

COAL TAR CONTAMINATION NEAR RANDLE REEF, HAMILTON HARBOUR

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Management Perspective

Bioassay studies discovered an area of severe sediment toxicity between Randle Reef, the Sherman Street combined sewer, and the southwest and northwest Stelco outfall pipes. Samples were found with more than 1000 µg/g of the 16 priority pollutant polynuclear aromatic hydrocarbons (PAHs). These sediments were acutely toxic to zooplankton, bacteria, rainbow trout, and mayfly nymphs. The acute toxicity of the sediments of Hamilton Harbour is significantly correlated to the PAH concentration.

To accurately determine the extent and nature of toxicity, a detailed study of sediment chemistry and toxicity was conducted with 81 sediment cores. A simple spectrophotometric method was developed to measure the PAH concentration of over 2000 samples. Approximately 40 samples were processed with gas chromatography/mass spectrometry for calibration.

Approximately 70,000 m³ of sediments between Randle Reef and the southwest Stelco outfall pipe contain more than 200 µg/g of PAHs. This PAH concentration is 4-50 times higher than reported apparent threshold effect concentrations, i.e., the lowest acutely toxic concentration of PAHs. In our bioassays, the 200 µg/g contour line is approximately the concentration of PAHs resulting in the mean death of 50% of the animals in three bioassays.

The most common concern with PAHs is their potential to induce cancer in wildlife at concentrations below the acute toxicity concentration. Comparisons of our data to several other sites with PAHs, and one Department of Fisheries and Oceans study in Hamilton Harbour, strongly indicated that these highly contaminated sediments have the potential to induce tumours in fish. A main RAP/Stakeholder goal for Hamilton Harbour is a healthy fishery. This goal can not be achieved without removal of these carcinogenic substances.

These contaminated sediments are in shallow water where boats and barges resuspend them; moreover, the Hamilton Harbour Commission would like to dredge much of this area to improve access to pier 15.

Perspectives de gestion

Des essais biologiques ont permis de déceler une zone de forte contamination des sédiments entre le Randle Reef, l'émissaire de l'égout unitaire de Sherman Street et les émissaires sud-ouest et nord-ouest de la Stelco. Certains échantillons renfermaient plus de 1 000 µg/g de 16 hydrocarbures aromatiques polynucléaires (HAP), polluants prioritaires. Ces sédiments avaient une toxité aiguë pour le zooplancton, les bactéries, la truite arc-en-ciel et les nymphes d'éphémères. Il existe une corrélation significative entre la toxicité aiguë des sédiments du port de Hamilton et la concentration d'HAP.

Pour déterminer avec exactitude l'étendue et la nature de la toxicité, une étude détaillée de la chimie et de la toxicité des sédiments a été entreprise grâce au prélèvement de 81 carottes de sédiments. Une simple méthode spectrophotométrique a été mise au point pour mesurer la concentration d'HAP dans plus de 2 000 échantillons. Environ 40 échantillons ont été analysés par chromatographie en phase gazeuse et spectrométrie de masse à des fins d'étalonnage.

Environ 70 000 m³ de sédiments entre le Randle Reef et l'émissaire sud-ouest de la Stelco renfermaient plus de 200 µg/g d'HAP. Cette dernière valeur est de 4 à 50 fois plus élevée que les concentrations seuils entraînant des effets apparents,

autrement dit les concentrations les plus faibles d'HAP présentant une toxicité aigue. Dans nos essais biologiques, la ligne de contour de 200 µg/g correspond à peu près à la concentration d'HAP qui tuait 50 % des animaux dans les trois essais.

Le plus grand danger des HAP est leur pouvoir d'induire le cancer chez des espèces fauniques à des concentrations inférieures à celle correspondant à la toxicité aigue. La comparaison de nos données avec celles de plusieurs autres endroits contaminés par les HAP, ainsi qu'une étude de PCC portant sur le port de Hamilton montrent de façon à peu près certaine que ces sédiments fortement contaminés entraînent l'apparition de tumeurs chez les poissons. Dans le cadre du Plan de mesures correctives, une pêcherie en bonne santé représente un objectif et un enjeu majeurs pour le port de Hamilton. Cet objectif ne pourra être atteint que si on élimine les substances cancérigènes.

Ces sédiments contaminés se trouvent dans des eaux peu profondes, où les bateaux et les barges les remettent en suspension; de plus, la "Hamilton Harbour Commission" a l'intention de draguer une grande partie de ce secteur pour améliorer l'accès au quai 15.

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Abstract

To support the remedial action plan of Hamilton Harbour, and to determine the extent of coal tar contamination in a toxic area of the harbour, 81 sediment cores were collected for chemical and biological study. Approximately 55,500 m³ of sediments bounded by Randle Reef, pier 15, and Stelco are contaminated with coal tar. The coal distribution tar is variable but the concentrations are near the Stelco outfall pipes and the Hamilton-Wentworth combined sewer outfall pipe. The total concentration of the 16 polynuclear aromatic hydrocarbons (PAHs) in 48,300 m³ of near-surface sediments exceeds 200 µg/g. The concentration of PAHs that results in the death of 50% of Daphnia magna and Hexagenia is less than 244 μ g/g and 329 μ g/g, respectively. Sediments containing more than 89 μ g/g of PAHs suppress at least half of the photoactivity of Photobacterium phosphoreum. The acute toxicity of the sediments of all of Hamilton Harbour is significantly correlated to the PAH concentration.

