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Chemical and Biological Profiles of sediment as Indicators
of sources of Genotoxic Contamination in Hamilton
Harbour, Part I: Analysis of Polycyclic Aromatic
Hydrocarbons and Thia-Arene Compounds
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MANAGEMENT PERSPECTIVE

- **Title:** Chemical and Biological Profiles of Sediment as Indicators of Sources of Genotoxic Contamination in Hamilton Harbour, Part I: Analysis of Polycyclic Aromatic Hydrocarbons and Thia-Arene Compounds, ~~and: Part II: Bioassay-Directed Fractionation Employing the Ames Salmonella/Microsome Assay.~~
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- **NWRI Publication #:** 99-231
- **Citation:**
- **EC Priority/Issue:** Great Lakes 2000 Program, Hamilton Harbour RAP. This work supports the EC priority of implementing ecosystem initiatives focused on ecosystems of national priority including AOCs in the Great Lakes and Atlantic Coastal Areas. Business Line = Nature, Outcome = Conservation of biodiversity in healthy ecosystems, Result = Priority ecosystems are conserved and restored, Sub-result = Great Lakes AOCs restored under GL2000.
- **Current Status:** This work is an investigation of chemical and bioassay response profiles as tracers of sources of contamination in Hamilton Harbour and is presented as a series of two papers. The findings in both phases of the study are complementary in that the presumed presence of two primary sources of organic contaminants to the harbour are substantiated; contamination originating from areas of historically contaminated sediments, and contamination originating in the watershed and entering the harbour through a tributary. This conclusion is based on samples from Redhill Creek and Windermere Arm exhibiting chemical and bioassay profiles characteristic of mobile combustion emissions while samples from the open harbour exhibited profiles suggesting the influence of both mobile and industrial emissions.

- **Next Steps: Publish in a scientific journal and communicate to RAP processes. Any continuation of this work is contingent upon funding.**



Chemical and biological profiles of sediments as indicators of sources of genotoxic contamination in Hamilton Harbour. Part I: Analysis of polycyclic aromatic hydrocarbons and thia-arene compounds

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Abstract

Bottom sediment and suspended sediment samples from Hamilton Harbour (western Lake Ontario) and from a major tributary were profiled using polycyclic aromatic hydrocarbons (PAH) and thia-arenes as source apportionment tracers. Ratios of selected PAH and ratios of monomethyl and dimethyl/ethyl dibenzothiophenes to the parent dibenzothiophenes were calculated. Thia-arene and PAH profiles of Standard Reference Material SRM 1649 (urban dust/organics), SRM 1650 (diesel), SRM 1597 (coal tar), Hamilton coal tar and a composite Hamilton air particulate sample provided source sample data. The gas chromatography-mass spectrometry (GC-MS) chromatograms of all sample extracts were dominated by homocyclic PAH but interpretation of PAH profiles with respect to source was difficult. In contrast, thia-arene analyses revealed more distinct differences in profiles of samples collected in different areas of the harbour, including the tributary. These results indicated that areas of coal tar-contaminated sediment are potential contributors to the overall contaminant burden of sediments and suspended sediments in Hamilton Harbour. These data also indicated that contaminants related to mobile combustion sources were entering the harbour via a major tributary. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polycyclic aromatic hydrocarbons; Suspended sediments; Thia-arenes; Source apportionment

1. Introduction

Hamilton, Ontario, Canada is located at the western end of Lake Ontario and represents a unique urban and industrial environment. Hamilton, the seventh largest

city in Canada (population 320,000), is dominated by heavy industry including the nation's two largest integrated steel mills and a number of other industries, some associated with steel production. Hamilton Harbour, an embayment of western Lake Ontario, has been designated as an Area of Concern by the International Joint Commission. High levels of contaminants including organochlorine compounds, heavy metals, polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAH) have been identified in Hamilton Harbour

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sediments (Poulton, 1987; Murphy et al., 1990). Of particular concern is an area of grossly coal tar-contaminated sediments near the south shore, east of Randle Reef (Fig. 1). Total PAH content (sum of concentrations of 16 priority pollutant PAH) in some sediments from this area has been reported to exceed 1000 $\mu\text{g/g}$ (Murphy et al., 1990). We previously reported the results of a chemical and biological investigation of Randle Reef sediment (Marvin et al., 1993) in which a bioassay-directed fractionation methodology employing the Ames *Salmonella typhimurium*/microsome assay was used to identify compounds responsible for mutagenic activity in the sediment extract. Benzo[a]pyrene, the benzofluoranthenes, indeno[1,2,3-cd]pyrene, ben-

zo[ghi]perylene and dibenz[a,h]anthracene were identified as significant mutagens in the sample extract. Resuspension and transport of material from areas of sediment contaminated by coal tar are commonly thought to be source of genotoxic PAH identified in harbour-wide sediments (Harlow and Hodson, 1988; Murphy et al., 1990; Mayer and Nagy, 1992). As a result, contaminated sediments near Randle Reef have been targeted for remediation.

