Annual Loading Estimates of Selected Metals and PAHs in CSOs, using a Continuous PCSWMM Approach

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Hamilton Harbour, Ontario, is an industrial port principally for the steel manufacturing industry, but also is a waterbody that increasingly supports recreational activities such as sailing, windsurfing, and fishing. While extensively used by a diverse group of interests, the harbour has been designated by the International Joint Commission (IJC) as one of 43 Areas of Concern (AOCs) around the Great Lakes due to environmental impairments. These impairments include: loss of habitat; high bacteria levels; fish consumption advisories; and high levels of metals and organic compounds in bottom sediment, particularly along the industrialized south eastern shore (e.g. IJC, 1989; Murphy et al., 1991; RAP, 1992; Poulton et al., 1996). Most of the contamination of the harbour is the result of long-term stormwater runoff, combined sewer overflows, sewage treatment plant input, atmospheric input, and direct industrial discharges (Paul Theil and Beak Consultants, 1991; RAP, 1992; Charlton and LeSage, 1996; Diamond and Ling-Lamprecht, 1996).

Remedial programs to control contaminant discharges to the harbour have been implemented over the last 15 years and this work has resulted in improved water quality (e.g. IJC, 1989; Murphy et al., 1995; Diamond and Ling-Lamprecht, 1996). One of these programs has been the development and implementation of Hamilton-Wentworth Region's Pollution Control Plan (PCP). The PCP was

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developed by Paul Theil Associates and Beak Consultants (1991) under the direction of the Region and in consultation with the Province. Using SWMM to estimate flows, the PCP indicated that typically 23 combined sewer overflow (CSO) events occurred per year (May 1 to October 31) at each of more than twenty outfalls, resulting in a discharge of approximately 4.33 million m³ of combined sewage to Hamilton Harbour and Cootes Paradise. Since the adoption of the PCP in 1992, Hamilton-Wentworth Region has begun implementation of several of the recommendations. For example, the construction of four off-line storage tanks was completed between 1993 and 1997 at a cost of approximately \$43 million. These tanks have a storage capacity of approximately 123,000 m³ and complement the previous (1988) construction of the Greenhill CSO tank that provides 70,000 m³ of storage (Stirrup, 1996). In addition, an in-line CSO storage tunnel is being considered, a microcomputer-based real-time control system is being implemented to optimize operation of the combined sewer system, and work has begun on improvements at the Woodward Avenue sewage treatment plant (Stirrup, 1996).

The PCP developed contaminant loading estimates for the CSOs in addition to examining overflow frequency, duration, and volume. However, due to budget constraints, a sampling program was not conducted under the PCP to determine contaminant concentrations for the loading estimates. Instead, the PCP relied on a literature search to determine representative pollutant concentrations (Paul Theil Associates and Beak Consultants, 1991). There clearly is some need to assess contaminant levels from CSOs based on actual sample collection.

Our group recently has focused on source evaluations to an industrial boat slip area of Hamilton Harbour that has undergone a demonstration *in situ* remediation of contaminated bed sediment. The intent of this source evaluation project is to determine the relative loadings of metals and PAHs (polynuclear aromatic hydrocarbons) to the boat slip from CSOs, non-point industrial stormwater runoff, coalpile runoff, and direct industrial discharges. Contaminated sediment remediation is being increasingly considered as a cleanup option for aquatic ecosystems, but it is important to understand how current contaminant loadings may affect the success of the remediation effort. The objectives of this chapter are:

1. to discuss the levels of selected metals and PAHs associated with CSOs from one major outfall, the Kennilworth St. outfall, to the study boat slip based on a preliminary sampling program conducted in 1996. These data also will begin to fill knowledge gaps identified in the PCP; and
2. to estimate the annual load of selected metals and PAHs for a "typical" year from CSOs. These loading estimates eventually will be compared with loading estimates from other sources to the boat slip.