Resumé

Pour appuyer le plan de mesures correctives dans le port de Hamilton et pour déterminer l'étendue de la contamination par le goudron de houille dans une zone toxique du port, 81 carottes de sédiments ont été prélevées pour des études chimiques et biologiques. Un volume d'environ 55 500 m³ de sédiments, limité par le Randle Reef, le quai 15 et Stelco, est contaminé par le goudron de houille. La répartition de ce dernier est variable. les concentrations les plus fortes se situant près de l'émissaire de la Stelco et de celui de l'égout unitaire de Hamilton-Wentworth. La concentration totale de 16 hydrocarbures aromatiques polynucléaires (HAP) dans un volume de 48 300 m³ de sédiments près de la surface dépasse 200 µg/g. Les concentrations d'HAP qui entraînent la mort de 50 % de Daphnia magna et d'Hexagenia sont respectivement inférieures à 244 et 329 µg/g. Des sédiments renfermant plus de 89 µg/g d'HAP réduisent d'au moins la moitié la photoactivité de Photobacterium phosphoreum. Il existe une corrélation significative entre la toxicité aigue des sédiments de l'ensemble du port de Hamilton et la concentration d'HAP.

1 INTRODUCTION

Hamilton Harbour services a heavily industrialized region at the western end of Lake Ontario (43°17'N, 79°50'W) (Harlow and The harbour receives the Hodson 1988, Metcalfe et al. 1988). treated wastes of 500,000 people and many factories, including Canada's two largest steel mills. Studies by Nagy (1973) found that the sediment in the eastern portion of the harbour contained up to 1 μ q/q of oil and grease. The Ontario Ministry of the Environment (MOE) studied the polynuclear aromatic hydrocarbon (PAH) composition of six sediment samples collected from different sites of the harbour and determined that the highest concentrations were near Randle Reef (Fig. 1, Ontario Ministry of the Environment Metcalfe et al. (1988) found that a sediment sample from Randle Reef containing approximately 40 µg/g of PAHs was mutagenic in the Ames test and extracts could induce hepatocellular carcinomas in rainbow trout.

The intent of this study was to map the spatial distribution of PAHs in Hamilton Harbour, to establish a relationship between acute toxicity (LC₅₀) and PAHs in three bioassays (<u>Daphnia magna</u>, <u>Hexagenia</u>, and <u>Photobacterium</u>), and to consider the effects of our studies on remedial actions. To accomplish these objectives we used a simplification of Riggin et al.'s (1982) ultraviolet (UV) spectrophotometric PAH analysis and standardized the method with gas chromatography/mass spectrometry and bioassay analyses. The harbour west of Stelco, north of pier 15, and east of Randle Reef was studied in the most detail because

preliminary studies of this area found severely toxic sediment contaminated with coal tar. Assays for other regions of the harbour are included to aid interpretation.

2 METHODS

2.1 Core Collection

On April 11, 1989, a total of 46 sediment cores were collected from Hamilton Harbour in the area north of pier 15 and west of Stelco (Fig. 1). On July 11, 1989, another 35 sediment cores were collected adjacent to the first 46 cores. The launch CSL Shark was used to collect the cores. The locations of the sample sites were measured with a T2 theodolite with a DI3000 distomat; the instrument is accurate to 1 mm but ship movement decreases the accuracy. A Techops corer with an additional 20 kg weight was used to collect sediment cores (Mawhinney 1987). sampling sites were approximately 90 m apart (Fig. 2). The exact locations of these sites from the survey points are shown in Table 1. The sediment cores were divided into 2 cm sections with a hydraulic extruder; observations of sediment appearance, texture, and odour were made. At various times in 1988, 12 sediment samples were collected with an Ekman dredge sampler. These sites, labelled M1-M12 on Fig. 3 were located by sighting landmarks and relative to the coring sites, were located less accurately $(\pm 10\text{m})$.

2.2 Chemical Analysis

To estimate the organic content of the sediments, loss on ignition (LOI) was determined for 28 samples southeast of Randle Reef and for another 18 sediment samples elsewhere in the harbour. Freeze-dried sediment samples were weighed before and after combustion at 490°C.

Metal concentrations of sediment samples were determined by extracting freeze-dried samples (0.5 g) with aqua regia (25 mL of 3:1 hydrochloric acid, nitric acid). After boiling to near dryness, an additional 25 mL of aqua regia was added to the samples and again boiled to near dryness. Ten mL of 1:1 HNO₃:H₂O was added to the samples and after 30 min the samples were filtered through #44 Whatman filters. The extracts were analyzed by atomic absorption (Environment Canada 1979). Metal concentrations were also analyzed in sediment samples extracted with distilled water for 16 h.

2.2.1 Polynuclear Aromatic Hydrocarbon (PAH) Analysis Gas Chromatographic/Mass Spectrographic (GC/MS) Procedure

Fifty-two, 1-5 g samples of homogenized, freeze-dried sediment were blended with anhydrous sodium sulphate and soxhlet extracted with dichloromethane. Subsamples of the concentrated extracts were evaporated to near dryness and redissolved in hexane:toluene (2:1). The resulting solutions were analyzed for 16 selected PAHs by selected GC/MS under the conditions described below.

GC: Hewlett-Packard model 5890

30 m fused silica capillary column, DB-5

Splitless injection

Injection temperature 250°C, detector temperature 280°C

Program: 50°C to 149°C at 10°C/min, 2°C to 280°C, held at 280°C for 10 min

MS: Hewlett-Packard series 5970 mass detector

Electron ionization 70 eV

Select ion monitoring (SIM) mode

2.2.2 Spectrophotometric PAH Analysis

Approximately 800 freeze-dried sediment samples (100 mg) were placed into 20-mL screw cap vials (lined with ashed aluminum foil) with 5 mL of iso-octane. Samples were sonicated for 30 seconds and placed on a shaker at 250 rpm for 17 h. Samples were then decanted into centrifuge tubes and centrifuged at setting 5 on a IEC centrifuge for 5 min (1200 g). Very yellow solutions were diluted with iso-octane and pale yellow extracts were not diluted for analysis. Absorption was measured at the wavelengths 210, 220, 230, 240, 250, 260, 280, and 300 nm using a base line correction on a Varian DMS UV/visible spectrophotometer. Total UV absorption was determined by integrating the area under the curve from 210 to 300 nm. To determine if the UV/PAH analysis could be used to monitor dredging, a subset of 27 samples were processed as above, with the

exception that 1.0 mL of fresh wet sediment was shaken with isooctane for 1 min.