It would be useful to develop an analytical methodology to determine the extent to which coal tar-contaminated sediment contributes to the contaminant burden in Hamilton Harbour. Specific PAH have been identified as indicators of contamination from automo-

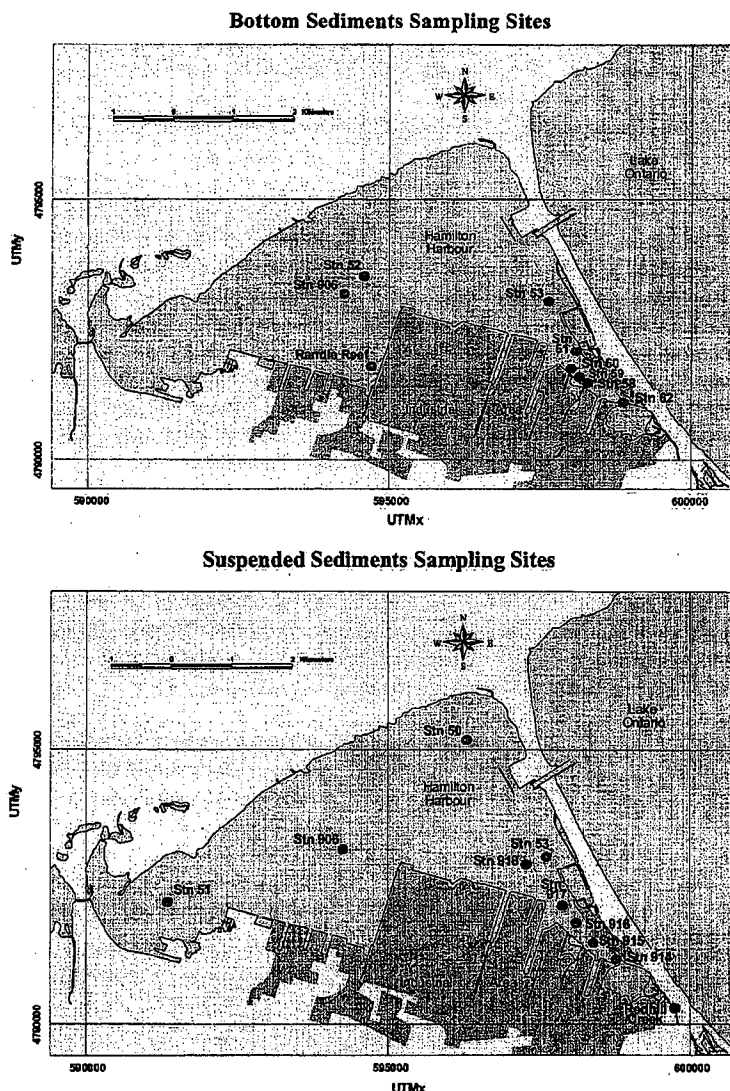


Fig. 1. Maps of Hamilton Harbour showing bottom sediment and suspended sediment sampling sites.

tive emissions, industrial emissions and crude oils (Gordon and Bryan, 1973; Greenberg et al., 1981; Hering et al., 1984; Cretney et al., 1985; Miguel and Pereira, 1989; Pistikopoulos et al., 1990; De Raat and de Meijere, 1991; Li and Kamens, 1993) but data interpretation can be confounded when contamination arises from multiple sources, such as in Hamilton Harbour. We have previously shown that dibenzothiophene or naphthothiophene isomers, their monomethyl derivatives and their dimethyl and ethyl derivatives are useful in distinguishing between coke oven emissions and diesel/urban emissions in samples of Hamilton air particulate (McCarthy et al., 1996). Thia-arene profiles of 24-h Hamilton air particulate sample extracts were divided into two profile groups based upon wind direction. One group exhibited profiles that were characteristic of vehicular emissions (i.e., diesel); the other group exhibited profiles that were characteristic of coke oven emissions. The thia-arene profile of a composite Hamilton air particulate sample (35 individual 24-h samples) appeared to be a composite of the profiles of diesel emissions and coke oven emissions.

Unlike PAH which are produced by the combustion of carbon-based fuels, thia-arenes are produced only by the combustion of fuels containing sulfur, such as coal and diesel fuel. We propose that thia-arenes might also be useful source apportionment tracers for Hamilton Harbour sediments and suspended sediments considering that resuspended coal tar-contaminated sediment and mobile combustion emissions are thought to be primary contributors to polycyclic aromatic compound (PAC) contamination in the harbour. We have examined PAH and thia-arene profiles of Hamilton Harbour bottom sediments and suspended sediments to evaluate the suitability of these compounds as tracers to distinguish between coal tar-contamination and contamination arising from other sources. This study was designed to assess the contribution of resuspended coal tar-contaminated sediment to the chemical profile of sediments throughout Hamilton Harbour and to identify other potential sources of contaminants (e.g., tributaries and sewage treatment plants) by comparison of profiles of sediments and suspended sediments from Windermere Arm and Redhill Creek with other areas of the harbour. The second paper in this volume describes the biological characterization of these samples using the Ames *Salmonella typhimurium*/microsome assay.

