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Environment Canada

Water Science and Technology Directorate

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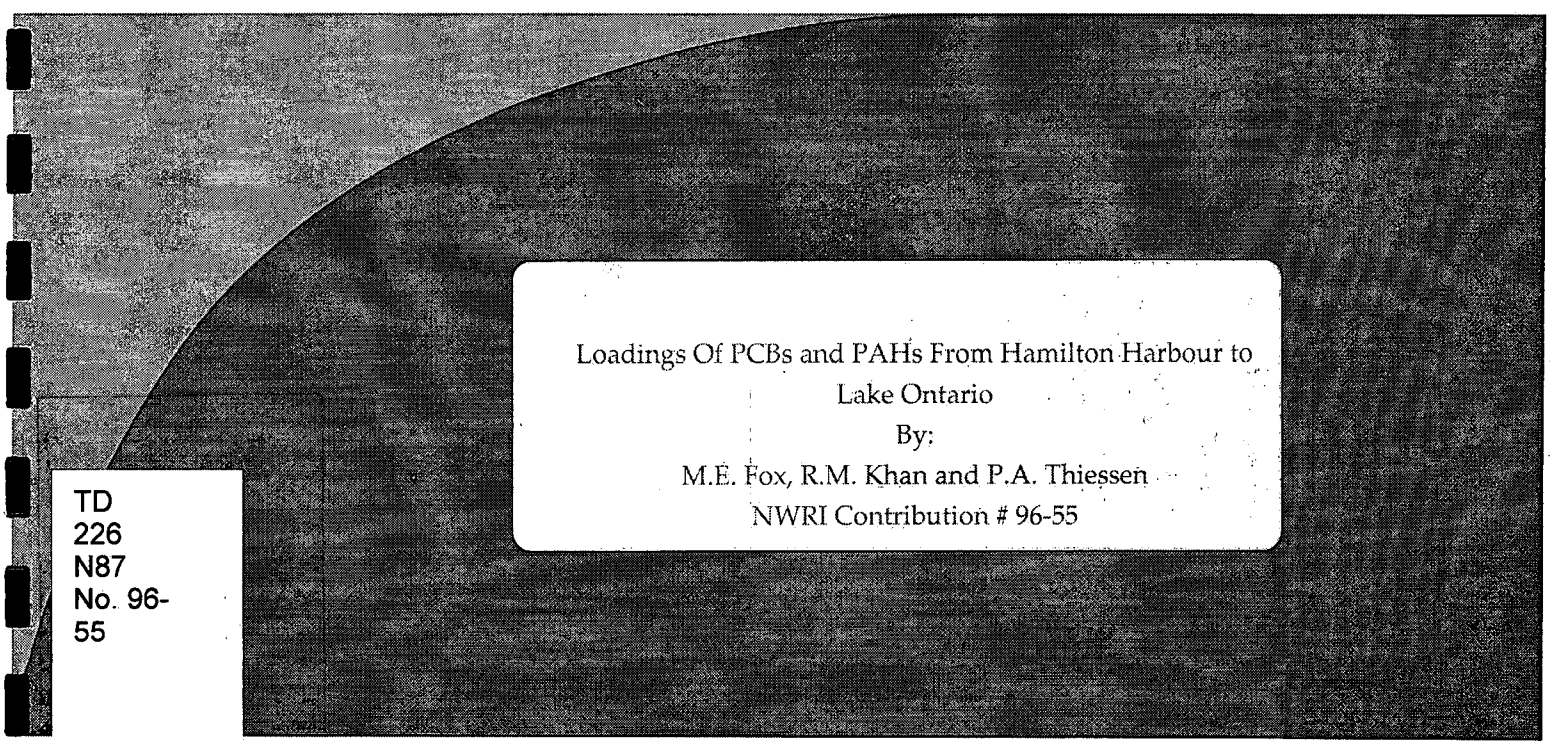

Loadings Of PCBs and PAHs From Hamilton Harbour to Lake Ontario

By:

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NWRI Contribution # 96-55

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MANAGEMENT PERSPECTIVE

LOADINGS OF PCBS AND PAHS FROM HAMILTON HARBOUR TO LAKE ONTARIO

M. E. Fox, R. M. Khan and P. A. Thiessen
Aquatic Ecosystem Restoration Branch, NWRI
1 February 1996

PCBs and PAHs are the major persistent organic pollutants of Hamilton Harbour water and sediments.

Export of PCBs and PAHs from Hamilton Harbour to Lake Ontario was measured to enable comparison with other sources to the lake and existing levels in the harbour.

Net loadings of PCBs and PAHs from Hamilton Harbour to Lake Ontario were 2.8 and 37.5 kg/ year respectively. These loadings are lower than reported loadings from the Niagara River by factors of 500 for PCBs and 800 for PAHs and from the atmosphere by 600 for PCBs and 30 for PAHs.

A major proportion of the present day loading of PAHs to Hamilton Harbour is not exported to Lake Ontario.

Annual export of PAHs to Lake Ontario was equivalent to <0.5 % of the amount of PAHs in the Randle Reef coaltar hotspot. Therefore natural export to the lake does not represent a significant amelioration mechanism for coal tar deposits in the harbour.

ABSTRACT

Large volume water samples were collected from the Ship Canal connecting Hamilton Harbour and Lake Ontario while detailed simultaneous measurements of water speed and direction were made. The 10 day sampling period in July 1989 and a 14 day sampling period in March 1991 were considered representative of typical stratified summer and unstratified winter flow regimes. The water samples were analysed for PCBs and PAHs which are known major organic contaminants in Hamilton Harbour. Supporting physicochemical measurements were also made. The water movement data was combined with the contaminant concentrations and the uniform channel dimensions to calculate annual loadings of 2.8 kg/ year PCBs and 37.5 kg/ year PAHs from Hamilton Harbour to Lake Ontario. These estimates were compared to other published estimates of loadings of these compounds from Hamilton Harbour and also from the atmosphere and the Niagara River. It was concluded that Hamilton Harbour is not a significant source of these compounds in comparison to the atmosphere and the Niagara River. The PAH export estimate was found to be small when compared to in situ sediment burdens of PAHs and also present day discharges to the harbour.

INTRODUCTION

In 1985, the International Joint Commission (IJC) identified 42 "Areas Of Concern" in the Great Lakes Basin. Hamilton Harbour, located at the western end of Lake Ontario, was included because of elevated levels of heavy metals, nutrients and toxic organics, including polychlorinated biphenyls (PCBs), and polyaromatic hydrocarbons (PAHs) (IJC, 1985) . Studies have identified large deposits of PAHs in the form of coal tar at the Randle Reef site as a major obstacle to remediation of Hamilton Harbour (Murphy et al., 1990) and the Hamilton Harbour Remedial Action Plan has proposed removal and containment/destruction of the most contaminated zone of Randle Reef (Hamilton Harbour RAP, 1995). According to a report of Ontario Ministry of the Environment (OME, 1986), Hamilton Harbour may be a significant source of PAHs to Lake Ontario via the Burlington Ship Canal, a 91m x 820m x 9.5m deep channel connecting the lake to the harbour. However, accurate quantification of organic contaminant loading from the Harbour to Lake Ontario has been thwarted by the complexity of water movement within the canal and difficulties in accurate quantitation of the low concentrations of these contaminants in the dissolved phase. Reliable loading data is needed to accurately determine whether significant amounts of PCBs and PAHs are exported to Lake Ontario.

Hamilton Harbour is a source of PAH, PCB and heavy metal contaminant loading to Lake Ontario (MOE, 1986; Rodgers et al, 1988; Poulton, 1987). The harbour received large quantities of PAHs from industrial operations in the past which substantially remains in the sediments to this day (Murphy et al., 1990). Present day PAH loadings are much lower; about 0.9 kg/day in 1988 (Hamilton Harbour RAP, 1992), and derive from STP effluents and stormwater runoff in addition to the steel industry. Historically, high concentrations of PCBs in sediment and the water column have been recorded adjacent to the site of a previous transformer

manufacturing plant (Harlow and Hodson, 1988; MOE, 1985), while current PCB sources of loadings to the harbour are believed to be minor and diffuse .