20.1 Methods

20.1.1 Kennilworth Sewershed

The Kennilworth Sewershed has a contributing area of 265.5 ha that is serviced principally by a combined sewer system (Figure 20.1). Because the sewershed is located on the glacial lake plain below the Niagara Escarpment, surface slope is relatively flat, ranging between 1 and 1.2%. Much of the land use in the upper part of the sewershed is older residential, single family dwellings, with commercial ribbons along major streets (e.g. Kennilworth, Barton, Main). A portion of the Greater Hamilton Shopping Centre paved parking lot (approximately 2.8 ha) is within the sewershed, although sanitary flow from the mall is discharged to an adjacent sewershed. The residential lots almost uniformly are 7.6-9.1 m x 30.5 m and downspouts on the majority of the houses are directly connected to the sewer system. The upper sewershed has a mix of pervious and impervious surfaces typical of an older, downtown residential area and includes four schoolyards and part of a large park. In total, approximately 52% of the upper sewershed can be considered impervious land. Paul Theil and Beak Consultants (1991) indicated that much of Hamilton below the Niagara Escarpment discharges a limited quantity of sewage to the sanitary interceptor and based on measurements in the adjacent Strathearne sewershed (Figure 20.1), determined a typical dry-weather flow rate to be 1.38 l s^{-1} per impervious hectare.

The lower sewershed (approximately 9% of the total contributing area) is dominated by a mix of industry, including steel mills, railcar manufacture, metal fabrication, construction material recycling, and lead recycling facilities. Several of the large industrial lots are semi-pervious and unpaved (e.g. staging areas for steel mill heavy equipment; storage areas for rolled steel; railway land; railcar storage areas). Approximately 66% of the industrial area can be considered impervious.

20.1.2 Loading Estimate Approach

A simple, volumetric approach often is used to estimate contaminant loadings on an annual basis (e.g. Marsalek and Ng, 1989; Marsalek, 1990; Irvine et al., 1993; Pratt et al., 1995) according to the following equation:

$$L_j = \sum (Q_i \cdot C_{ji}) \quad (20.1)$$

where:

- L_j = the annual load of pollutant, j
- Q_i = the volume of each overflow event, i
- C_{ji} = the event mean concentration of pollutant, j.

Figure 20.1 Kennilworth sewershed and sample site locations.

In this study, a variation of Equation 20.1 was used to calculate annual loads. PCSWMM was run in continuous mode with one year of rainfall data to calculate the annual overflow volume. The total overflow volume for the entire year therefore was the user-designated model output. A continuous modeling approach was used in the PCP development and, in general, continuous modeling avoids the problem of defining discrete, independent events and associated antecedent conditions. Gregory and James (1996) further summarize advantages of a continuous modeling approach and James (1994) argues that event-based and design storm modeling should be abandoned. Equipment availability necessitated that only discrete grab samples could be collected during a sub-set of overflow events throughout the year. Therefore, the mean values of individual metals and PAHs for all discrete grab samples were used for C_{ji} in Equation 20.1. Marsalek (1990) reviewed several methods by which *representative* concentrations could be calculated for Equation 20.1, including the direct average method, flow-weighted-concentration method, and the regression method. Marsalek (1990) ultimately recommended use of a probability distribution model approach to define event mean concentrations. The probability approach is attractive, but for this preliminary study the data were not sufficient for a rigorous and meaningful probability application. In the future, flow-proportioned composite sampling with automated systems (e.g. Irvine et al., 1993) should be done for individual events to provide data that could be used to define appropriate probability distributions for event mean concentrations.

Rainfall data in the Hamilton area have been or are collected by various groups, including: Environment Canada, Atmospheric Environment Service (AES); Hamilton-Wentworth Conservation Authority; the Regional Municipality of Hamilton-Wentworth; and McMaster University. For planning level loading estimates on an annual basis, it was decided to use AES hourly rainfall data collected at the Mount Hope Airport which is located approximately 10.5 km southwest of the sewershed. The Mount Hope data were available on disk for the period 1970-1995 and this extended rainfall record will be used for future statistical analysis of overflow volume. Data from the Mount Hope gauge also were used in the development of the PCP.