2. Experimental

Samples were collected with the assistance of Mr. Murray Charlton of the National Water Research Institute, Environment Canada, Canada Centre for Inland Waters, Burlington, Ontario. The sediment trap design was previously described by Charlton (1983).

Sediment traps were deployed over an 8-month period (October to May) resulting in 5–10 g (dry weight) accumulations of material per trap tube. Sediment traps were deployed at 2 depths (2 m from surface and 2 m from bottom). Centrifuge sediment samples were collected in October using two Westfalia flow-through centrifuges operated in tandem. Each centrifuge was operated at 5 l/min; total volume of water sampled was 1000 l per site. Centrifuges were mounted on a truck for sampling at station 914 and the Redhill Creek site. Twenty litres of post-centrifuge effluent water from five sites was extracted in dichloromethane for 24 h and the extracts were analysed by GC-MS. These data showed over 99% of the total PAH by mass was retained in the centrifuges. Sediment samples were dried prior to extraction in a desiccator over CaCl_2 (Drierite) until a constant weight was achieved.

A diesel particulate reference standard (SRM 1650), an urban air reference standard (SRM 1649) and a coal tar reference standard (SRM 1597) were obtained from the National Institute of Standards and Technology (Gaithersburg, MD). The composite Hamilton, Ontario air particulate extract was prepared from 35 filters collected at two sites in Hamilton. Air particulate samples were collected for 24 h at 40 ft³/min (1630 m³ sampled) on Teflon-coated glass fibre filters using an Anderson PM-10 air sampler (General Metal Works, Village of Cleves, OH).

Soxhlet extraction: Bottom sediments (50–90 g), reference standards and air filters were extracted in a Soxhlet extractor with dichloromethane (350 ml) for 24 h and for an additional 24 h with methanol. The extracts were combined and an aliquot of the crude extract was weighed after solvent evaporation for calculation of the percentage of organic material extracted.

Ultrasonication: Suspended sediment samples were extracted using a 300 watt Dismembrator Model 300 Ultrasonicator with a 0.75 in. diameter titanium probe (Fisher Scientific). Samples ranging from 2 to 7 g were placed in glass beakers containing 50 ml of dichloromethane. Eight consecutive pulses of 15 s duration each were applied at full power. An interval of one minute was maintained between pulses and the beaker was immersed in ice to minimize solvent heating. The suspension was filtered and re-extracted with 50 ml of fresh dichloromethane. The procedure was then repeated with 50 ml of methanol. The extracts were then combined.

Extracted material was adsorbed to alumina (3 g, Brockman activity I activated at 170°C for 48 h) by solvent reduction using a rotary evaporator. The sample, adsorbed to alumina, was applied to the top of fresh alumina (6 g) contained in a glass column (1 cm × 30 cm). Hexane (60 ml) was added to the column to elute aliphatics. Non-polar PAC were eluted by sequential addition of benzene (50 ml) then dichloromethane/ethanol (70 ml, 99:1 v/v), which were combined to afford a

single fraction. The non-polar PAC fraction was subjected to an additional clean-up step using a Sephadex LH20 gel column (hexane/methanol/dichloromethane, 6:4:3 v/v, 3 ml/min) to remove any remaining aliphatic compounds and reduce interferences; these non-polar aromatic compound fractions were then analysed by gas chromatography–mass spectrometry (GC–MS).

GC–MS experiments were performed on a Model 5890 Series II gas chromatograph with an on-column injector and a Model 5971A mass selective detector operated in selected ion monitoring mode (Hewlett-Packard Mississauga, ON). The following temperature program was used: 130–300°C at 1.6°C/min; final time at 300°C, 30 min. The column was a 30 m or 60 m × 0.25 mm i.d. DB-5ms or DB-17ht with a 0.25 µm stationary phase film coating (J&W Scientific, Folsom, CA). The internal standard was benzo[a]anthracene-d₁₂. Between-run precision ranged from 4% for benzo[a]pyrene to 11%

for chrysene. Using a signal-to-noise ratio of 2.5:1, the estimated detection limits were 60 pg for 178 amu and 202 amu PAH; 100 pg for 228 amu and 252 amu PAH; and 130 pg for 276 amu PAH. Total PAH were expressed as the sum of the 16 priority PAH as identified by the US EPA.