Net water flow must be from the harbour to the lake since the harbour receives numerous industrial and municipal effluents, as well as runoff from several watersheds. Hence, PAHs, PCBs and heavy metals are transported from the harbour to the Lake. However, there are other, major sources of organic contaminant loading to Lake Ontario such as the Niagara River (Environment Canada, 1990) and the atmosphere (Chan and Perkins, 1989). The Niagara River is the major source of contaminant loading to the lake, discharging 2000 kilograms PCBs and 44384 kilograms PAHs into the lake annually (IJC, 1980; MOE, 1986). An accurate estimate of net organic contaminant loading from the harbour to the lake requires a knowledge of the patterns of exchange flow through the canal itself. These patterns were first characterized by Dick and Marsalek (1973), who observed two main flow regimes within the canal: unidirectional "plug" flow, and stratified exchange flow. In the first regime, bulk exchange flow occurs unidirectionally and is governed by relative differences in lake-harbour water levels. This flow regime persists throughout the year. The second regime occurs mainly during the stratification period in the summer months where a layer of warm harbour water flows into the lake over a layer of cool lake water flowing into the harbour. More recently, studies have shown the flow regimes in the Burlington Ship Canal to be more complex where flow in the top layer of the canal sometimes occurs in the direction of the harbour, and occasionally three-layer flow has been observed (Palmer and Poulton, 1976), (Kohli, 1977, 1979a,b).

Several estimates of organic contaminant loading from Hamilton Harbour to Lake Ontario via the Burlington Ship Canal have been made in the past but they have suffered from various limitations. For example, the 1986 study conducted by the Ontario Ministry of the Environment estimated the total PAH loadings from Hamilton Harbour to Lake Ontario of 180 to 1050 kg PAH's per year using broad-

assumptions derived from very limited measurements (MOE, 1986). In another study by Poulton (1987), the PCB loading estimate was based on PCB concentrations in the Harbour proper rather than the Ship Canal and neglected the important phenomenon of reverse flow. In this study we attempted to make more precise loading estimates based on detailed measurements of both water flow and contaminant concentrations made simultaneously in the connecting channel itself under the conditions of both summer stratification and winter uniform plug flow.

EXPERIMENTAL

1. Collection and Processing of Water Samples

Twenty-litre water samples were collected daily during nine days in July 1990 and fifteen days in March 1991. The samples were collected at midspan from the Burlington Canal lift bridge at 2m and 8m depths. Temperature observations were recorded immediately. Conductivity measurements were made after the samples were taken to the laboratory. A 1 L subsample was analyzed for suspended solids and the remainder (18 L) was immediately filtered through a glass fibre filter (nominal pore size, 1um) and the resulting suspended solids and filtrate separately extracted with dichloromethane (Fox, 1986).

Baseline source (Hamilton Harbour) and receiving body (Lake Ontario) samples were collected on three occasions during the study.

2. Analysis of extracts for PCBs and PAHs

The concentrated extracts were cleaned up on Florisil minicolumns and analysed by dual column electron capture gas chromatography for PCBs and by selected ion gas chromatogaphy-mass spectrometry for PAHs.

3. Canal Water Flow Measurement and Analysis

Measurements of water velocity and direction were made with the aid of an Acoustic Doppler Current Profiler (ADCP) which measured current velocity and direction at 1 m intervals in the water column using an acoustic transponder

(R D Instruments, 1989). Measurements were recorded continuously by the ADCP at ten minute intervals throughout the duration of the study. The ADCP was installed on the ship canal floor 150 m west of the lift bridge and 5 m from the base of the north canal wall. Although this location does not correspond to the water sampling site, its close proximity and the uniform cross section of the canal suggests that the flow regimes are similar at both sites.

Raw data was transmitted from the ADCP to a standard personal computer and the raw data stored on floppy diskettes after transformation of the direction vectors relative to magnetic north . Since loading only occurs if the water mass is travelling "east" from the harbour to the Lake (positive loading), or "west" from the lake to the harbour (negative loading), only the current measurements along the "east-west" axis of the canal were considered in the present study. The neglected "north-south" velocity components were frequently either negligible or non-existent. The edited ADCP data was imported into a spreadsheet for manipulation and statistical summaries.

RESULTS AND DISCUSSION

Analysis of water movement data

Even after discarding the "north-south" velocity measurements, more than 3000 depth current profiles remained in the database. The resolution available in the database was much higher than the corresponding analytical database which consisted of daily measurements at two depths. For this reason, each ADCP depth profile was condensed into a "top layer mean" and a "bottom layer mean" where each layer occupied 5 m of the 10 m total depth of the connecting channel. In addition to matching the resolution of flow and analytical data, this simplification can accomodate almost any flow regime from simple plug flow to complex two layer exchange. The summary of water flow regimes at all depths in both the summer and winter periods shown in Figure 1 illustrates the utility of both the flow data

simplification and the choice of sampling depths at 2 m and 8 m. Figure 1 also shows the dominance of seasonal stratified flow in the summer period and its absence in the winter period.

In the stratified summer period of 9.2 days the mean top layer velocity was +5.77 cm/sec (towards the lake) producing a net volume exchange of +2.27E+06 m^3/day and -6.73 cm/sec (towards the harbour) in the bottom layer for a net volume exchange of -2.65E+06 m^3/ day. The sum of these values yields a total net volume exchange for the channel of -0.38E+06 m^3/ day, ie negative loading which is clearly impossible over significant time periods because of tributary inputs to the harbour. Negative loadings over the stratified summer period have been observed by others (Dick and Marsalek, 1973; Spigel, 1989) and may be attributed to very large volumetric excursions through the canal, much of which reverses direction without leaving the immediate environment of the channel (Hamblin, pers. comm. 1996). The frequent flow reversals, which can occur at intervals of less than one hour are caused by wind and barometric pressure variations on Lake Ontario. Diurnal periodicities, which bias the flow towards the harbour in daylight hours during the summer stratified period (Spigel, 1989), would not distort the ADCP measurements which were continuous throughout the study period.

In the unstratified winter period of 14.9 days the predominant plug flow regime was observed to change direction frequently with approximately equal distribution at the surface and increasingly dominant flow towards the lake with increasing depth (Figure 2). The mean velocity was +2.03 cm/ sec (towards the lake) for a net volume exchange of 1.60E+06 m^3/ day (Table 3).

Although extrapolating to a full calendar year from these limited observations is not fully justified, we have assumed a stratified period of five months from mid May to mid October (Charlton, pers. comm.) and calculated a year round mean volume exchange of 0.8E+06 m^3/ day which is quite close to the estimate of tributary and STP loadings of 1E+06 m^3/ day (Klapwijk and Snodgrass, 1985).

Temperature and conductivity measurements

The temperature and conductivity of each sample was recorded immediately after sample collection and proved especially useful in the summer period as a means of distinguishing between lake water, harbour water or mixtures of both. The conductivity of western Lake Ontario is usually 300-320 µS/ cm while that of the harbour is usually >650 µS/ cm. Similarly, Lake Ontario July temperatures are frequently below 16 C, while the corresponding harbour temperatures are often above 20 C. The data presented in Figures 3 & 4 show that during the summer period the outflowing top layer water is almost 100% harbour water, while the inflowing bottom layer varies from almost 100% lake water to lake water with a significant harbour water component.

PCB measurements

Concentrations of total PCBs (both dissolved and suspended solids phases separately determined) in the Ship Canal are shown in Figures 5 & 6 for the summer period and Figure 7 for the winter period. Lake Ontario and Hamilton Harbour total PCBs are shown in Figure 8. "Totals" were calculated by multiplying the sum of 13 individually determined significant congeners by an empirically derived factor. The selected congeners (Table 1) were chosen on the basis of known local abundance and complete separation under the analytical system used. The distribution between the dissolved and solid phases varied between 30 and 70 % in each phase with a mean of approximately 50 %. The higher proportion on the particulate phase was usually associated with higher levels of suspended solids. As observed earlier in an unpublished study on the spatial, temporal and phase distribution of PCBs in Hamilton Harbour the congener distribution was biased towards more of the higher chlorine number congeners and less of the lower chlorine number congeners on the particulate phase. Summer period whole water total PCBs (dissolved + particulate) in the ship canal ranged from 6.3 - 11.4 ng/ L

in the upper layer and 4.0 - 8.9 ng/ L in the lower layer. Concentrations in Hamilton Harbour at the CCIW dock on three occasions ranged from 9.1 to 12.7 ng/ L. Triplicate measurements on samples from mid western Lake Ontario averaged 2.3 ng/ L while triplicate measurements on samples 1 mile offshore from the canal averaged 3.3 ng/ L . It is evident from these measurements that although PCBs are exported into Lake Ontario, where an excess over background levels is detectable at the 1mile marker buoy, a significant quantity of PCBs discharged in the upper layer becomes entrained in the inflowing lower layer and reenters the harbour. Winter period whole water total PCBs ranged from 4.7 to 9.3 ng/ L. Export of PCBs is likely to be more complete than in the summer period because of the absence of stratified reverse flow. Although there were frequent reversals of plug flow direction, the strong lower level return flow of the summer period was not observed.

