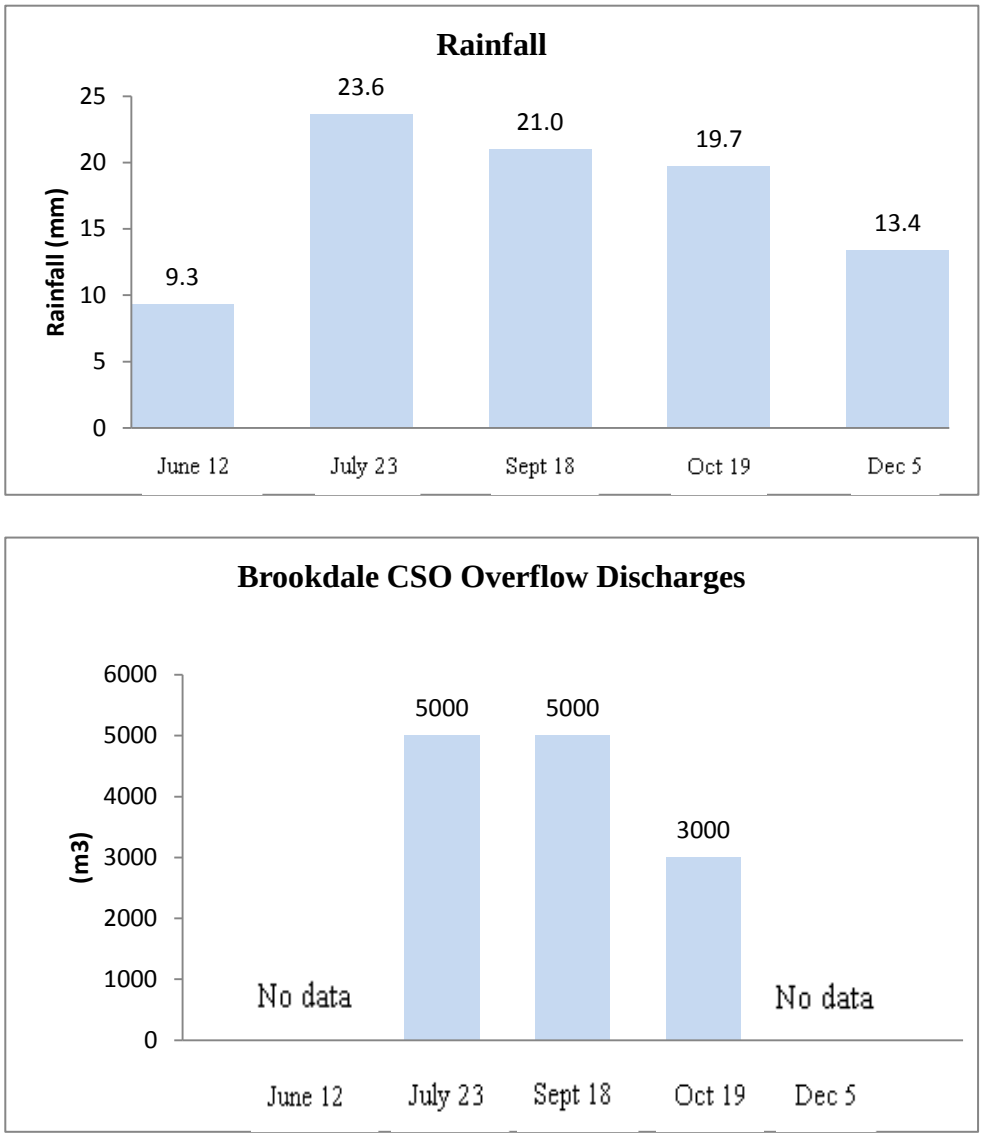


Figure 2. Rainfall during the 24-hr period prior and during sampling events and corresponding discharges at the Brookdale CSO.