2.3 Bioassays

All <u>Daphnia magna</u>, <u>Hexagenia</u> and <u>Photobacterium</u> bioassays were conducted in the National Water Research Institute (NWRI) laboratories. To calculate an LC_{50} (concentration in which 50% died) or EC_{50} (concentration effecting 50% of photoactivity), a dilution series was made in each bioassay by mixing varying amounts of one large sediment sample from Station M2* with relatively clean sediment from Station 80 (Fig. 4). Sediments from Station 80 were used as a control in all bioassays.

2.3.1 Photobacterium Bioassay

A sediment contact bioassay was developed using <u>Photobacterium phosphoreum</u>. Sediments were shaken with the bacteria, the sediments were centrifuged from the bacteria, and the light output from the bacteria was measured with a Beckman Microtox photometer. An internal standard of ¹⁴C-labelled bacteria was used to determine the proportion of bacteria removed by centrifugation. The photoactivity (light emission) of the <u>Photobacterium</u> was compared in each set of analyses to that of <u>Photobacterium</u> in sediments from Station 80, a relatively uncontaminated site in the northwest corner of Hamilton Harbour. Full details of this new method can be found in Brouwer et al. (1990).

Sediment dilutions were also used for the <u>Photobacterium</u> bioassay with sediments from five stations (A1, B2, C4, D6, and E8) at depths of 0-1, 2-4, and 10-12 cm.

2.3.2 Daphnia Bioassay

Within two weeks of collection all samples were extracted with equal volumes of distilled water on an end-over-end shaker for 16 h. After extraction, the sediment extracts were centrifuged for 20 min at 1000 g. We chose to follow the original elutriate test guideline (Cheam et al. 1976) and centrifuge, not filter, the extracts; filtration can remove colloidal material that would not settle from disrupted sediment and that may contain toxic metallic or organic contaminants. The extracts were then diluted 1:5 with dechlorinated Burlington City water. Prior to all experiments, the sediment extracts were oxygenated by bubbling with purified air for 16 h.

2.3.3 <u>Hexagenia Bioassay</u>

Hexagenia (mayflies) eggs were obtained from Windsor University (Elizabeth Hanes) after collection at Riverside Drive at Lauzon in Windsor. The eggs were 65% Hexagenia limbata and 35% Hexagenia rigida. Mayfly nymphs were raised at 20°C in uncontaminated sediment from Honey Harbour, Georgian Bay, Lake Huron. Sets of ten mayfly nymphs were exposed for 21 days to the control sediment from Honey Harbour or to dilutions of sediments

collected from Station M2* with a Ponar dredge sampler. The nymphs were 123 days old at the start of the 21-day bioassays.

Repetitions were performed in triplicate for the mayfly bioassays. Wide mouth 2-L jars were filled with 3 cm of sediment (300 cm³) and 1200 mL of dechlorinated Burlington City water to obtain a water:sediment ratio of 4:1 (v/v). Sediment and water mixtures were allowed to settle for 24 h. Aeration was provided 1 h prior to addition of the test organisms and continued throughout the duration of the experiment. These experiments were carried out under static conditions. Water loss was replaced with distilled water. Dissolved oxygen, pH, conductivity, and temperature were monitored routinely during the experiments. Mortality was checked at the termination of the incubations.

2.4 <u>Data Processing</u>

Lotus 123 and Statgraphics were used for calculations. Corel Draw was used to produce most maps.

3. RESULTS

3.1 Physical Observations

The appearance and odour of sediments varied greatly (Fig. 5) and some sediments had distinctive colours and chemical odours. There were three pronounced zones of shiny black sediment. Near the southeast outfall pipe of Stelco and the outlet of the Sherman Street Creek the underlying sediment was continuously jet black.

Further north along the Stelco property near the northeast outfall pipe of Stelco was another similar but smaller deposit of jet black sediment. The sediments from both of these areas were viscous and balls of coal tar were obvious after freeze-drying. Further north along the Stelco dock was the third deposit of visually contaminated sediment. This deposit was also black, but it was watery and coal tar was not obvious after freeze-drying. The sediment of this most northern site had less naphthalene odour and more oil smell. Away from the three sites, the sediments were streaked with the black tar/oil.

The depth of the visual contamination varied greatly. The deepest deposits of approximately 52 cm were found near the outfall pipes of Stelco. About 40 cm of contaminated sediments were found in the most northern and southern hotspots, including the area that was dredged in 1978 (Fig. 3). Two cores indicated that the sediments in the middle hotspot are shallow (<20 cm); however, our corer was unable to penetrate the most contaminated tarry sample (site #All). Away from the two southern hotspots the depth of contamination decreased to less than 10 cm.

The extent of the northern hotspot is not fully characterized and it appears that the northern hotspot extends into the main deep depositional basin. Unlike the southern hotspots, the sediments of the northern hotspot are in deep water.

The small loss of mass after combustion of sediment samples which varied from 6% in the deepest portions of the cores, away from the outfall pipes, to 16% near the outfall pipes indicates a

high inorganic content (Table 2). Although the bottom of some cores were clay-like, most of the samples more than 500 m away from the centre of the coal tar area were predominately sand.