PAH measurements

Concentrations of total PAHs (both dissolved and suspended solids phases separately determined) in the Ship Canal are shown in Figures 9 & 10 for the summer period and Figure 11 for the winter period. Lake Ontario and Hamilton Harbour total PAHs are shown in Figure 12. "Total" refers to the EPA designated 16 "priority" PAHs shown in Table 1 and may be conservatively considered to represent in excess of 70% of all PAHs.

The distribution between the dissolved and solid phases was similar to that observed for the PCBs with the solid phase accounting for 30 - 80 % of the total and a mean of approximately 50 %. Summer period whole water PAH concentrations ranged from 65 - 190 ng/ L in the upper layer and 50 - 123 ng/ L in the lower layer. Winter period whole water PAH concentrations ranged from 22 -103 ng/ L with a higher proportion associated with the suspended solids than observed during the summer period. Concentrations of whole water total PAHs in Hamilton Harbour at the CCIW dock on three occasions in the summer and fall of 1990 ranged from 58 to 149 ng/ L. On other occasions concentrations have ranged from below 20 ng/ L to more than 200 ng/ L with much more rapid changes in concentration than those

observed with PCBs. This variability is probably a reflection of the more recent nature of PAH contamination in Hamilton Harbour where large deposits still exist at the sediment- water interface in the Randle Reef area.

Triplicate measurements on samples from mid western Lake Ontario averaged 8.3 ng/ L while triplicate measurements on samples 1 mile offshore from the canal averaged 12.4 ng/ L. As with the PCBs, the summertime lower layer measurements shows that significant amounts of PAHs from the upper layer fail to escape the mouth of the canal before becoming entrained in the often inflowing lower layer and returned to the harbour.

Loadings to Lake Ontario

The daily loadings of total PCBs and total PAHs for each study period was calculated by multiplying the mean concentrations for each layer by the corresponding net volume exchange between the harbour and lake (Table 3). The annual loadings were calculated by extrapolation to a five month summer period and a seven month winter period as discussed earlier. Although the summer period net volume exchange was towards the harbour, a positive chemical loading was observed due to the higher concentrations of contaminants in the upper layer. Thus, the annual total PCB loading of PCBs was estimated to be 2.8 kg/ year and the annual total PAH loading estimated to be 37.5 kg/ year. To cross check these values we calculated the loadings to the lake based on the total natural flow plus various treated and untreated effluents of 1.23E+06 m^3/ day into the harbour (MOE, 1978) and the mean contaminant concentrations in the canal from the summer period upper layer and the winter period. The net contaminant loading to the lake from this calculation was 3.3 kg/ year for total PCBs and 46.6 kg/year for total PAHs.

Poulton (1987) estimated the annual loading of PCBs to be 24 kg/ year, approximately nine times the estimate of this study. His estimate is believed to be less precise than the present study, because of extrapolation of PCB measurements made in Hamilton Harbour rather than the ship canal. Poulton's flow

and contaminant concentrations were also made in different years. Poulton did not make a loading estimate for PAHs. Ling et al. (1993) modeled the fate of a number of chemicals in Hamilton Harbour and compared the results with available sediment and water column concentrations. They predicted the net export of total PCBs to Lake Ontario to be 4.1 kg/ year. This is quite a good agreement between prediction and direct measurement, considering the many assumptions and approximations in both studies.

Lake Ontario has many minor point source inputs of PCBs and PAHs but only two major sources; the Niagara River and the atmosphere. The International Joint Commission in 1980 estimated loadings of total PCBs from the Niagara River to be approximately 2000 kg/ year. Strachan and Eisenreich (1990) estimated loadings to Lake Ontario of total PCBs from the atmosphere of 2540 kg/ year. These estimates exceed the loading estimate of this study by a factor of 500 - 800. Similarly for total PAHs, the Ontario Ministry of the Environment estimated the Niagara River contribution to be 44,000 kg/ year (MOE, 1986) while Chan and Perkins (1989) reported precipitation concentrations of PAHs equivalent to an atmospheric loading of 1780 kg/ year. These atmospheric loading estimates for total PAHs exceed the Hamilton Harbour loading estimate of this study by a factor of 600 for the Niagara River and 30 for the atmosphere. On the basis of our estimates of loadings from Hamilton Harbour and the comparisons of loading estimates from other sources, we conclude that Hamilton Harbour is not a major source of PCB and PAH loadings to Lake Ontario.

Present day inputs of approximately 325 kg/ year total PAHs to the harbour (Hamilton Harbour RAP, 1992) exceed the calculated discharge by almost an order of magnitude. These ongoing supplies derive largely from combined sewer overflows and urban runoff together with a significant industrial discharge. The results of this study suggest that much of this ongoing input settles to the sediments or is broken down by biological mechanisms.

Since a major concern of the Hamilton Harbour RAP (1995) is the area most heavily contaminated with PAHs known as Randle Reef, it may be instructive to relate the export loadings of PAHs presented here to an estimate of the quantity of PAHs potentially available for export. Murphy et al. (1990) reported that 70,000 m^3 of sediments in the Randle Reef area contained more than 0.2 mg/ g total PAH. An inspection of the figures in this report suggests that 0.4 mg/ g is a reasonable average. The Hamilton Harbour RAP (1995) has recommended removal of sediments with more than 0.8 mg/ g. concentration. Assuming a mean grain density of 2.5 g/cm^3 and a water content of 368% (dry weight) from measurements made in the Randle Reef area (Rukavina and Versteeg, 1995), the total amount of PAHs in the Randle Reef area is close to 20,000 kg. Thus, the annual loading of PAHs to the lake is <0.5% of the Randle Reef burden suggesting that decisions to remediate the Randle Reef area should be based solely on the potential for in Harbour improvements.

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TABLE 1: PCB Congeners analysed

2,2',5-trichlorobiphenyl	(PCB # 18)
2,2',3,5'-tetrachlorobiphenyl	(PCB # 44)
2,2',4,5'-tetrachlorobiphenyl	(PCB # 49)
2,2',5,5'-tetrachlorobiphenyl	(PCB # 52)
2,2',4,5,5'-pentachlorobiphenyl	(PCB # 101)
2,3,3',4,4'-pentachlorobiphenyl	(PCB # 105)
2,3',4,4',5-pentachlorobiphenyl	(PCB # 118)
2,2',3,4,4',5'-hexachlorobiphenyl	(PCB # 138)
2,2',3,4',5',6-hexachlorobiphenyl	(PCB # 149)
2,2',3,5,5',6-hexachlorobiphenyl	(PCB # 151)
2,2',3,4,4',5,5'-heptachlorobiphenyl	(PCB # 180)
2,2',3,4,4',5',6-heptachlorobiphenyl	(PCB # 183)
2,2',3,3',4,4',5,5'-octachlorobiphenyl	(PCB # 194)

TABLE 2: PAH compounds analysed

Napthalene
Acenapthylene
Acenapthene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Benz(a)anthracene
Chrysene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene
Indeno(1,2,3-cd)pyrene
Dibenz(a,h)anthracene
Benzo(g,h,i)perylene