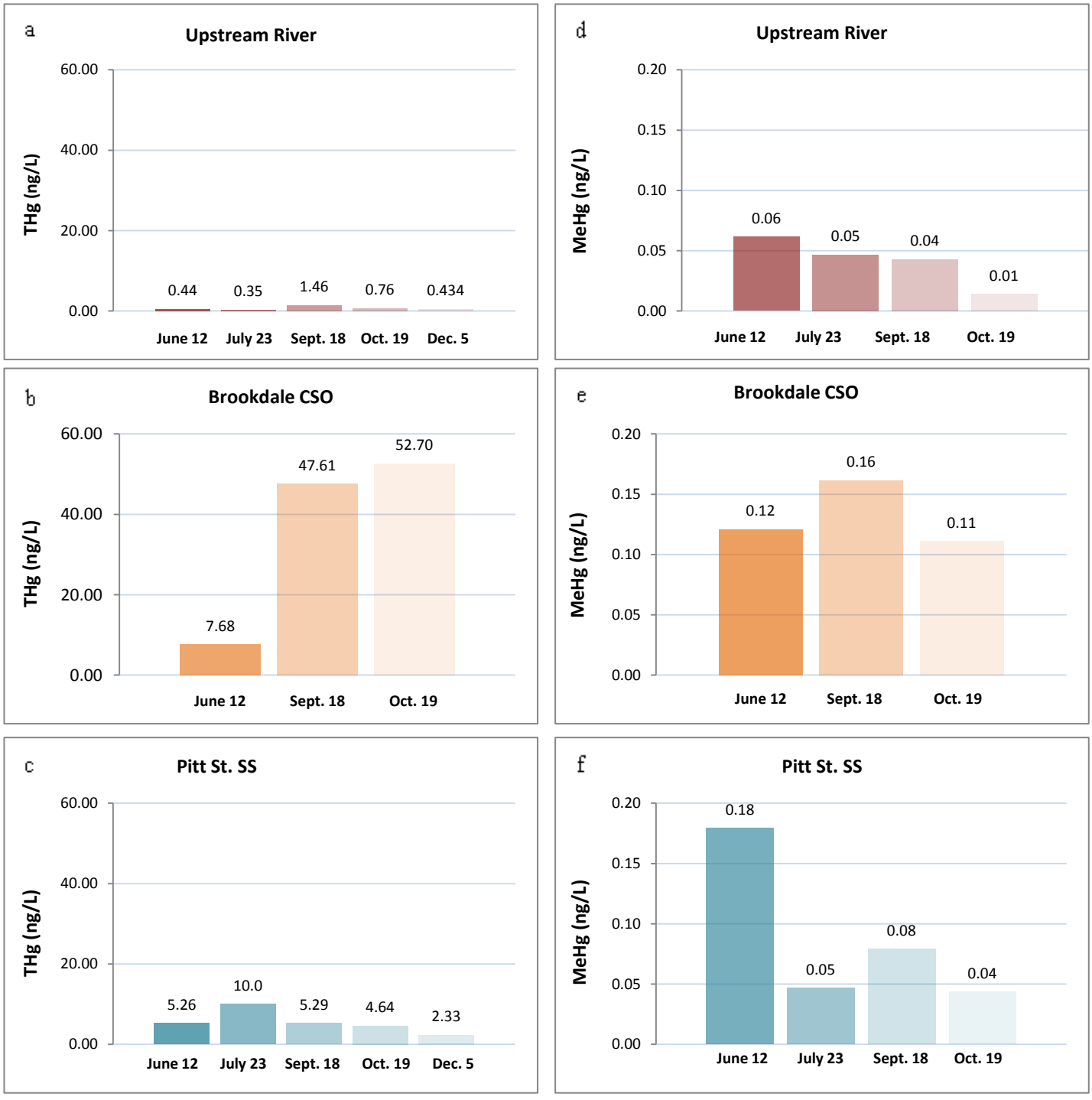
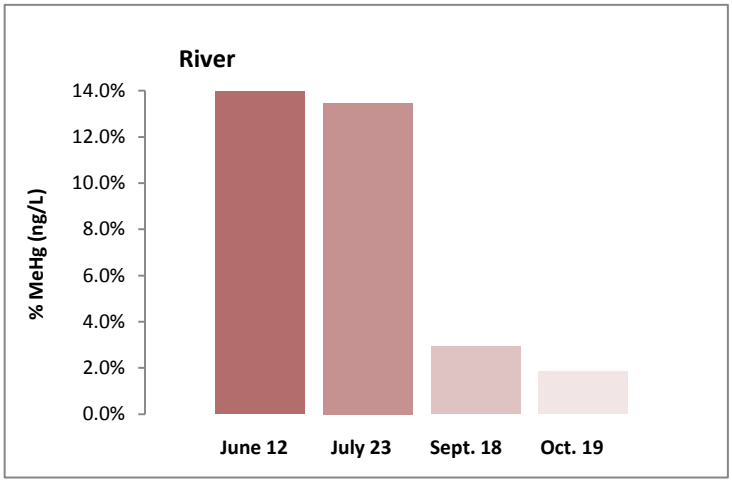
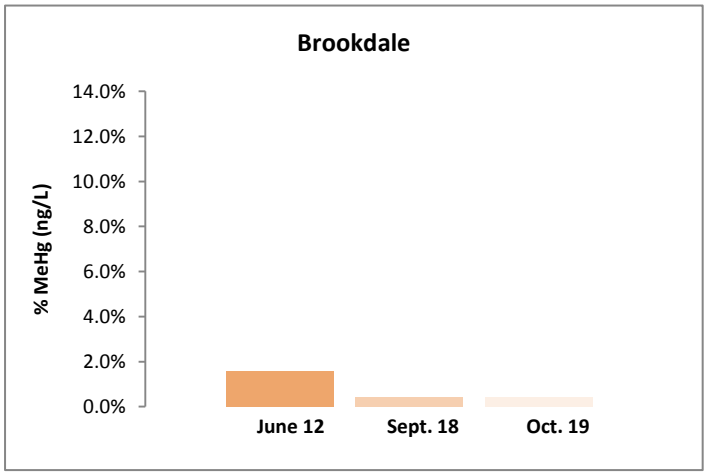