3. Results and discussion

Sediment traps were deployed in the fall (October) and collected in the spring (May) at three Environment Canada sites in Hamilton Harbour (stations 50, 51 and 53, Fig. 1). These sites reflect a variety of conditions dictated by water exchange with Lake Ontario and point source and non-point source discharges (Mayer and Nagy, 1992). Centrifuge samples were collected in October at two depths at station 906 (sub-surface and

Table 1

Selected polycyclic aromatic hydrocarbon ratios for source samples and Hamilton Harbour sediment samples^a

Station number/sample	Fluor/Pyrene	I[cd]P/B[ghi]P	B[a]P/B[e]P	Pery/B[e]P
<i>Centrifuge samples</i>				
Redhill Creek	1.22	1.00	0.71	0.21
914	0.97	0.86	0.81	0.20
915	1.10	1.00	1.00	0.35
916	1.08	0.96	0.79	0.30
917	0.98	0.95	0.91	0.33
918	0.98	0.98	0.91	0.33
906 – 1 m depth	0.93	1.06	0.76	0.27
906 – 24 m depth	1.12	0.93	0.98	0.33
<i>Sediment trap samples</i>				
50 top	1.14	1.15	1.05	
50 bottom	1.08	1.19	1.30	
51 top	1.25	1.26	1.04	0.38
51 bottom				
53 top	0.98	1.10		
53 middle	1.10	1.36		
<i>Bottom sediment samples</i>				
62	1.38	0.86	0.58	0.40
58	1.20	1.13	0.73	0.36
59	1.14	1.01	0.56	0.30
60	1.46	1.11	0.98	0.48
61	1.25	1.13	0.68	0.30
52	1.22	1.10	0.76	0.31
53	1.24	0.98	0.74	0.31
906	1.26	1.04	1.00	0.38
Randle Reef	1.45	1.55	1.64	0.67
<i>Reference samples</i>				
SRM 1597 (coal tar)	1.31	1.10	1.91	0.51
Hamilton coal tar	1.29	1.02	1.81	0.49
Coke oven condensate	1.29	1.02	1.45	0.42
SRM 1649 (urban air)	1.26	0.83	0.75	0.13
SRM 1650 (diesel)	1.10	0.82	0.15	<0.1
Composite Hamilton air	1.27	0.96	0.61	0.11

^a Ratios are expressed as the relative peak areas from the GC–MS ion chromatograms.

1 m from bottom) and at a sub-surface depth (0.5-1 m) at two sites in the harbour and six sites extending up the Windermere Arm to a site in Red Hill Creek, upstream of the Hamilton sewage treatment facility outfall. Bottom sediments were collected at three sites in the harbour and at four sites in Windermere Arm. Table 1 lists the sampling sites and Fig. 1 shows their locations in the harbour.

Samples were dried and extracted with dichloromethane, then methanol. The method of extraction (Soxhlet versus ultrasonication) was dictated by sample size; we have previously shown these techniques to be equally efficient for the extraction of PAH from sediment samples ranging in weight from 0.5 to 5 g (Marvin et al.,

1992). The masses of dry sediment ranged from 2.5 to 6.8 g for centrifuge sediments to over 90 g for bottom sediments. Rapid extraction by ultrasonication is the preferred method in our laboratory but was not applicable to the large masses of the bottom sediment samples. The percentages of extracted organic material ranged from 0.5% to 4.8% of the dried sediment masses.

3.1. Analysis of polycyclic aromatic hydrocarbons

The GC-MS chromatograms of the non-polar aromatic fractions of all sample extracts were dominated by PAH. Figs. 2 and 3 depict spatial variation in total PAH content of suspended sediments and bottom sediments,

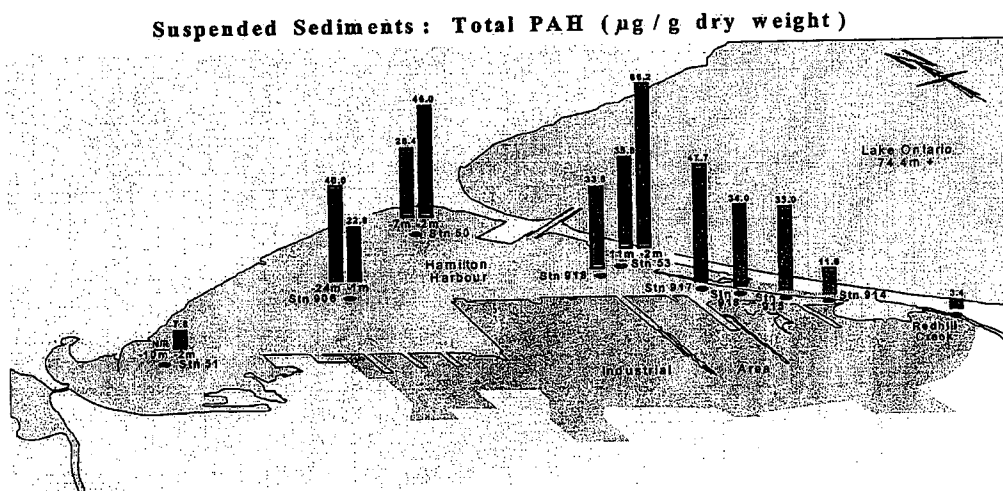


Fig. 2. Spatial variation in PAH loadings (μg PAH per g dry weight) in bottom sediment samples.