TABLE 3: PCB and PAH loading calculations

Stratified period: July 17-27 1990

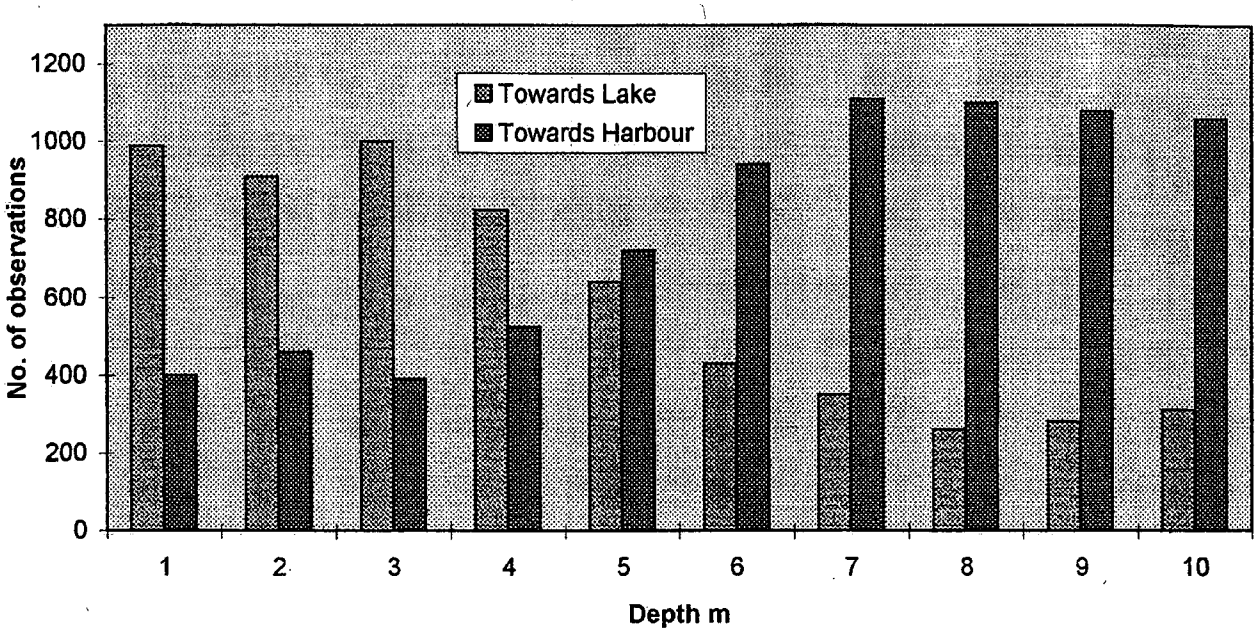
		PCB	PAH
Study duration	9.2 days		
Av. velocity - top layer	5.77 cm/ sec (to lake)		
Av. velocity - bot. layer	-6.73 cm/ sec (to HH)		
Net vol. exchange top	2.27E+06 m^3/ day		
Net vol. exchange bot.	-2.65E+06 m^3/ day		
Av. concn. contaminant - top layer		8.5 ng/ L	143.4 ng/ L
Av. concn. contaminant - bot. layer		5.6 ng/ L	84.0 ng/ L
Contaminant loading - top		19.3 g/ day	325.6 g/ day
Contaminant loading - bot.		-14.8 g/ day	-222.0 g/ day
Net contaminant loading to lake		**4.6 g/ day**	**103.6 g/day**

Unstratified period: March 11 - 25 1991

Study duration	14.9 days		
Av. velocity	2.03 cm/ sec		
Volume exchange	1.60E+06 m^3/ day		
Av. concn. contaminant		6.1 ng/ L	63.5 ng/ L
Contaminant loading to lake		**9.8 g/ day**	**102.0 g/ day**

LIST OF FIGURES:

Fig. 1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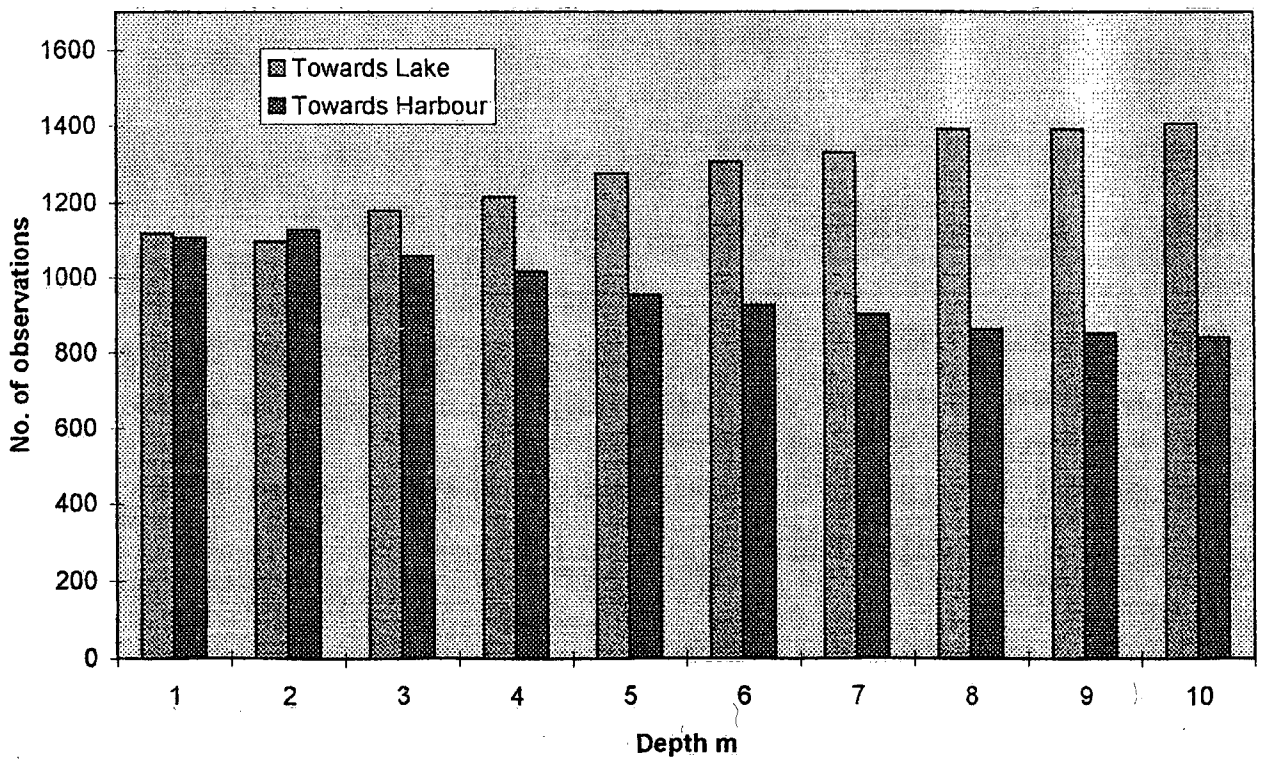
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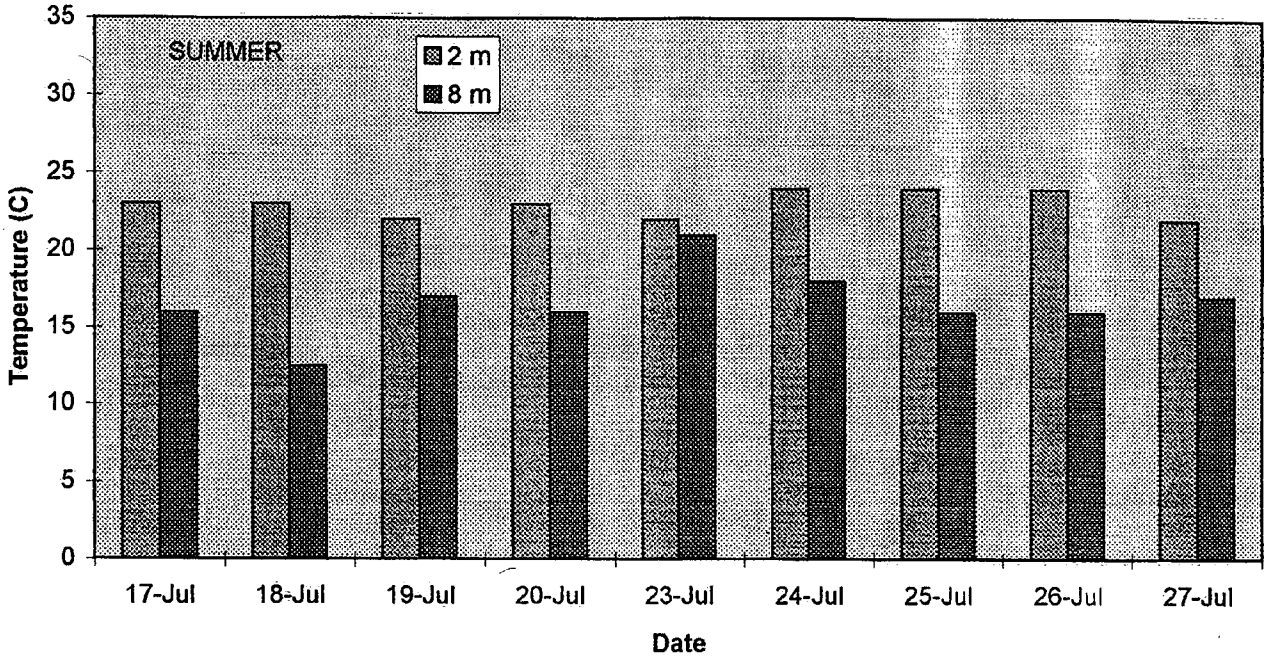
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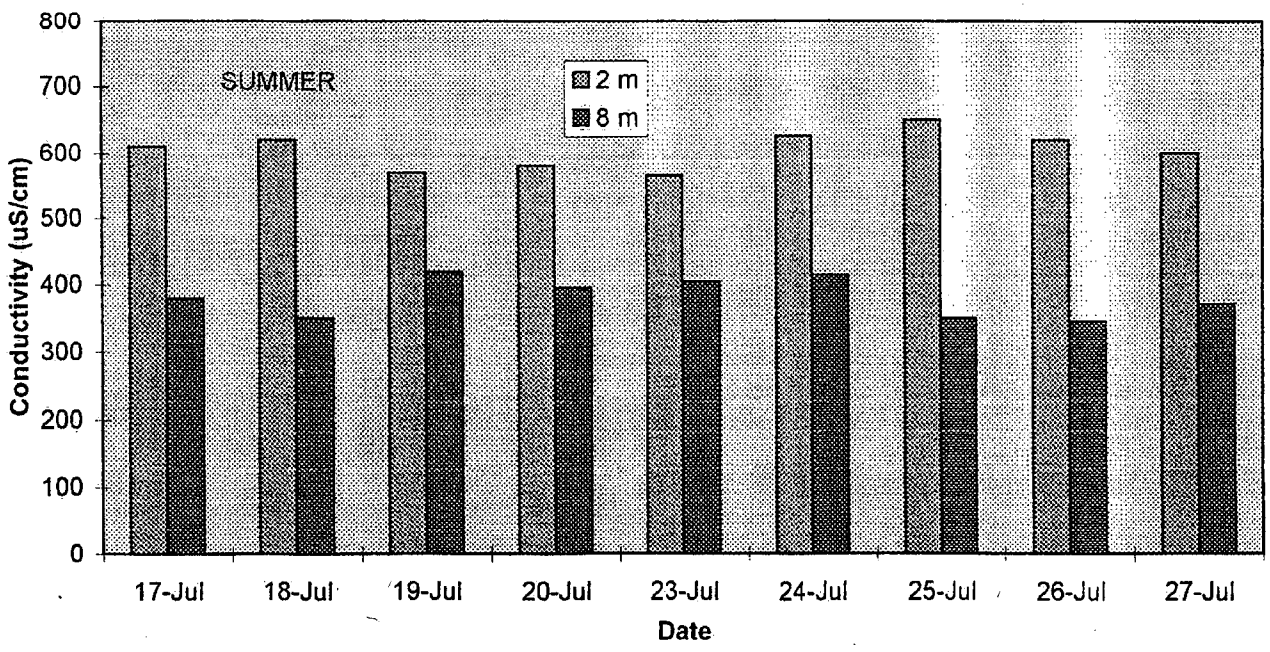
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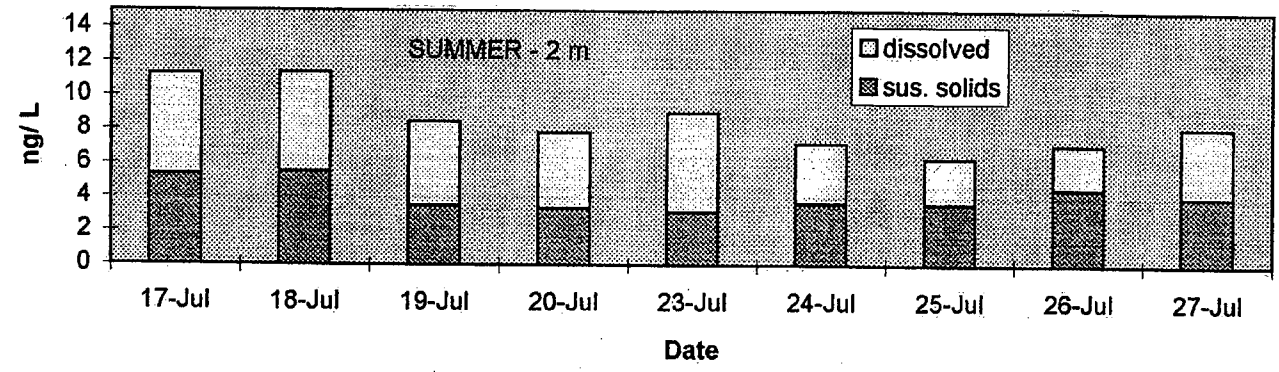
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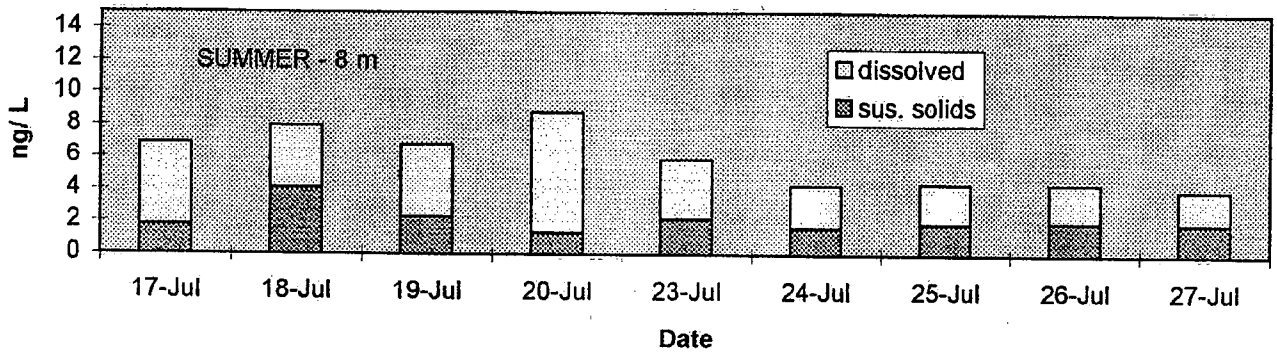
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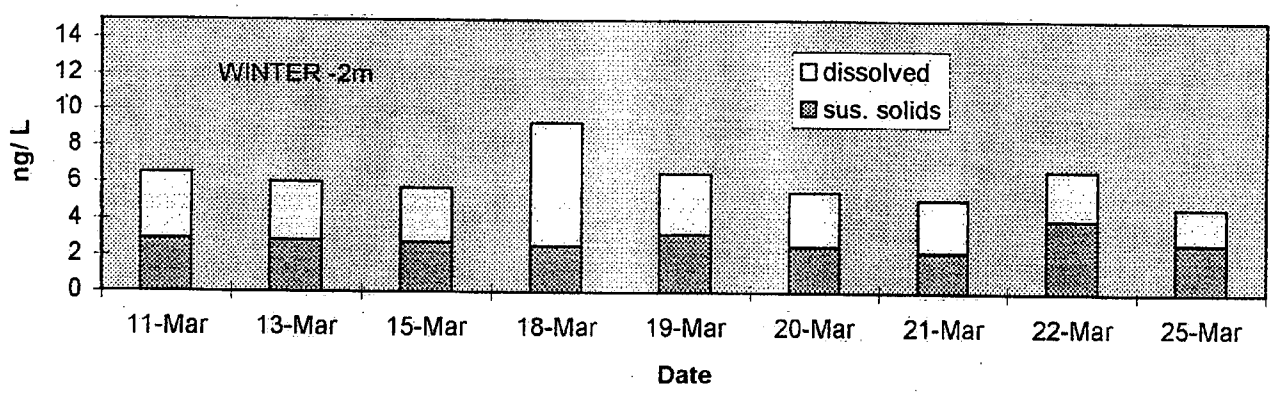
Date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dissolved
sus. solids
ng/ L
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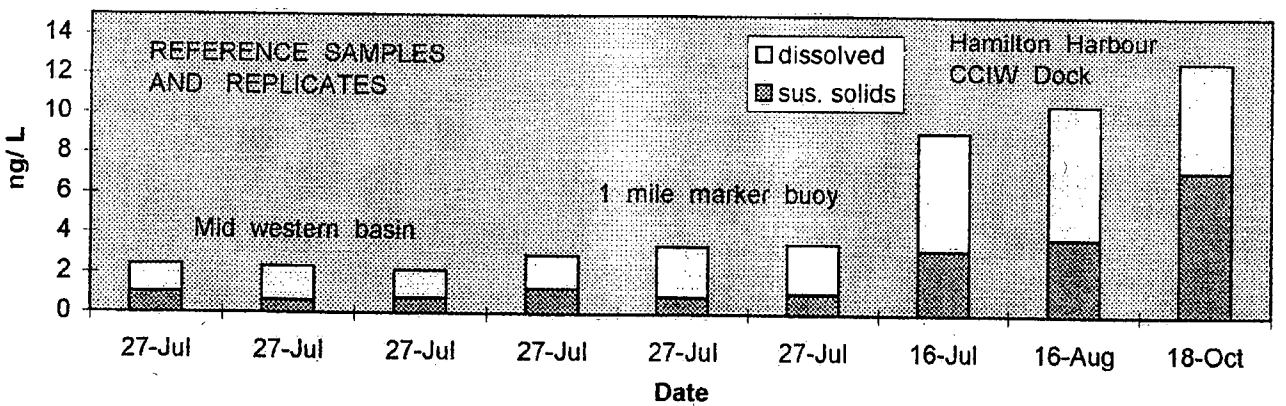
Date