Figure 3.Comparison of total mercury (THg) and methyl mercury (MeHg) results for river, Brookdale CSO and Pitt St. storm water samples.





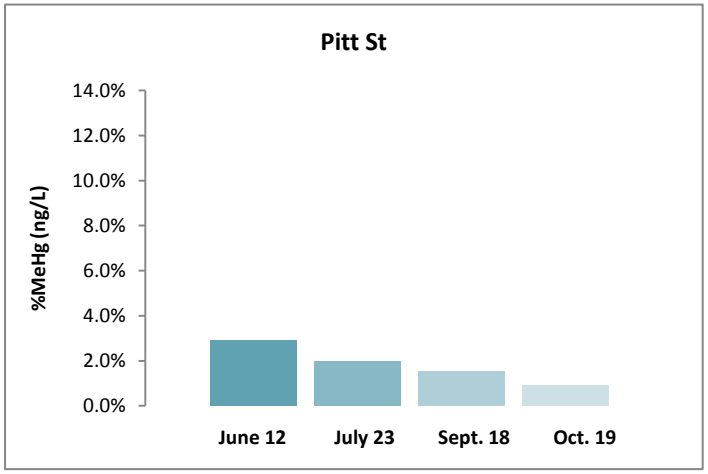


Figure 4. Percent of Total mercury that is methylmercury for the three sampling stations. Shown are averages of all samples for the sampling dates.