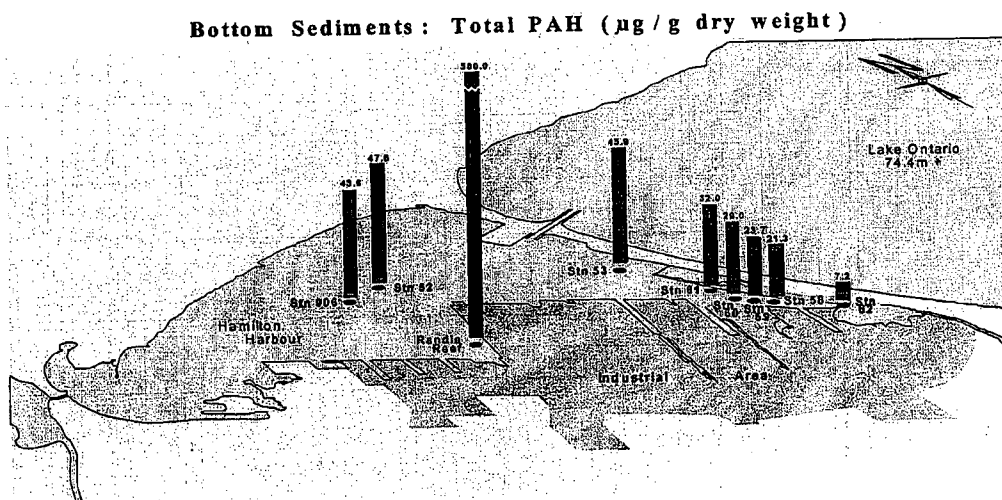


Fig. 3. Spatial variation in PAH loadings (μg PAH per g dry weight) in bottom sediment samples.

respectively. The PAH data from Randle Reef sediment were previously reported (Marvin et al., 1993), and was within the range reported by Murphy et al. (1990) for sediments from the same area. The PAH levels in sediment trap samples were within the range reported by Mayer and Nagy (1992) for extracts of centrifuge samples collected near sites sampled in our study. Centrifuge samples had total PAH contents that were generally within 20% of the station 906 bottom sediment with the exception of Redhill Creek and station 914; the latter samples exhibited roughly thirteenfold and fourfold lower PAH levels, respectively, than the station 906 bottom sediment, indicating that loadings of PAH to the harbour via Redhill Creek were quite low. The station 906-24 m centrifuge sediment sample had a PAH content (40 $\mu\text{g/g}$) within 10% of the station 906 bottom sediment (44 $\mu\text{g/g}$). Bottom sediments were sampled in close proximity to centrifuge sites and to the station 53 sediment trap sample site. Windermere Arm centrifuge sediments generally had higher PAH contents than corresponding bottom sediments.

The ratios of selected PAH, e.g., fluoranthene:pyrene, indeno[1,2,3-cd]pyrene: benzo[ghi]perylene, benzo[a]pyrene:benzo[e]pyrene and perylene:benzo[e]pyrene, were calculated for all source and harbour samples analysed in this study (Table 1). Canton and Grimalt (1992) reported that the ratios of fluoranthene:pyrene and indeno[1,2,3-cd]pyrene:benzo[ghi]perylene could be used

as indicators to differentiate PAH from coal tar and mobile emissions. However, we found that the fluoranthene:pyrene and indeno[1,2,3-cd]pyrene:benzo[ghi]perylene ratios for all source and harbour samples were similar; these ratios do not appear to be useful discriminators in the present work. We observed that the benzo[a]pyrene:benzo[e]pyrene and perylene:benzo[e]pyrene ratios in source samples related to the manufacturing of steel (coal tar and coke oven condensate) were much greater than the corresponding ratios in source samples related to mobile combustion sources. With the exception of coal tar-contaminated sediment from Randle Reef, benzo[a]pyrene/benzo[e]pyrene ratios for harbour samples appeared to approximate those of mobile combustion source samples while perylene:benzo[e]pyrene ratios were generally intermediate to values for steel industry-related source samples and mobile combustion source samples. None of these PAH ratios (or other PAH ratios we explored) showed a significant differentiation to allow us to distinguish between these two source types.