The colour of the surface sediments changed with the seasons. All of the cores collected on April 11, 1989 were covered with a thin layer of light brown sediment overlying black sediments. On an earlier sampling trip in January 1989, only two of six sediment cores were covered with this light brown layer. The light brown sediments were not observed in summer. The seasonal change in the appearance of the surface sediments probably indicates that the sediments become oxidized in late winter and are reduced for most of the year. A complete record of our visual observations can be found in Appendix 1.

3.2 Distribution of PAHs

Figure 7 indicates the known spatial distribution of PAHs before the sediment cores west of Stelco were analyzed. Thirty-seven Ekman grab samples were analyzed by GC/MS to prepare the map; thus, only general trends are apparent. Most of the PAH contamination in Hamilton Harbour appears to emanate from the hotspots located north of the Sherman Street Creek and west of Stelco.

Currently, 15 samples from sediment cores from the southern hotspot have been analyzed for PAHs by GC/MS (Table 3). The surface sediments (0-2 cm) have an average of 246 μ g/g of PAHs. Near the southwest outfall pipe of Stelco the surface concentration

of PAHs is lower than the deeper sediment but further away the surface sediments appear to be more contaminated than the deeper sediments. This interpretation is consistent with the visual observations but it is based on a small data set.

Data from the loss on ignition (LOI) analysis was not accurate in predicting PAH concentrations, but the two data sets of LOI data were significantly correlated to PAH data within 95% and 90% confidence limits, respectively, for a whole harbour set and a hotspot subset. For a set of 46 samples from the whole harbour, the r value was 0.34 (y = -1.5 + 0.65 x) and for a subset of 28 southeast of Randle Reef, the r value was 0.32 (y = 6.3 + 29.7 x).

The ultraviolet absorption analysis is a good estimator of PAH concentrations and a larger data set is able to provide a more detailed interpretation than the limited number of samples processed by GC/MS analysis. The ultraviolet absorption of isooctane extracts of 52 sediments from the complete harbour is highly correlated to the PAH analysis by a GC/MS method (r = 0.81, The correlation of a subset of 16 samples immediately Fig. 8). adjacent to the Stelco property was similar (r = 0.81, Fig. 9). of the equations lines were slightly different; y = 41.5 + 33.4 x for the complete set and y = 28.6 + 37.5 xthe subset of 16 samples near Stelco.

Although either equation would be useful to predict PAH concentrations in sediment, neither equation is completely satisfactory. Based on the equations above, the minimum predicted PAH concentrations from the equations above are 29 and 42 μ g/g for

the subset and complete sets of data, respectively. The three lowest concentrations of total PAHs by GC/MS analysis were 0.9, 1, and 0.8 μ g/g. To provide the best estimate of PAH concentration from the UV data, the data from four outliers of the complete set of 52 samples were removed from the calculation. This operation improves the r value to 0.88, changes the equation of the line to $y = -6.3 + 41.3 \times 10^{-2} \, \text{m}^{-2}$ and results in a more realistic background PAH concentration of $-6 \, \mu$ g/g (Fig. 10).

The four outlier samples were all near the outfall pipes of Two of the outlier samples contained the two highest concentrations of PAHs from samples collected in 1988. samples contained more than twice as much PAHs as any other sample $(>1000 \mu g/g)$, and although their extracts highly absorbed UV light and only one was outside the 90% confidence limits, they greatly biased the x intercept. Analyses from the other two outlier samples were repeated with GC/MS and spectrophotometric analyses. Repeat analyses confirmed that one sample had a particularly low concentration of PAHs and a high UV absorption, and one sample had a high concentration of PAHs and low UV absorption. The latter sample (Station A15) had only small streaks of black. Station A15 is near another deviating, but not excluded data point, M6. The UV (111 μg/g) gave a poor prediction of PAH analysis of M6 concentration as determined by GC/MS (276 μ g/g). Station A15 is near and M6 is in the black sediment near the northwest corner of the Stelco dock. The UV analysis may not be a good predictor of the PAH concentrations in the northern Stelco hotspot.

With the exception of one important constraint, the UV absorption analysis has excellent utility in mapping the distribution of PAHs near the southwest and northwest Stelco outfall pipes. Approximately 2% of the samples cannot be relied upon to predict PAH concentration, and another 10% of the points could have a considerable error (±50%) in predicting PAH concentration. Four outliers are near outfall pipes but further analyses would be required interpret why outliers are grouped. The bioassay analyses indicate that the PAH concentration is not a perfect indicator of sediment toxicity. No one assay in this study is a perfect quide in assaying sediment contamination.

3.2.1 Mapping

Although UV absorption analysis enables detailed maps of the areal distribution of PAHs to be prepared (Figs. 11-14), the distribution of PAHs within the hotspot is patchy. For example, the most contaminated core at the 0-2 cm sample depth is not necessarily the most contaminated core at the 2-4 cm depth. Visual observations of over 3000 sediment samples confirms that the distribution of coal tar is patchy.

The variability of the PAH distribution can be reduced in these three ways:

1) plot the spatial distribution of the maximum observed concentration of PAHs in the surface samples (0-2, 2-4, 4-6,and 10-12 cm) (Fig. 15);

- 2) integrate the concentration of total PAHs and plot the areal distribution of PAHs (Fig. 16, Appendix 2); and
- 3) calculate and plot the mean concentration of total PAHs (Fig. 17, Appendix 2).

Most of the PAHs were found near the southwest and northwest Stelco outfall pipes. The distribution of PAHs around the northwest Stelco pipe suggests that Stelco was the source of these PAHs and that currents moved the PAHs south and southwest. The distribution of PAHs near the southwest Stelco pipe is more complicated. Although the highest concentration of PAHs is near the Stelco outfall pipe, the worst of the PAH contamination is deep (35-45 cm) and probably old (Fig. 18). Also, the depth of the maximum concentration of PAHs is closer to the surface south of this outfall pipe (Fig. 18). Although the currents may have moved the PAHs from the southwest Stelco outfall pipe south, the data cannot dispute that another source of PAHs might have existed in the sewershed of the Sherman Street combined sewer.