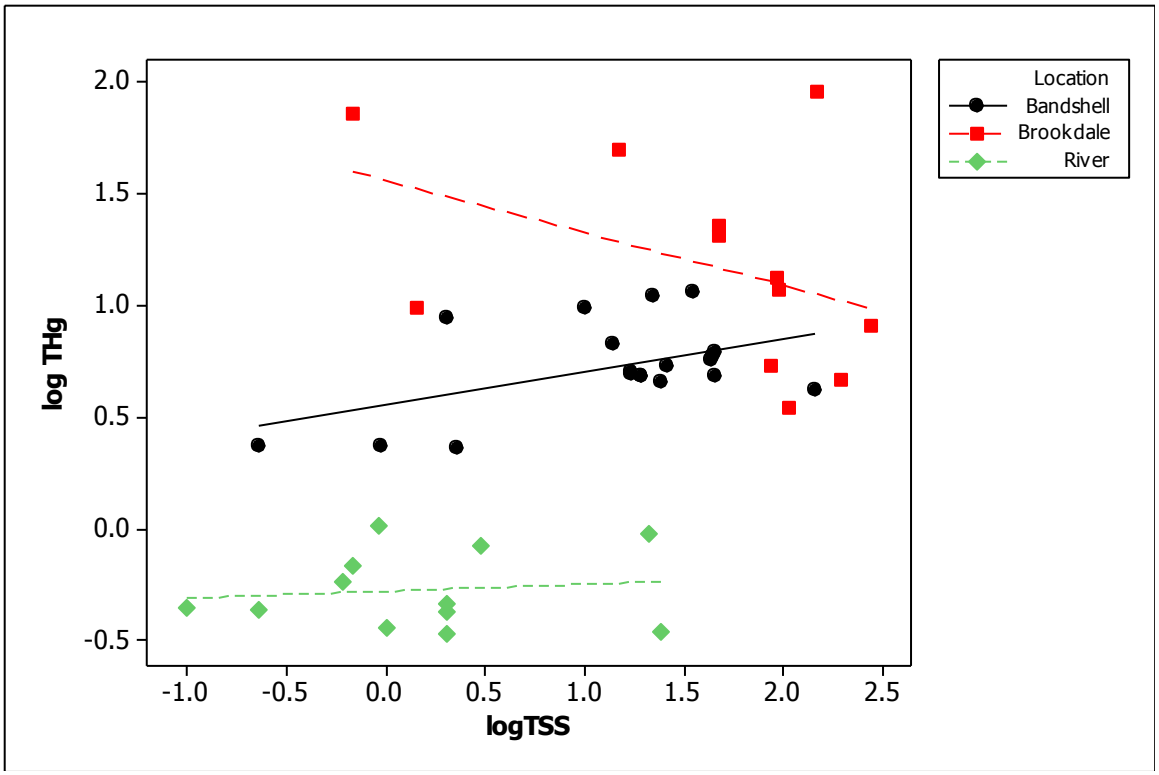


Figure 5. Relationship between log total mercury concentration (log THg) of unfiltered stormwater and Log Total suspended sediment (TSS) for the three different water systems sampled during this study. The only statistically signficant relationship is for the Pitt St. (Bandshell) stormwater data: log THgl = 0.555 + 0.147 logTSS ($p=0.034$, $r^2 =0.19$).