3.2. Analysis of thia-arenes

Fig. 4 shows reconstructed ion chromatograms corresponding to molecular ions of the parent dibenzothiophene and naphthothiophene isomers (m/z 184), the monomethyl derivatives (m/z 198) and the dimethyl/

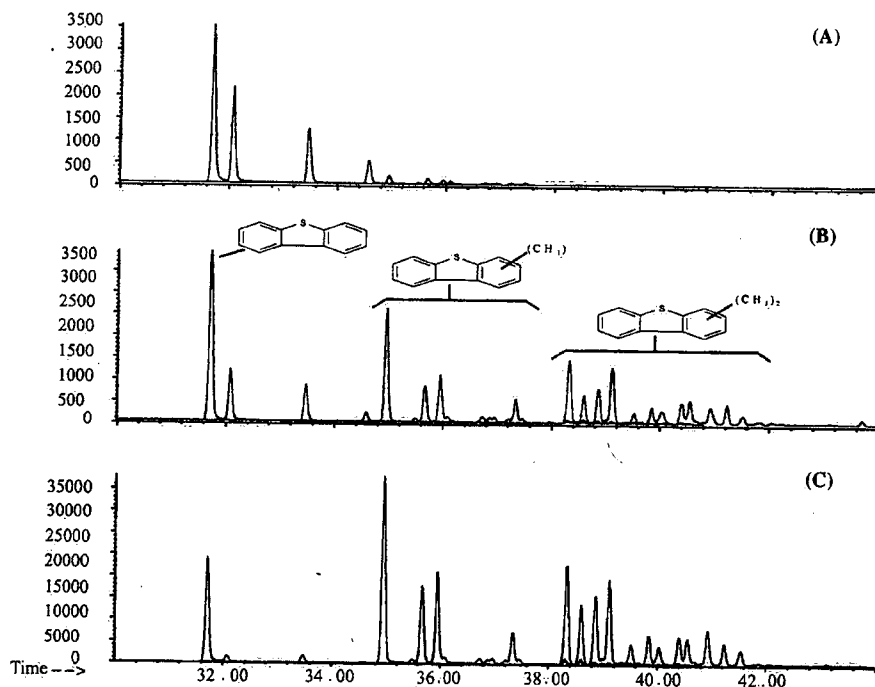


Fig. 4. GC-MS ion chromatograms of m/z 184, m/z 198 and m/z 212 for SRM 1597 (A), SRM 1649 (B) and SRM 1650 (C).

ethyl derivatives (m/z 212) for the coal tar reference standard (SRM 1597), the urban air reference standard (SRM 1649) and the diesel reference standard (SRM 1650). In the urban air reference standard (Fig. 4B) and the diesel reference standard (Fig. 4C), the ion abundances of the alkylated derivatives (m/z 198 and m/z 212 ions) greatly exceed the ion abundances of the parent compounds (m/z 184). In contrast, ion abundances of alkylated derivatives in the coal tar reference standard were very low compared to the parent thia-arenes (Fig. 4A). Thia-arene ratios for these samples were calculated by determining the area under the peaks in the m/z 198 and m/z 212 ion chromatograms and then dividing by the area under peaks in the m/z 184 ion chromatogram.

Thus, the area corresponding to the non-alkylated parent compounds (m/z 184) would have a normalized value of 1.0 for any sample. The m/z 198: m/z 184 and m/z 212: m/z 184 ratios for all samples analysed are listed in Table 2. The thia-arene ratios for the source samples showed very different values; this difference formed the basis for source discrimination. Thia-arene profiles of sediment trap samples exhibited a greater degree of alkylation than the Randle Reef sediment, indicating contamination from sources in addition to coal tar-contaminated material. The mean m/z 198: m/z 184 ratio (1.7 ± 0.76) and mean m/z 212: m/z 184 ratio (4.1 ± 1.5) for the sediment trap samples were intermediate between values reported for urban air SRM 1649 and diesel SRM

Table 2
Thia-arene ratios for source samples and Hamilton Harbour samples^a

Station number/sample	m/z 198: m/z 184	m/z 212: m/z 184	Total PAH ($\mu\text{g/g}$)
<i>Centrifuge samples</i>			
Redhill Creek	1.8	11.9	3.4
914	2.8	17.4	11.6
915	0.76	2.3	35.0
916	1.1	3.8	34.0
917	1.9	6.6	47.7
918	2.9	10.5	33.8
906 – 1 m depth	1.5	5.7	22.9
906 – 24 m depth	0.70	1.7	40.0
Mean	1.9 ± 0.9	8.8 ± 5.6	
<i>Sediment trap samples</i>			
50 top	1.1	2.5	46.0
50 bottom	1.0	2.8	28.4
51 top	3.0	5.6	7.6
51 bottom	1.7	5.0	
53 top	1.2	3.0	66.2
53 middle	2.0	5.8	35.8
Mean	1.7 ± 0.76	4.1 ± 1.5	
<i>Bottom sediment samples</i>			
62	0.87	2.1	7.2
58	0.74	1.9	21.3
59	0.78	1.3	23.7
60	1.2	2.5	29.0
61	1.2	3.1	32.0
52	0.50	1.0	47.6
53	0.68	1.3	45.9
906	1.3	3.6	43.6
Randle Reef	0.25	0.37	483
Mean	0.9 ± 0.3	2.1 ± 0.9	
<i>Reference samples</i>			
SRM 1597 (coal tar)	0.12	0.03	
Hamilton coal tar	0.11	0.03	
Coke oven condensate	0.16	0.04	
SRM 1649 (urban air)	1.5	2.7	
SRM 1650 (diesel)	2.9	4.2	
Composite Hamilton air	0.86	1.9	

^a The ratios are expressed as the areas under the m/z 198 ion peaks (monomethyl derivatives) and m/z 212 ion peaks (dimethyl and ethyl derivatives) relative to the m/z 184 ion peaks (parent thia-arene compounds).