The maps generated by the UV method of measuring PAHs can be used to calculate the volume of contaminated sediments (Table 4). Calculations using only the surface (0-2 cm) concentration of PAHs exceeding 200 μ g/g indicate the volume of contaminated sediments is as low as 30,000 m³. This cleanup standard would minimize the effect of PAHs on the water column but it would not provide optimal protection for benthic invertebrates and fish. If sediments containing greater than 200 μ g/g of PAHs in the surface 0-12 cm of

sediment were removed, wildlife would be better protected but the volume of contaminated sediments increases to 55,000 m³.

Note that these volumes are not necessarily the volumes of sediment that would be removed in an actual cleanup. The efficiency of dredging would be greatest where the contaminated sediments are deepest (near outfall pipes) and least at the edge of the hotspot (thin layer of contamination). If only the worst sediments were dredged with simple equipment, the volume of sediment dredged would likely increase by 50%, but if the edges of the hotspot were also dredged, the volumes of sediment removed could double or triple. The use of precision dredging equipment would reduce the extent of overdredging required to remove the contaminated sediments.

3.2.2 Rapid UV Analysis of Sediments

The 1-min UV absorption analysis of fresh sediments was significantly correlated to the 17-h extraction protocol at the 99% confidence limits. However, the r value of 0.48 reflects that there were many outliers (Fig. 19). Presumably, the varying water content of the sediments created some of the variability. Rather than use the 1-min UV absorption, a dredging operation would be guided as well by visual observations of the sediments, and better by predetermining the toxic concentration of PAHs in laboratory analyses.

3.3 Metal Concentrations

The concentrations of copper, lead, and zinc are very high in the sediments nearest the southwest Stelco outfall pipe (Table 5). Although the metals are likely less toxic than the coal tar, any remedial action must consider the metal content of the sediments. For example, if the most contaminated sediments are combusted, the gases and ashes must be treated. Also, if a tank farm or other microbial treatment is utilized, the metals may restrict the microbial degradation of organic contaminants.

3.4 Bioassays

3.4.1 Photobacterium

The correlation between the PAH concentration and the toxicity of the sediment samples from all of the harbour (n = 48) was statistically significant (r = 0.37) within the 99% confidence limits (Fig. 20). However, several outliers weakened the correlation. Station 14, which was an outlier in the PAH/UV analysis, is again an outlier in the PAH/Photobacterium analysis. Surface samples from cores B-2 and C-4 also had high PAH concentrations and little toxicity. It is interesting that Station 14 had little water soluble iron or manganese (Table 5) and the surface of B-2 and C-4 were light brown (no metal data). These three outliers were likely oxidized.

Another set of data indicates that toxicity is a function of the oxygen concentration. The EC_{50} values for <u>Photobacterium</u> were

lower at positions deeper in the sediment cores (Table 6), and it is likely that oxygen concentration influenced this trend.

Several outliers that were toxic with low PAH concentrations were also found. Some of these outliers had low concentrations of metals thus the cause of the toxicity is not clear. Moreover, some of these sites were also toxic to Daphnia. All but one of these outliers had one thing in common; they were near outfall pipes. removing all sampling stations that were near outfall pipes, the correlation between PAH concentration and toxicity to Photobacterium becomes 0.85 (n = 19, Fig. 21). This is a verv strong correlation and indicates that PAHs or closely associated compounds are responsible for much of the acute toxicity of Hamilton Harbour sediments.

Similar analysis with the concentration of zinc extracted from the sediments with water, and toxicity of the sediments to $\frac{Photobacterium}{Photobacterium}$ led to analogous but weaker correlations. For the complete data set (n = 30), the correlation was weak (r = 0.33) and significant only at the 90% confidence limits. For the subset of sediments more than 100 m from outfall pipes, the r value is 0.55 (n = 16) and it is significant at the 95% confidence limits.

The EC $_{50}$ for the sediment dilution study with sediment from Station M2* was approximately 71 μ g/g of PAHs (Fig. 22). This calculation is derived from the observation that the concentration of diluted sediment suppressing 50% of the light output of Photobacterium was 86% uncontaminated sediment and 14% of the sediment containing 507 μ g/g of PAHs. The sample used for the

dilution assay was not one of the outlier samples but it was near an outfall pipe.

The mean EC_{50} for all <u>Photobacterium</u> analyses was 89 µg/g. Note that the variability in the EC_{50} for the <u>Photobacterium</u> bioassays for 15 samples was large (Table 6). In general, the surface samples were less toxic than the deeper samples and the EC_{50} values were lower in the deeper sediments (Figs. 23-27). It is believed that the deeper sediments are more toxic because of greater reducing conditions which increase the availability of metals.

3.4.2 <u>Daphnia Bioassay</u>

The elutriates in the dilution series with sediments from Station M2* were toxic to <u>Daphnia magna</u> (Fig. 22). The LC₅₀ was approximately 254 μ g/g of PAHs. In an earlier evaluation of a sediment from M1, all of the <u>Daphnia</u> died in an elutriate from sediment containing 231 μ g/g of PAHs. Thus, the mean LC₅₀ must be less than 244 μ g/g of total PAHs.

3.4.3 <u>Hexagenia Bioassay</u>

As with the <u>Daphnia</u> bioassay, the diluted sediments from Station M2* were toxic to <u>Hexagenia</u> (Fig. 28). The LC_{50} was approximately 456 μ g/g of PAHs. In an earlier 21-d bioassay with sediment from Station M1 containing 231 μ g/g of PAHs, all of the <u>Hexagenia</u> were killed. Thus, the mean LC_{50} must be less than 329 μ g/g.