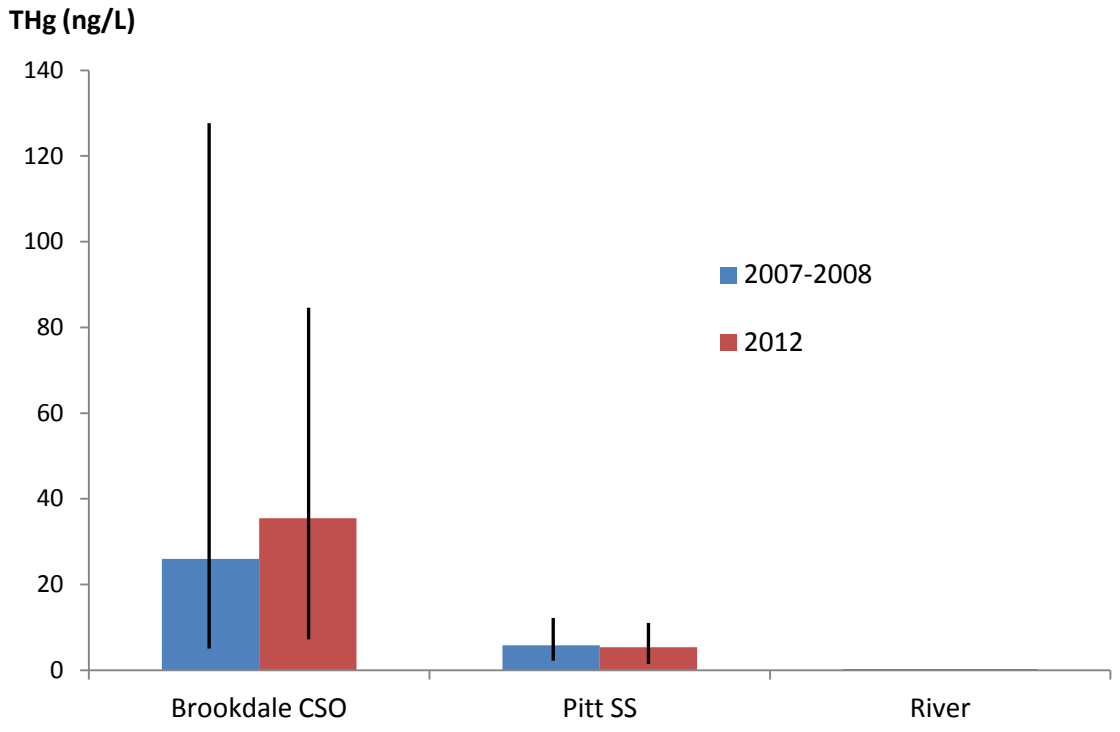


Figure 6. Comparison of mean values measured at the sampling sites for 2007/2008 and 2012. Comparison at Brookdale for confirmed overflow events only. Vertical bars indicate standard deviations of the measurements. There were no significant differences between the mean values $p>0.05$ at any of the sites between the two sampling (2007/8 vs 2012).

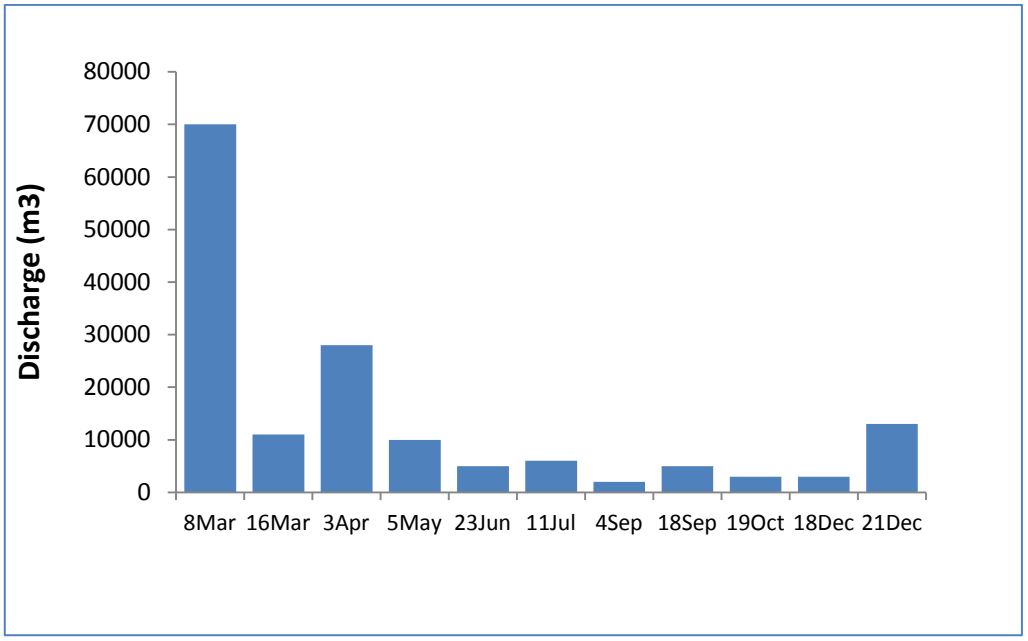


Figure 7. Discharge volumes of combined sewer overflow events in 2012 at the Brookdale combined sewer.