Selection of the annual rainfall series for use with PCSWMM was based on two criteria: (i) monthly mean rainfall depth should represent, to the extent possible, a *typical* year, as determined by the 30-year norm; and (ii) the year should be as close to present as possible, to represent current loading conditions. An initial examination of the 1970-1995 rainfall data identified six candidate years. The squared errors for each month (difference between observed monthly rainfall and 30-year norm) of the candidate years were summed and the rainfall record for 1986 minimized the sum of the squared errors (see Figure 20.2). Therefore, the hourly rainfall data for 1986 were used to drive PCSWMM in obtaining an estimate of overflow volume (Equation 20.1).

Figure 20.2 Comparison of monthly 30-year norm rainfall and monthly rainfall for 1986, Mount Hope Airport, Hamilton, Ontario.

20.1.3 Sampling Methods

Samples for metals analysis were collected at two manholes. The upstream site was located at the first manhole on Cope St. south of Britannia St. (Figure 20.1). Sanitary flow at this site almost exclusively represents residential inputs. Stormwater runoff at the site could include atmospheric deposition inputs from the industrial areas to the north (e.g. Vermette et al., 1987). Samples of both sanitary and wet-weather flow were collected at this site. The downstream site (hereafter referred to as the CSO site) was located at a manhole approximately 110 m south (upstream) of the outfall mouth (Figure 20.1). The sewer is a twinbox at the CSO sampling site, with each side being 2.13 m x 1.75 m. Sampling was done in the eastern box and it was assumed that both sides were equally mixed. There is no dry-weather sanitary flow at this site, but the combined sewer overflows would include sanitary discharge and stormwater runoff from the industries in the lower sewershed. Grab samples for PAHs analysis also were collected at this CSO site.

Grab samples for metals at both sites were collected using telescoping sample poles fitted with 500 ml polyethylene bottles. The bottles were pre-cleaned by soaking in 1% nitric acid for a minimum of 24 hours and then rinsed once, on-site, with sewage. Sampling was done at a point mid-width of the pipe and approximately half the total flow depth below the water surface.

Grab samples (1,000 ml) of combined sewage for analysis of PAHs were collected at the CSO site using telescoping sample poles fitted with previously unused amber glass bottles. Sampling was done at a point mid-width of the pipe and approximately half the total flow depth below the water surface.

Sampling for metals began in May, 1996 and was completed at the end of October, 1996. A greater number of events was sampled at the CSO site,

exclusively, to maximize sample size for use in the loading estimates. To the extent possible, samples were collected at evenly-spaced time intervals through an event. In order to compare the levels of metals as flow progressed down-pipe, samples were collected at both sites for a subset of the overflow events. For these comparison events, sampling was done at the Cope St. (upstream) site first, followed approximately 30 minutes later at the CSO site. This sample lag provided for flow travel time between the two sites. Dry-weather, sanitary flow samples were collected at the Cope St. site following the same methodology as the wet-weather sampling. Sampling for PAHs in the CSOs was conducted during October and November, 1996.

20.1.4 Laboratory Methods

Within two hours of collection, samples for metals analysis were fixed with 1 ml (1:1) of Seastar nitric acid in the laboratory facilities of the National Water Research Institute (NWRI), Burlington, Ontario. Total metals concentrations were determined for each sample by the National Laboratory for Environmental Testing, Burlington, Ontario, using inductively coupled argon plasma (ICAP) following the methods of Environment Canada (1979). Metals examined in this chapter are: Cd, Cr, Cu, Ni, Pb, Al, Fe, Mn, V, and Zn.

Samples for PAHs analysis were kept on ice in the field and upon returning to NWRI were submitted directly to the Wastewater Technology International (WTI) laboratory, Burlington, Ontario, for analysis. PAHs analysis was done following WTI Standard Operating Procedure 95.01. Briefly, each 1,000 ml sample was spiked with a surrogate mixture and serially extracted three times with dichloromethane under basic conditions. The combined extracts were dried over sodium sulphate. The solvent was evaporated from the extract to a final volume of 3 ml. The extract then was combined with an internal standard and analyzed by gas chromatography/mass spectrometry (GC/MS).