4 DISCUSSION

4.1 <u>Comparison of Hamilton Harbour Hotspot to Other Sites</u> Contaminated with PAHs and Impact of PAHs on Biota

The concentration of PAHs in the Hamilton Harbour hotspot is higher than those reported by Fabacher et al. (1988) for several sites on the Great Lakes and is higher than the PAH concentration reported by Shiaris and Jambard-Sweet (1986) for contaminated estuaries of the world. Recent publications indicate that the PAH contamination of the Hamilton Harbour hotspot is similar to that of the Grand Calumet River, Indiana (Simmers et al. 1989), Eagle Harbor, Washington (Swartz et al. 1989), Thunder Bay, Lake Superior (Lake Sediment Studies - Thunder Bay 1988), and Elizabeth River, Norvolk, VA (Hargis et al. 1984). At least two of these contaminated sites, Eagle Harbor and Thunder Bay, are smaller than the Hamilton Harbour hotspot.

PAHs in the sediments of the Elizabeth River are acutely lethal to fish (Hargis et al. 1984) and the fish also suffer from lesions and erosion of tissue. The sediments of Eagle Harbor and other areas of Puget Sound with lower concentrations of PAHs than the Hamilton Harbour hotspot have been linked to the induction of hepatic lesions in the bottom fish English Sole (Myers et al. 1987). Induction of fish neoplasms from sediments in the Black River, Ohio, was observed by Fabacher et al. (1988); these sediments contained a lower concentration of PAHs than the hotspot of Hamilton Harbour. Induction of neoplastic and preneoplastic lesions has also been linked to PAH concentrations in the sediments

these sediments contain Harbour and of Vancouver concentrations of PAHs (maximum of 300 $\mu g/g$) than the Hamilton Harbour hotspot (Goyette et al. 1988, Brand and Goyette 1989, Burrard Inlet Environmental Improvements 1990). The work of Metcalfe et al. (1988) with a sample outside of the Hamilton Harbour hotspot (near Randle Reef) with 40 $\mu g/g$ of total PAHs indicated that neoplasms in fish in Hamilton Harbour are likely caused by PAHs. It is highly probable that the sediments in the hotspot of Hamilton Harbour with 200-1200 µg/g of PAHs are producing tumours in any bottom fish able to live there.

Swartz et al. (1989) found in dilution experiments with a marine amphipod Rhepoxynius abronius that the LC50 for total PAHs was 666 µg/g. This measurement was done with wet sediment and must translate to less than 200 μ g/g of total PAHs for dry sediment. This value is lower than we measured for Hexagenia (<329 μ g/g), close to what we observed with Daphnia ($<244 \mu g/g$), and is higher than we found with Photobacterium (89 μ g/g). Both Athey et al. (1989) and Newstead and Giesy (1987) found that Daphnia magna and Microtox bioassays are more sensitive than several other bioassays. sensitive assav. The Microtox assay was the most Photobacterium/Microtox bioassays may seem esoteric but they are less sensitive to PAHs than an acute toxicity bioassays with oyster larvae (Barrick et al. 1988) and there are probably juvenile fresh water organisms with at least a similar sensitivity to PAHs.

Studies in the Puget Sound area of Washington determined that the total PAH concentrations in sediments greater than 3.8 $\mu g/g$

impair biota (Chapman 1986, Chapman 1989). At Kettle Creek, Port Stanley, Ontario, the gradient of total PAH contamination was steep but provides similar evidence (Griffith 1988). A sample with $37~\mu g/g$ was not toxic, but the next most contaminated sediment with $80~\mu g/g$ suppressed the diversity and intensity of benthic invertebrates.

4.2 Choosing a Cleanup Standard for PAHs

Choosing a concentration of PAHs to guide a dredging project is difficult. Well established guidelines for PAH cleanup do not exist. A large portion of Hamilton Harbour sediments exceeds the IJC objective that sediments not have more than 1 μ g/g of the PAH benzo (a) pyrene.

Recently the state of Washington released recommendations for sediment cleanup that includes PAHs. Their protocol gives standards for individual PAHs, i.e., naphthalene 99 μ g/g, low molecular weight PAHs 370 μ g/g, and high molecular weight PAHs 960 μ g/g. Their standards are much higher than the apparent effects threshold. If only PAHs were considered, only the sediment in Hamilton Harbour containing more than 800 μ g/g of total PAHs would require treatment. However, the Washington cleanup protocol for zinc is 410 μ g/g and zinc concentrations in the sediments of the Hamilton Harbour hotspot exceed 4000 μ g/g.

The Washington protocol advises that site specific evaluations be conducted using bioassays. The bioassay standardization of the

PAHs in Hamilton Harbour expresses toxicity as a function of PAHs, but it must also measure zinc toxicity.

Proposing a cleanup standard using the mean LC50 of the Daphnia, Hexagenia and Photobacterium bioassays is similar to the Washington protocol in that it is more conservative than the is also consistent with apparent effects threshold. It recommendations of the Remedial Action Plan for Hamilton Harbour. The best estimate now is that the LC₅₀ is less than 230 μ g/g. Further biological analysis is required, but we have adequate confidence in our analyses and related harbour studies to recommend an interim standard. For simplicity and because our most accurate bioassay analysis is the smallest value, a concentration of 200 μ g/g is proposed. This proposal provides a focus on the worst sediments and avoids the uncertainties of assessing moderately contaminated sediment. At least two American studies have recommended similar bioassay criteria (Athey et al. 1989, Porcella 1983).

There would be several difficulties in proposing to adopt an apparent threshold effect as a cleanup standard for PAHs. A very large area of Hamilton Harbour contains sediments with PAH concentrations that exceed the apparent threshold effect concentration. Justifying such a large project with current data would be difficult. Comparison with other studies should be done cautiously. The reporting of total PAHs varies between laboratories in the number of compounds studied. Moreover, the most commonly reported 16 PAHs represent only about 20% of the total PAHs in sediments (Alden and Butt 1987). Also, the bioavailability of PAHs is not the same at every site.