1650 (1.5/2.9 and 2.7/4.2, respectively, Table 2); these data indicate that urban air and diesel inputs through direct deposition, or via runoff from the watershed, contributed to the flux of contaminants entering the water column in Hamilton Harbour. Conversely, the Randle Reef sediment exhibited only a slightly greater level of alkylation than the coal tar reference sample (SRM 1597) and Hamilton coal tar, indicating that PAH contamination in the area east of Randle Reef was due primarily to coal tar.

Thia-arene profiles obtained from Windermere Arm centrifuge sediment samples (stations 914–918) were generally characterized by high m/z 212: m/z 184 ratios (Fig. 5). The mean m/z 198: m/z 184 ratio (1.9 ± 0.9) was intermediate between urban air SRM 1649 and diesel SRM 1650 (Table 2) while the mean m/z 212: m/z 184 ratio (8.8 ± 5.6) exceeded the ratios of any of the reference samples. The SRM 1650 diesel reference sample was derived from a single engine using a single diesel fuel; we are currently investigating the variability of thia-arene profiles between diesel engine sources to produce thia-arene profile information potentially more representative of diesel emissions in urban centres. We have also observed m/z 212: m/z 184 ratios in the range of 7.5–8.5 for some 24-h air particulate samples collected adjacent to a major highway in southern Ontario (data not shown). We believe that the primary source responsible for the high m/z 212: m/z 184 ratios is diesel emissions. Stations 915 and 916 exhibited lower thia-arene ratios than other centrifuge samples from Windermere Arm which are possibly due to coal tar-

contaminated material entering Windermere Arm from a source located near these sites. It is possible that the Windermere Arm and Redhill Creek centrifuge samples are not fully representative of material entering the harbour via the watershed as these samples were “snapshots” of material present in the water column at the time of sampling and were not time-integrated as in the case of the sediment trap and bottom sediment samples. However, these data implicated Redhill Creek and Windermere Arm as vectors of contamination into Hamilton Harbour.

Thia-arene profiles of bottom sediments in both the open harbour and Windermere Arm were characterized by generally lower degrees of alkylation than suspended sediments (Fig. 6, Table 2). There appeared to be no differences in thia-arene profiles of Windermere Arm bottom sediments compared to open-harbour bottom sediments. Mean m/z 198: m/z 184 and m/z 212: m/z 184 ratios for bottom sediments (with the exception of the Randle Reef sediment sample) were 0.9 ± 0.3 and 2.1 ± 0.9 , respectively. Mean thia-arene ratios of bottom sediments were similar to the ratios determined for a composite Hamilton air particulate sample (prepared from 35 24-h air particulate filters). We believe that the composite Hamilton air particulate sample represents roughly equal contributions from the two primary sources of PAC contamination in Hamilton, diesel (vehicle) emissions and coke oven emissions. The thia-arene profiles of Hamilton coke oven condensate and the two coal tar samples were virtually indistinguishable. These data are consistent with the interpretation that two