REFERENCE SAMPLES
AND REPLICATES
dissolved
sus. solids
Hamilton Harbour
CCIW Dock
1 mile marker buoy
Mid western basin
ng/ L
0
2
4
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8
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27-Jul
27-Jul
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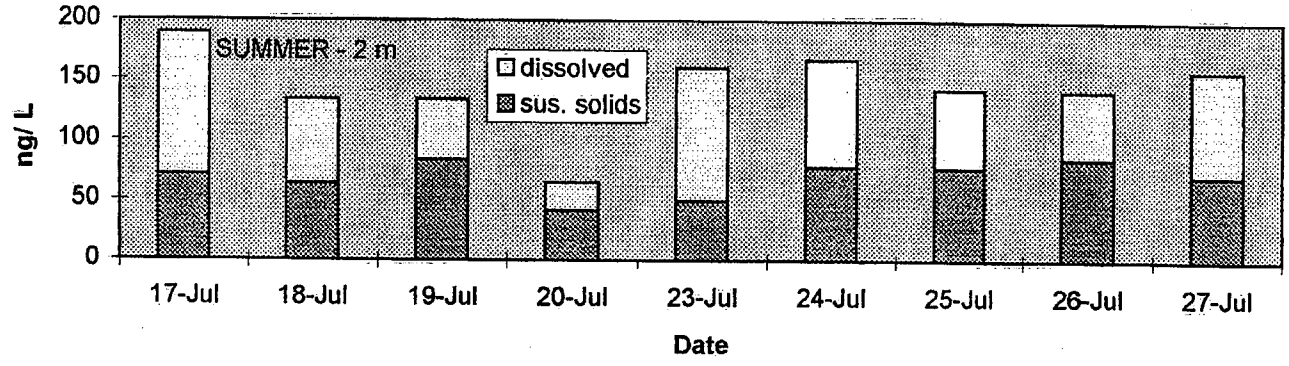
16-Jul
16-Aug
18-Oct
Date

Fig. 4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sus. solids
ng/ L
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150
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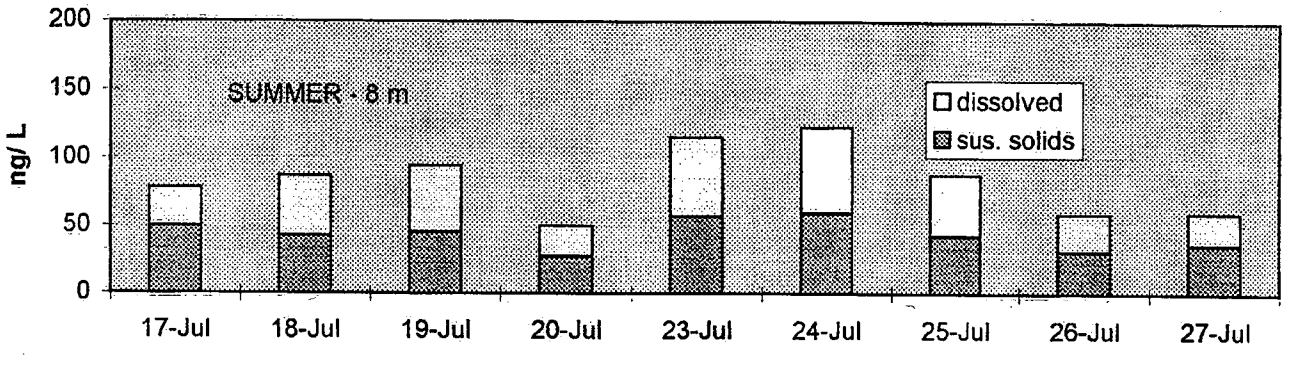
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dissolved
sus. solids
ng/ L
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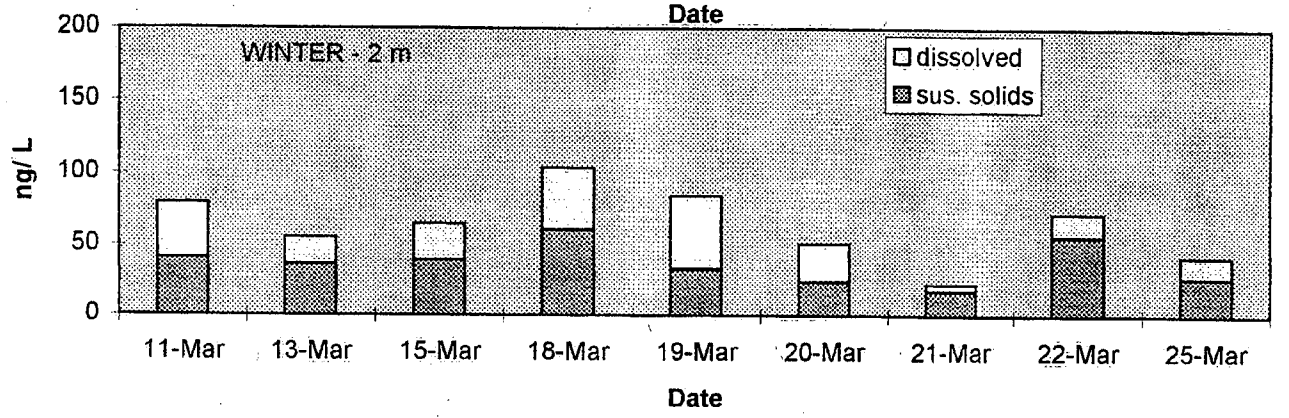
26-Jul
27-Jul
Date


WINTER - 2 m
dissolved
sus. solids
ng/ L
200
150
100
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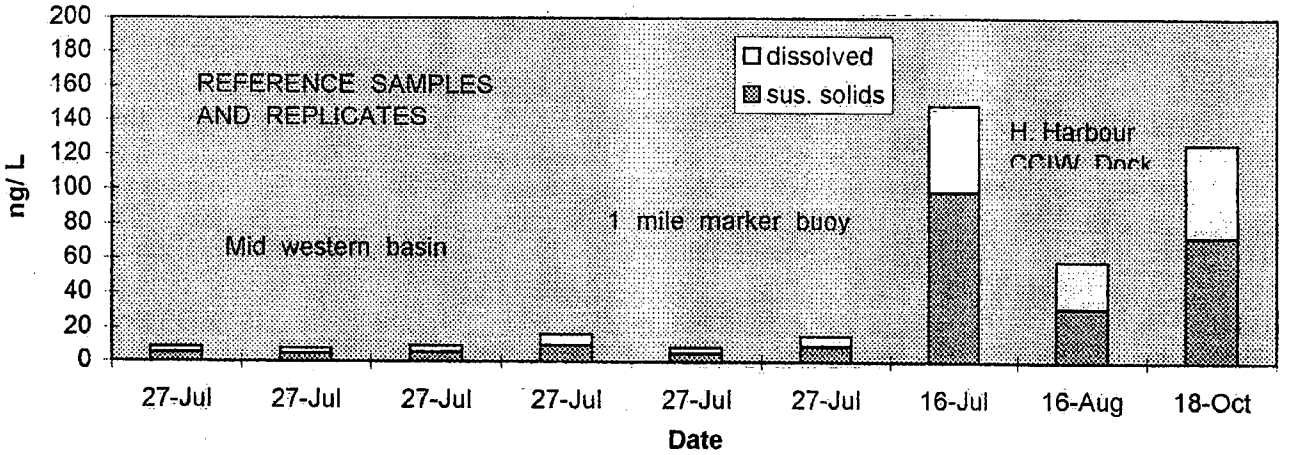
0
11-Mar
13-Mar
15-Mar
18-Mar
19-Mar
20-Mar
21-Mar
22-Mar
25-Mar
Date


REFERENCE SAMPLES
AND REPLICATES
dissolved
sus. solids
Mid western basin
1 mile marker buoy
H. Harbour
ng/ L
200
180
160
140
120
100
80
60
40
20
0
27-Jul
27-Jul
27-Jul
27-Jul
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27-Jul
16-Jul
16-Aug
18-Oct
Date

Reviewer No. 2

Comments on manuscript by *Fox et al* numbered as per manuscript evaluation sheet

3. Abstract:

The high quality and extensive nature of water flow data should be mentioned in abstract.