The uncertainties with the outliers in all analyses need clarification, not necessarily verification. This report contains no more outliers than the extensive study of PAH contamination in Puget Sound (Barrick et al. 1988). The variability in the PAH/toxicity analyses could be related to interactions between metallic and organic toxins, and varying bioavailabilities of toxins. For example, coal dust contains PAHs but relative to coal tar and creosote it is apparently biologically inert (Alden and Butt 1987). The concentration of coal dust is unknown in our samples, but it must be present. Also, like metals, the bioavailability of PAHs can be suppressed by organic matter (Landrum et al. 1987) or presumably other reactive compounds.

The black sediment at the northwest end of the Stelco property may contain high concentrations of coal dust. The coal piles are immediately adjacent to this site. Although Alden and Butt (1987) said coal dust was relatively biologically inert, these sediments are toxic to <u>Daphnia</u> and <u>Photobacterium</u>. The UV/PAH analysis indicates that these sediments contain less PAHs than the sediments of the southern hotspot; however, few GC/MS analyses of PAHs were done in the area. More GC/MS analyses, data in related sediment studies and MISA studies should be evaluated before taking any direct physical action to restore the northern hotspot. The sediments of the northern site are in much deeper water and they should been much less prone to resuspension and more likely to be

buried by newly formed sediment. Moreover, the source of the contamination in the northern hotspot must be established and controlled before any rehabilitation proposal is considered. Coal dust is the most likely source. The management of the coal piles has improved and berms are being constructed to further reduce coal dust pollution.

With the exception of the 81 cores collected in this study, all other PAH analyses in Hamilton Harbour were processed on samples collected with Ekman dredge samplers. These samples were composed of a mix of the surface sediments and deeper sediments (<10 cm). It is highly likely that the surface sediments in the deep depositional basin have reduced concentrations of PAHs at the surface, as did the cores near the Stelco property. There may be no need to treat the contaminated sediments in the deeper portion of the harbour; they should be naturally buried by recently formed cleaner sediment.

If only sediment resuspension was important, the optimal way to interpret the core data for a cleanup program would not be obvious. The depth that ships can resuspend sediment is not well documented but our sampling vessel, which is small compared to commercial ships, did resuspend sediment. All of the sediments in the southern hotspots are in relatively shallow water and the most contaminated sediments are only under 3-5 m of water (Fig. 15b).

Sediment benthos can move through the top 12 cm of sediment; thus, to protect wildlife, the spatial distribution of the maximum observed concentration of PAHs in the surface samples (0-2, 2-4, 4-

6, and 10-12 cm) should be considered as a guide for dredging (Fig. 15). Using Fig. 15 as a guide increases the volume of the most contaminated sites by 15% relative to the area containing sediment contaminated at a depth of 4-6 cm (Table 4). The extension would ensure that Randle Reef was part of the cleanup plan. The water depth is less than 3 m and waves may increase the release of contaminants from these sediments (Fig. 15b).

4.3 Impact of NWRI Studies on Remedial Options

4.3.1 Natural Recovery

Natural recovery of the hotspot would likely be very long and delaying a cleanup of the hotspot will delay the anticipated recovery of the main harbour. PAH analysis from sediment traps in the harbour appears to indicate a current source of PAHs (Charlton unpublished), but the Stelco MISA data indicates low industrial loadings of PAHs. Some of the hotspot is in water only 3-5 m deep and sediment resuspension could be the current source of PAHs. Although no data exists to assess sediment resuspension from wave action, graphic evidence exists to illustrate the impact of ships. Rukavina (unpublished) has recorded sediment resuspension from ships and Rodgers (unpublished) has observed substantial sediment resuspension and a large oil-like slick when a barge was flipped over above the hotspot.

The discharges of coal tar in process water from the west side of Stelco have ceased; thus, the hotspot should not be recontaminated if a cleanup operation was conducted. However,

spills of coal tar may still be a problem. In 1985, Stelco spilled about 4000 m³ of coal tar near the northern half of the southern hotspot. In 1978, approximately 35,000 m³ of sediment was removed from this area. Either the coal tar spill was not adequately cleaned or the coal tar to the south is moving.

Coal tar was also spilled in March 1990 and oil spilled in May 1990 into the hotspot. Although Stelco appears to be the only current potential major source of PAHs, samples from the creek into which the Sherman Street combined sewer discharge should be analyzed to confirm this hypothesis. All sources of contamination should be controlled before a major dredging program is initiated.

4.3.2 <u>In Situ Treatment</u>

The options for in situ sediment treatment appear limited. unpublished studies by NWRI and MOE, it was observed that sediment treatment with oxygen, ferric chloride, or lime were more effective in reducing toxicity of sediments contaminated with metals than PAHs, and treatments had no effect on PAH bioaccumulation by Oxidizing sediments should enhance Hexagenia. microbial degradation of PAHs (Racke and Frink 1989), but an unpublished NWRI study did not observe this effect. Possibly, the high concentrations of metals restricted bacterial metabolism. Perhaps increasing the oxygen concentration of the harbour would expedite the recovery of the marginally contaminated sediments, but oxidation of the hotspot sediments would not remove the risk to fish and benthic invertebrates.

4.3.3 <u>Dredging and Sediment Disposal</u>

Disposal of the dredged PAH contaminated sediment is beyond the focus of this study but some obvervations should be made. Disposal of this sediment in a confined disposal facility (CDF) should be considered carefully. The sediment is approximately a hundred times more toxic than the Windermere Basin sediment of Hamilton Harbour, a current dredging project. Workers must be protected from the fumes and direct contact with the sediment, especially the dust from the dried sediment. At least, a CDF should be lined to prevent leakage. The CDF should be covered as soon as possible to minimize wildlife exposure to PAHs. The covering cap of the CDF should be impervious to water (i.e. asphalt), to minimize water movement through the CDF.