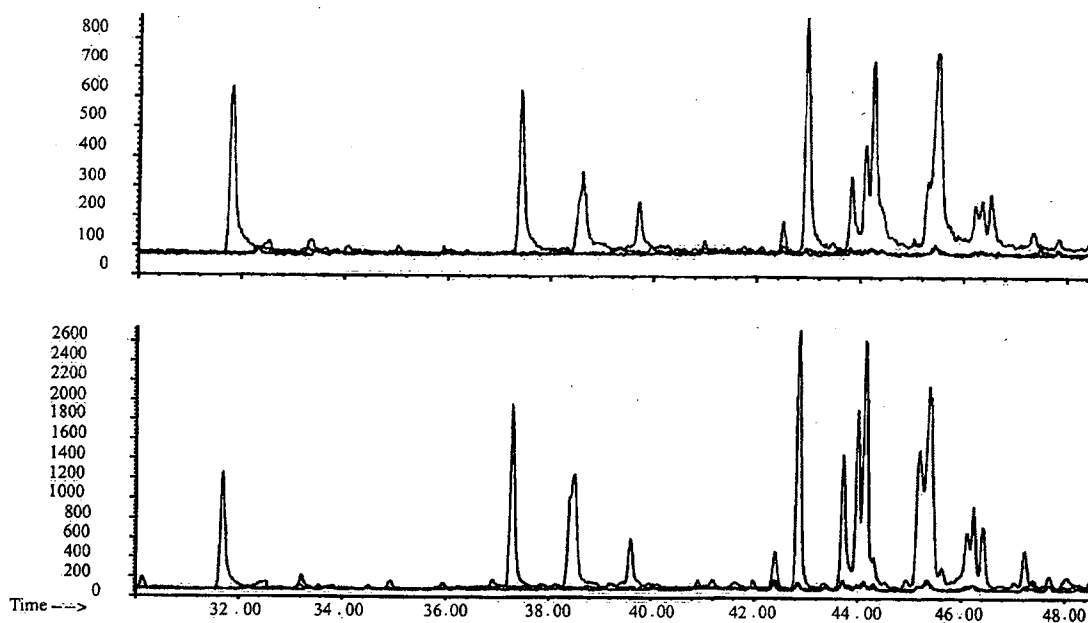


Fig. 5. GC-MS ion chromatograms of thia-arenes for selected Windermere Arm centrifuged sediment samples.

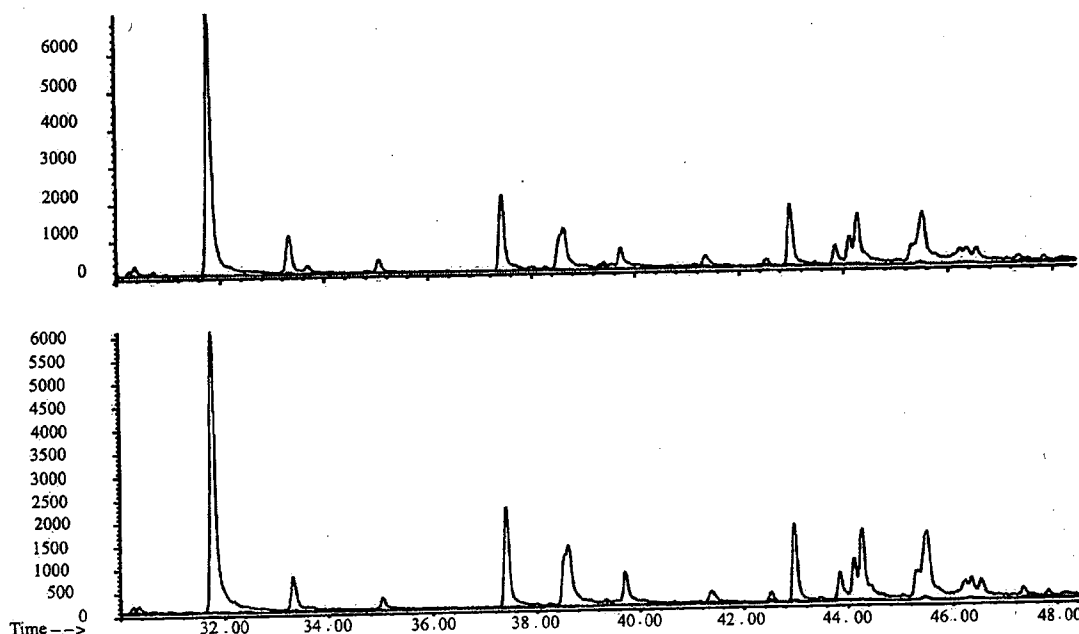


Fig. 6. GC-MS ion chromatograms of thia-arenes from selected Hamilton Harbour bottom sediment samples.

primary sources of contamination in Hamilton Harbour sediments are also the primary sources of contamination in Hamilton air particulates, i.e., vehicle emissions and contamination arising from the manufacturing of steel (McCarthy et al., 1996).

4. Conclusions

Thia-arene profiles of reference and sediment samples showed that harbour contamination could be distinguished as arising from two primary sources of contamination: mobile emissions and emissions related to steel manufacturing. Chemical profiling and source apportionment approaches using PAH ratios were much less conclusive than approaches using thia-arene ratios.

The Randle Reef sediment had the highest level of PAH contamination and had a thia-arene ratio very similar to those obtained from coal tars and coke oven condensate, indicating PAH contamination in this sample arose from coal tar. Bottom sediments and suspended sediments collected elsewhere in the harbour had thia-arene ratios similar to that determined for a reference urban dust sample (SRM 1649) and a composite Hamilton air particulate sample. While some Windermere Arm centrifuge sediment samples had thia-arene ratios that exceeded those of the reference samples, we speculate that the sources of these high ratios are diesel emissions. The thia-arene profiles of harbour and Windermere Arm bottom sediments were characterized by

lower degrees of alkylation than suspended sediments. The ratios for bottom sediments were very similar to the ratios calculated for a composite Hamilton air particulate sample. These thia-arene data are consistent with the interpretation that the two primary sources of contamination in Hamilton Harbour sediments are mobile combustion emissions and contamination arising from the manufacturing of steel. Thia-arene ratios have been shown to be very useful in distinguishing between coal-based contamination and diesel-based contamination in environmental samples.

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