20.2 Results

20.2.1 Overflow Volume Estimates

Model Development

The RUNOFF and TRANSPORT blocks of PCSWMM4 (distributed by Computational Hydraulics International) were used to estimate the CSO volume that would discharge from the Kennilworth sewershed to the boat slip in a *typical* rainfall year. The Kennilworth sewershed was discretized into fifteen subcatchments for the RUNOFF computational block. This is a finer discretization than that used by Paul Theil Associates and Beak Consultants (1991), but many of the physical parameter values for the RUNOFF block were taken from the earlier modeling effort. Paul Theil Associates and Beak Consultants (1991) had

determined RUNOFF parameter values for the Kennilworth area based on flow monitoring and model calibration/validation of the adjacent Strathearne sewershed (see Figure 20.1). Model estimates of flow volumes for seven events (four calibration, three validation) were within 20% of measured volumes, except for one calibration event that was within 25% of the measured volume (Paul Theil Associates and Beak Consultants, 1991).

Constant dry-weather flow rates were calculated for each of the fifteen subcatchments as a function of impervious area, following the methods used by Paul Theil Associates and Beak Consultants (1991). Evapotranspiration rates were calculated on a monthly basis using the Blaney-Criddle method (e.g. Ponce, 1989):

$$f = p(0.46t + 8.13) \quad (20.2)$$

where:

- f = evapotranspiration (mm d^{-1})
- t = the daily mean temperature for each month ($^{\circ}\text{C}$) of 1986, taken from the Mount Hope Airport
- p = the ratio of mean daily daytime hours for a given month to the total daytime hours in the year as a percent and is a function of latitude (values of p were interpolated from Table A-3, Appendix A of Ponce (1989)).

The calculated evapotranspiration rates from the Blaney-Criddle method are summarized in Table 20.1. The evapotranspiration rates used in this study are higher than those from the Paul Theil Associates and Beak Consultants (1991) (see Table 20.1 for comparison).

A schematic of the sewer system used in the TRANSPORT block is provided in Figure 20.3. A greater number of pipes and nodes was used in this study than the PCP modeling effort. All pipe slope steepnesses and dimensions were determined from the Hamilton-Wentworth Region 1:1200 sewer maps. Flow is diverted out of the sewershed at five locations upstream of the primary diversion (node 1425) to the sewage treatment plant (Figure 20.3). Diversion rates for this study were similar to the common diversion sites modeled in Paul Theil Associates and Beak Consultants (1991). However, as compared to the PCP, additional flow at nodes 325 and 1275 was removed from the sewershed in this study.

Overflow Volume Estimate for a Typical Rainfall Year, 1986

The hourly rainfall intensity data from 1986 for the Mount Hope Airport were run with the RUNOFF and TRANSPORT blocks in continuous mode. Total rainfall for 1986 was 775 mm, which produced 295 mm of surface runoff from the sewershed. The estimated overflow volume for 1986, considering both surface runoff and sanitary flow, is 311,000 m^3 .

Figure 20.3 Schematic of pipe network for Kennilworth sewershed modeled with the TRANSPORT block of PCSWMM4.

20.2.2 Metals and PAHs Levels

A total of twenty samples were collected for metals analysis at the CSO site, representing nine different overflow events and metals levels are summarized in Table 20.2. As evidenced by the standard deviations (Table 20.2) there can be considerable variability in the metals levels at the CSO site. A qualitative examination of the data indicated that there was variability both between samples within an overflow event and between sets of samples from different events, indicating that antecedent conditions and storm characteristics may influence metals levels in the CSOs. This variability clearly increases the uncertainty of the loading estimates for this study. The concept of a *first flush* effect has been well-established in the literature, although it has been argued that the first flush phenomenon is not always observed (e.g. Revitt and Ellis, 1982; Weeks, 1982; Thornton and Saul, 1987; Granier et al., 1990; Moffa, 1990; Saget et al., 1996). In this study, metals levels in the first sample collected through the CSO event often were the highest, supporting the concept of a first flush. However, higher concentrations in the first sample were not universally observed, as some metals concentrations for some storms were higher later in the event.

Canadian Water Quality Guidelines (Canadian Council of Resource and Environment Ministers, 1993) for the individual metals also are shown in Table 20.2. All samples in the case of Al, Cu, Fe, Pb, and Zn exceeded the water quality guidelines. Half of the samples exceeded guidelines for Cd and 40% of the samples exceeded guidelines for Cr. The mean levels of all metals in the CSOs, except for Ni, exceeded the water quality guidelines (there are no guidelines for Mn and V).