5. Materials and Methods:

The sections dealing with the extraction and analysis of PCBs and PAHs (and of section 1 and section 2) should be expanded to include some details of extraction methods, clean-up method, GC column(s) used and methods of quantitation. I presume all compounds quantified were on hand as authentic standards.

6. Quality Assurance:

There is no indication of any QA/QC being done as part of this project. The PCB and PAH data are presented only in summary form in figures. It would be most useful to have average and standard deviation data (and range of values) included for each PCB and PAH in Tables 1 and 2, respectively. Tables 1 and 2 should be consolidated into one table. Some indication of detection limits of analyses would also be appropriate.

8. Discussion:

Many of the values for PCB and PAH concentrations are only given as ranges. While range data are useful, average values and standard deviations are more useful and more meaningful. In some cases averaged values are mentioned without a standard deviation.

The water flow data in Table 3 should also have standard deviations included (and perhaps ranges).

9. There is no separate "conclusions" section in the text. The conclusions drawn in the paper would be much stronger once the data issues addressed in sections 6 and 8 above are dealt with.

10. As mentioned under point 6 above, Tables 1 and 2 should be consolidated into one Table. Average and standard deviation values for analyses would be included in this new table as column.

11. This manuscript has a large number of figures. I suggest that Figures 5 and 6 and Figures 9 and 10 be consolidated into two figures. This would make comparisons easier. I don't know the editorial policy of this journal re figure numbers, but Figures 7 and 11 could even be combined with two scales differing by a factor of ten. These consolidations would still leave the manuscript with 10 or 9 figures, respectively. The editor may wish to ask that some data be put into a large table and save 4 - 6 figures. The average values for various parameters were undoubtedly plotted in the figures. The standard deviations from the new tabular data should also be included on the figures so that the significance of the data in the figures can be evaluated at a glance.

WATER QUALITY RESEARCH JOURNAL OF CANADA
Manuscript Evaluation

Manuscript Title: **Loadings of PCBs and PAHs from Hamilton Harbour to Lake Ontario**

Author(s): ***Fox et al.***

Date: Jan. 8/96 **Reviewer No. 2**

		YES	NO
1.	**Does the manuscript present new knowledge, a useful review or assessment ?**	☑	☐
2.	**Does the title reflect accurately the substance of the work?**	☑	☐
3.	**Does the abstract reflect accurately the most important findings of the work?**	☐	☐ See comments
4.	**Does the introduction include all important guide posts for orienting the reader?**	☑	☐
5.	**Does the Materials and Methods section adequately describe all important elements of :** •materials ☐ •methods ☐ •conditions ☐ •time frame ☐ •location ☐ ?	see comments	
6.	**Are the quality assurance tests and statistics adequate for the work?**	☐	☐ See comments
7.	**Are the results given in sufficient detail?** if actions taken as per #6	☑	☐
8.	**Does the discussion address the results adequately?**	☐	☐
9.	**Are the conclusions drawn supported by the data?**	☑	☐
10.	**Are all tables necessary?** some consolidation.	☑	☐
	• **Are the table headings sufficiently detailed to understand the data?**	☑	☐
11.	**Are all figures necessary?**	☐	☑
	• **Are the figure captions sufficiently detailed to understand the figures?**	☑	☐
12.	**Are all important references given?**	☑	☐
13.	**Does the manuscript read well?**	☑	☐
14.	**Is the manuscript acceptable for publication:**		
	(a) as it stands or after minor changes?	☑	☐
	(b) after major revisions of the text?	☐	☐
	(c) after revisions of tables and/or figures?	☑	☐
	(d) after further work?	☐	☐
15.	**Did you make notations in the manuscript?** Some	☑	☐
16.	**Did you make additional comments on a separate page or overleaf?**	☑	☐
17.	**Do you wish to review this manuscript again after revisions?**	☐	☑

Reviewer No. 2

INTRODUCTION

In 1985, the International Joint Commission (IJC) identified 42 "areas of concern" in the Great Lakes Basin. Hamilton Harbour, located at western Lake Ontario, was included as an "area of concern" mainly for its elevated levels of polychlorinated biphenyls (PCBs), ~~polyaromatic~~ polycyclic aromatic hydrocarbons (PAHs) and heavy metals. According to the IJC, Hamilton Harbour is a significant source of contaminant loading to Lake Ontario via the Burlington Ship Canal, a 91m x 820m x 9.5m deep channel connecting the lake to the harbour. However, accurate quantification of organic contaminant loading from the Harbour to Lake Ontario has been thwarted by the complexity of water movement within the canal. Reliable loading data is essential for the Hamilton Harbour Remedial Action Plan to accurately assess whether the harbour continues to be a significant loading source to Lake Ontario.

Hamilton Harbour has been shown to be a source of PAH, PCB and heavy metal contaminant loading to Lake Ontario (MOE, 1986; Rodgers et al, 1988; Poulton, 1987). The harbour receives most of its PAHs from the coking operations of steel mills while current PCB sources of loadings to the harbour are minor and diffuse (Fox and Thiessen 1990). Historically, large quantities of PCBs entered the harbour as leachate from industrial sites such as the Westinghouse transformer plant (Harlow and Hodson, 1988; MOE, 1985; 1986). Net water flow must be from the harbour to the lake since the harbour receives numerous industrial and municipal effluents, as well as runoff from several watersheds. Hence, PAHs, PCBs and heavy metals are transported from the harbour to the Lake. However, there are other, major sources of organic contaminant loading to Lake Ontario such as the Niagara River (Kuntz, 1984) and the atmosphere (Chan and Perkins, 1989). The Niagara River is the major source of contaminant loading to the lake, discharging 3050 kilograms PCBs and ~~4384~~ 400 kilograms PAHs into the lake annually (MOE, 1986; MOE, 1985; Data Interpretation Group, 1986).

An accurate estimate of net organic contaminant loading from the harbour to the lake requires a knowledge of the patterns of exchange flow through the canal itself. These patterns were first characterized by Dick and Marsalek (1973), who observed two main flow regimes within the canal: unidirectional "plug" flow, and stratified exchange flow. In the first regime, bulk exchange flow occurs unidirectionally and is governed by relative differences in lake-harbour water levels. This flow regime persists throughout the year. The second regime occurs mainly during the stratification period in the summer months where a layer of warm harbour water flows into the lake over a layer of cool lake water flowing into the harbour. It must be appreciated, however, that flow in the Burlington Ship Canal is somewhat more complex than the above generalization, as suggested by Palmer and Poulton (1976) and Kohli (1977, 1979a,b). Indeed, flow in the top layer of the canal sometimes occurs in the direction of the harbour, and occasionally three-layer flow has been observed.

Several estimates of organic contaminant loading from Hamilton Harbour to Lake Ontario via the Burlington Ship Canal have been posited in previous studies (MOE, 1986; Rodgers et al., 1988; Poulton, 1987). However, because these estimates are based on limited measurements of both contaminant concentrations and flow regimes in the ship canal, they may not be very useful to the Hamilton Harbour RAP. For example, a 1986 study conducted by the Ontario Ministry of the Environment estimates the total PAH loadings from the Hamilton Harbour to Lake Ontario as 180 to 1050 kg PAHs per year using broad-based assumptions (MOE, 1986). In another study by Poulton (1987), the PCB loading estimate was based on PCB concentrations in the Harbour proper and neglected reverse flow. None of these studies have based loading estimates on detailed measurements of both water flow and contaminant concentrations made simultaneously in the connecting channel itself under the conditions of both summer stratification and winter uniform plug flow.

EXPERIMENTAL

1. Collection and Processing of Water Samples

Twenty-litre water samples were collected on a daily basis over a ten day period in July 1990 and a fourteen day period in March 1991. The samples were collected at midspan from the Burlington Canal lift bridge at 2m and 8m depths. Temperature observations were recorded immediately. Conductivity measurements were made after the samples were taken to the laboratory. A 1 L subsample was analyzed for suspended solids and the remainder (18 L) was immediately filtered through a glass fibre filter (nominal pore size, 1um) and the resulting suspended solids and filtrate separately extracted with dichloromethane (Fox, 1986).

Baseline source (Hamilton Harbour) and receiving body (Lake Ontario) samples were collected on three occasions during the study.

2. Analysis of extracts for PCBs and PAHs

The concentrated extracts were cleaned up on Florisil minicolumns and analysed by dual column electron capture gas chromatography for PCBs and by selected ion gas chromatogaphy-mass spectrometry for PAHs.

3. Canal Water Flow Measurement and Analysis

Measurements of water velocity and direction were made with the aid of an Acoustic Doppler Current Profiler (ADCP) which measured current velocity and direction at 1 m intervals in the water column using an acoustic transponder (R D Instruments, 1989). Measurements were recorded continuously by the ADCP at ten minute intervals throughout the duration of the study. The ADCP was installed on the ship canal floor 150 m west of the lift bridge and 5 m from the base of the north canal wall. Although this location does not correspond to the of water sampling site, its close proximity and the uniform cross section of the canal suggests that the flow regimes are similar at both sites.

Raw data was transmitted from the ADCP to a standard personal computer and the raw data stored on floppy diskettes after transformation of the

approximately equal distribution at the surface and increasingly dominant flow towards the lake with increasing depth (Figure 2). The mean velocity was +2.03 cm/ sec (towards the lake) for a net volume exchange of 1.60E+06 m^3/ day (Table 1). Extrapolating to a full calendar year from such limited observations is fraught with uncertainties; however, assuming a typical stratified period of 5 months from mid May to mid October (Charlton, pers. comm.), the year round mean volume exchange would be approx. 0.8E+06 m^3/ day which is quite in accordance with the estimate of tributary and STP loadings of approx. 1E+06 m^3/ day (Klapwijk and Snodgrass, 1985). A deduction from this loading estimate for summertime evaporation would probably produce a discharge estimate similar to that of this study.

Temperature and conductivity measurements

The temperature and conductivity of each sample was recorded immediately after sample collection and proved especially useful in the summer period as a means of distinguishing between lake water, harbour water or mixtures of both. The conductivity of western Lake Ontario is usually 300-320 uS while that of the harbour is usually >650 uS. Similarly , Lake Ontario July temperatures are frequently below 16 °C, while the corresponding harbour temperatures are often above 20 °C. The data presented in Figures 3 & 4 show that during the summer period the outflowing top layer water is almost 100% harbour water, while the inflowing bottom layer varies from almost 100% lake water to lake water with a significant harbour water component.

PCB measurements

Concentrations of total PCBs (both dissolved and suspended solids phases separately determined) in the Ship Canal are shown in Figures 5 & 6 for the summer period and Figure 7 for the winter period. Lake Ontario and Hamilton Harbour total PCBs are shown in Figure 8. "Totals" were calculated by multiplying the sum of 13 individually determined significant congeners by an empirically derived factor. The selected congeners (Table 1) were chosen on the basis of

The distribution between the dissolved and solid phases was similar to that observed for the PCBs with the solid phase accounting for 30 - 80 % of the total and a mean of approximately 50 %. Summer period whole water PAH concentrations ranged from 65 - 190 ng/ L in the upper layer and 50 - 123 ng/ L in the lower layer. Winter period whole water PAH concentrations ranged from 22 -103 ng/ L with a higher proportion associated with the suspended solids than observed during the summer period. Concentrations of whole water total PAHs in Hamilton Harbour at the CCIW dock on three occasions in the summer and fall of 1990 ranged from 58 to 149 ng/ L. On other occasions concentrations have ranged from below 20 ng/ L to more than 200 ng/ L with much more rapid changes in concentration than those observed with PCBs. This variability is probably a reflection of the more recent nature of PAH contamination in Hamilton Harbour where significant deposits still exist at the sediment- water interface. Triplicate measurements on samples from mid western Lake Ontario averaged 8.3 ng/ L while triplicate measurements on samples 1 Km offshore from the canal averaged 12.4 ng/ L. As with the PCBs, the summertime lower layer shows that significant amounts of PAHs from the upper layer fail to escape the mouth of the canal before becoming entrained in the often inflowing lower layer and returned to the harbour.

Loadings to Lake Ontario

The ADCP produced a very detailed picture of the complex and highly variable dynamics of water movement in the ship canal during the two study periods. Lake - Harbour oscillations were clearly evident. In addition, significant periods of "blocking" were observed as described by Spigel (1989). Spigel also observed the apparently anomolous net inflow over an extended period as was observed in this study over the entire summer study period of 9.2 days. Nevertheless, the estimate of annual outflow is consistent with that of other studies (Klapwijk and Snodgrass, 1985).

The loadings of total PCBs and total PAHs for each study period was calculated by multiplying the mean concentrations for each layer by the corresponding net

volume exchange between the harbour and lake (Table 3). The two periods were then extrapolated to a calender year loading based on a five-month estimate of stratified flow as discussed earlier.

Thus the annual total ~~PCB~~ loading of PCBs was estimated to be 2.8 kg/ year and the annual total PAH loading estimated to be 37.5 kg/ year. Poulton (1987) estimated the annual loading of PCBs to be 24 kg/ year, approximately ~~10x~~ ten times the estimate of this study. The 1987 estimate is believed to be less precise than this study, largely due to neglect of reverse flow in the ship canal and extrapolation of PCB measurements made in Hamilton Harbour rather than the ship canal. Poulton's flow measurements and contaminant concentrations were also made in different years. Poulton did not make a loading estimate for PAHs. Ling et al. (1993) modeled the fate of a number of chemicals in Hamilton Harbour based on measurements made in 1987. They estimated the net export of total PCBs to Lake Ontario to be 4.1 kg/ year. This is quite a good agreement between theoretical prediction and direct measurement considering the many assumptions and approximations in both studies. Ling et al. did not make a loading calculation for total PAHs but did present a loading estimate for benz(a)pyrene of approximately 100 kg/ year which would translate into a total PAH loading estimate of at least 1500 kg/ year based on the ratio of benz(a)pyrene to total PAHs commonly observed in Hamilton Harbour water. This very speculative value is about 40x the loading estimate of this study. and would seem to warrant further investigation.

Lake Ontario has many minor point source inputs of PCBs and PAHs but only two major sources; the Niagara River and the atmosphere. Loading data for the Niagara River published by the Joint Evaluation of Upstream/ Downstream Niagara River Monitoring Committee 1989-90 of the four agency binational Data Interpretation Group River Monitoring Committee (Environment Canda 1990), reported a mean loading of 344 kg/ year of total PCBs based on suspended solids only. The International Joint Commision in 1980 estimated loadings of total PCBs from the Nigara River to be approximately 2000 kg/ year. Estimates of loadings of

total PCBs from the atmosphere range from 85 to 2300 kg/ year (IJC, 1980; Strachan and Eisenreich, 1990). Although these estimates vary widely, they exceed the loading estimate of this study by a minimum factor of 30x. Similarly for total PAHs, the Ontario Ministry of the Environment estimated the Niagara River contribution to be 44,000 kg/ year (MOE, 1986) while Strachan and Eisenreich (1990) estimated loadings from the atmosphere to be >500 kg/ year. As with PCBs, these loading estimates for total PAHs exceed the Hamilton Harbour loading estimate of this study by a minimum factor of 13x. On the basis of our loading estimates and the comparisons of loading estimates from other sources, we conclude that Hamilton Harbour is not a major source of PCB and PAH loadings to Lake Ontario.

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Spigel, Robert. 1988. "Some Aspects of the Physical Limnology of Hamilton Harbour", NWRI Contribution # 89-08, Lakes Research Branch, NWRI, Burlington, Ontario.

Strachan and Eisenreich 1990

TABLE 2: PAH compounds analysed

Napthalene
Acenapthylene
Acenapthene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Benz(a)anthracene
Chrysene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene
Indeno(1,2,3-cd)pyrene
Dibenz(a,h)anthracene
Benzo(g,h,i)perylene

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