Table 20.1 Estimated daily evapotranspiration rates (mm d⁻¹), by month.

	J	F	M	A	M	J	J	A	S	O	N	D
This Study	1.1	1.3	2.3	3.6	4.9	5.7	6.2	5.3	4.2	3.0	1.9	1.4
PCP	0	0	0	3.26	3.70	4.15	4.80	4.10	2.70	1.54	0	0

Note: values of 0 for the PCP indicate that these months were not used in the modeling effort

Table 20.2 Summary of selected (total) metals levels (mg l⁻¹), CSO samples.

	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
Mean	3.87	0.0029	0.0244	0.0949	8.70	0.907	0.0102	0.0902	0.0180	0.676
S.D.	5.94	0.0039	0.0330	0.1149	12.42	1.529	0.0088	0.0777	0.0158	0.887
CWQG	0.1	0.0018	0.02	0.004	0.3	N.S.	0.15	0.007	N.S.	0.03

CWQG - Canadian Water Quality Guidelines; N.S. - no standard; n = 20; S.D. - standard deviation

Table 20.3 Mean (total) metals levels (mg l⁻¹), Cope St. wet-weather and sanitary flow.

	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
W.W.*	0.964	0.00076	0.00787	0.0427	2.02	0.150	0.0031	0.0288	0.0086	0.0919
Sanitary**	1.46	0.00032	0.0023	0.0372	0.707	0.0381	0.0026	0.0095	0.0016	0.0733

*n=7; **n=8

A total of seven wet-weather samples (representing three events) were collected at the Cope St. site on dates that overflow samples also were collected. The mean levels of all metals in the Cope St. and CSO sites for the common sample dates are compared in Figures 20.4a and 20.4b. In all cases there is an enrichment of metals levels as the flow progresses from the residential area, through the commercial ribbon and lower industrial area. The enrichment ratio (mean CSO level:mean Cope St. level) ranges from a low of 1.3 for Cu and V, to a high of 4.4 for Zn.

Sanitary (dry-weather) samples were collected at the Cope St. site throughout the day (8:00-17:00) on June 5 (6 samples) and individual grab samples were collected on October 2 and October 7. Results of the analyses are summarized in Table 20.3 and also are compared to the wet-weather concentrations at the same site.

Figure 20.4 Mean metals levels in combined flow for common sample dates at the CSO and Cope St. site (n=7).

Single grab samples for PAHs analysis were collected during the overflow events observed on September 9, 1996 and October 23, 1996. While a suite of PAHs were analysed, it was decided for illustrative purposes to focus on fluoranthene, phenanthrene, benzo(a)pyrene, pyrene, and chrysene. The mean concentrations of these PAHs for the two grab samples are summarized in Table 20.4.

20.2.3 Metals and PAHs Loading Estimates

The mean levels of metals presented in Table 20.2 and the mean levels of the PAHs in Table 20.4 were used as the *representative* concentrations to calculate loadings as presented in Equation 20.1. The modeled overflow volume of 311,000 m³ (section 20.2.1) for the year 1986 was used for the volumetric component of Equation 20.1 and the annual loading estimates for a *typical* year are presented in Tables 20.5 and 20.6.

20.3 Discussion and Conclusion

A planning level sampling and modeling program has provided preliminary insights to the levels and loadings of metals and PAHs associated with CSOs from a major, industrial-influenced outfall discharging to a boat slip area of Hamilton Harbour. The PCP loading estimates from CSOs for the entire city previously had been based on event mean concentration data obtained from the literature. For comparison purposes, the PCP *representative* concentrations are shown in Table 20.7. To calculate concentrations for CSOs from the data in Table 20.7, a weighted average should be used, assuming 93% of the CSO is associated with urban stormwater and 7% is associated with sanitary sewage. Comparing the levels for CSOs in Tables 20.2 and 20.7, values of Zn and Cu from the PCP are 2 and 2.4 times lower than in this study while the value of Pb from the PCP is 1.5 times higher than this study. Pratt et al. (1995) reported mean concentrations of 0.144 mg l⁻¹ for Pb and 0.148 mg l⁻¹ for Cu from combined sewage samples in south Buffalo, NY. D'Andrea and Maunder (1993) showed that mean levels of Zn, Cu, and Pb in CSO samples from Toronto, Ontario were in the range of 0.3, 0.1, and 0.12 mg l⁻¹, respectively. Moffa (1990) reported a mean concentration of 0.14 mg l⁻¹ for Pb from CSO samples in Rochester, NY. The levels of metals reported in Table 20.2 for this study are consistent with those used in the PCP loading estimates as well as those from sampling efforts in major cities around the Golden Horseshoe (Toronto, Buffalo, and Rochester).

Although there certainly is variability in our metals data, given the above brief review of the literature, it appears that the mean values used in Table 20.2 are reasonable for planning level loading estimates for the Kennilworth sewershed.

Table 20.4 Mean levels of PAHs ($\mu\text{g l}^{-1}$), CSO samples*.

Fluoranthene	Phenanthrene	Benzo(a)pyrene	Pyrene	Chrysene
0.99	0.52	0.35	0.90	0.64

n=2

Table 20.5 CSO loading estimates of metals (kg) for a typical year from the Kennilworth sewershed.

Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
1204	0.889	7.588	29.51	2706	282.1	3.172	28.05	5.598	210.2

Table 20.6 CSO loading estimates of PAHs (kg) for a typical year from the Kennilworth sewershed.

Fluoranthene	Phenanthrene	Benzo(a)pyrene	Pyrene	Chrysene
0.308	0.162	0.109	0.280	0.199

Table 20.7 Event mean concentration data (mg l^{-1}) used for loading calculations in the PCP (after Paul Theil Associates and Beak Consultants, 1991).

Metal	Sanitary Sewage	Stormwater Runoff, Urban Areas	Weighted Mean of Sanitary Sewage and Stormwater Runoff, Urban Areas
Zn	2.6	0.16	0.331
Pb	0.071	0.14	0.135
Cu	0.10	0.034	0.0386

A comparison of the metals levels in the Cope St. combined sewage samples and the CSO samples (Figure 20.4) indicates, however, that the values in Table 20.2 used for loading estimates may not be representative of areas in the city that are some distance from major contaminant sources. While studies have variously supported or rejected trends in contaminant concentration by land use (e.g. Novotny and Chesters, 1981; Marsh, 1991; D'Andrea and Maunder, 1993; Rhee et al., 1997), it does appear that there is some spatial variability in stormwater runoff and CSO quality within Hamilton. The variability may be related in some way to land use, but also to distance from major sources, as relative location can dictate deposition and redistribution patterns (e.g. Vermette et al., 1987; Irvine and Loganathan, in press).

Metals levels in storm flow at the Cope St. site generally are higher than in sanitary flow, indicating that washoff processes are important in contributing to pollutant loads. However, the metals levels in sanitary flow determined from this study are lower than those used in the PCP (see Table 20.7).

D'Andrea and Maunder (1993) found that event mean concentrations of phenanthrene and benzo(a)pyrene in CSOs from Toronto were in the range of 0.6 and 0.3 $\mu\text{g l}^{-1}$, respectively. The levels of phenanthrene and benzo(a)pyrene observed in Toronto are similar to those sampled in the Kennilworth sewershed. Data for individual PAHs in CSOs are relatively scarce and this study provides some limited, preliminary insights to the levels of these organic compounds.

The general modeling and loading estimate approach outlined in this paper can be used as a basis for future loading evaluations, as more CSO quality data become available. In addition, the approach can be used to evaluate loadings for other years (e.g. a specific year of interest, or extreme wet and dry years). These loading estimates can be compared to loadings from other sources discharging to the boat slip area of the harbour. The levels of most metals in the CSOs from the Kennilworth sewershed generally exceed Canadian Water Quality Guidelines and therefore are of some concern. As the different components of the PCP are implemented it is anticipated that the frequency and volume of overflows to Hamilton Harbour from all outfalls, including the Kennilworth site, will be significantly reduced, thereby resulting in improved water quality within the harbour.

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