4.3.4 Other Alternatives for Sediment Treatment

Other alternatives to a CDF should be considered for the most toxic sediments (IJC 1988). A pyrolysis system is available for the destruction of PAHs by reduction (Ecologic) but costs are not accurately known. The Superburn incineration process for 700,000 tonnes of sediment from the Sydney Tar Ponds Cleanup Project, will cost about \$34.3 million over the next ten years.

The Hamilton Harbour site should be studied in more detail with an underwater camera, such as NWRI's MERV, to determine the extent of the solid coal tar near the outfall pipes. Perhaps the solid coal tar could be recycled.

The Randle Reef area would be expensive to dredge in that most dredging equipment would remove as much as a metre of sediment to remove the 10-15 cm thick lens of contaminated sediment. If this area is treated, other options than dredging, such as capping or building a CDF over it could be considered.

CONCLUSIONS

Our studies indicate a higher correlation of PAH concentration and toxicity than is apparent with metals; PAHs appear to be a better guide for a cleanup standard for Hamilton Harbour than metal concentrations. Metallic contamination is important in that it acts as a biocide suppressing bacterial degradation of PAHs. Use of bioassays to measure PAH toxicity will incorporate metal toxicity into the standard.

Adoption of the mean 200 μ g/g PAH contour line would provide considerable protection for the wildlife of Hamilton Harbour. This cleanup standard is suggested as an interim standard to guide the removal of the worst of the contamination. The cleanup program should be developed in stages. Future research is required to more accurately assess the risk of the less contaminated sediments to wildlife and if necessary to develop cost-effective treatment.

Recommendations

- A) Needing immediate action.
- 1) Adopt the following cleanup standard; the mean concentration of PAHs in sediments resulting in the death of 50% of <u>Daphnia</u> and <u>Hexagenia</u>, and the suppression of 50% of the photoactivity of <u>Photobacterium</u> (200 μ g/g).
- 2) Use the best available safety procedures when handling the most contaminated sediments.
- Develop a cleanup protocol that includes advanced processing of the most contaminated sediments, i.e., recycling, pyrolysis, but not a simple CDF.
- 4) Examine existing MOE data to confirm that PAH discharges into combined sewers will not continue to result in the formation of contaminated sediments.
- 5) Expand upon the current limited data set to confirm that PCBs are not a major contaminant in the sediments of the hotspot.
- B) Needing future action.
- 1) Determine the environmental variables restricting bacterial degradation of the PAHs in Hamilton Harbour.
- 2) Develop a "finger print" assay to distinguish between coal tar and coal dust.
- 3) Determine if the black sediments at the northwest corner of Stelco contain high concentrations of coal dust.
- 4) Determine the relative contribution of coal tar and coal dust

to the elevated PAH concentrations in the deep basin of Hamilton Harbour.

- 5) Determine the relative bioavailability of PAHs in coal tar and coal dust.
- 6) Determine the effect of coal tar and coal dust on the distribution of benthic invertebrates.

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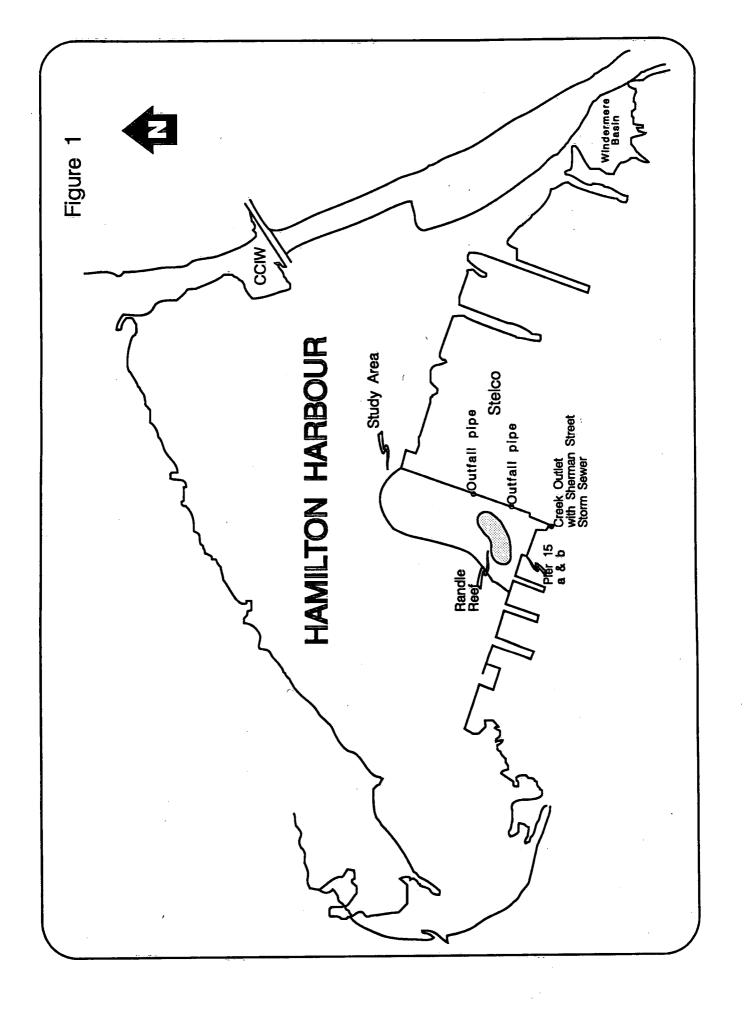


Figure 2

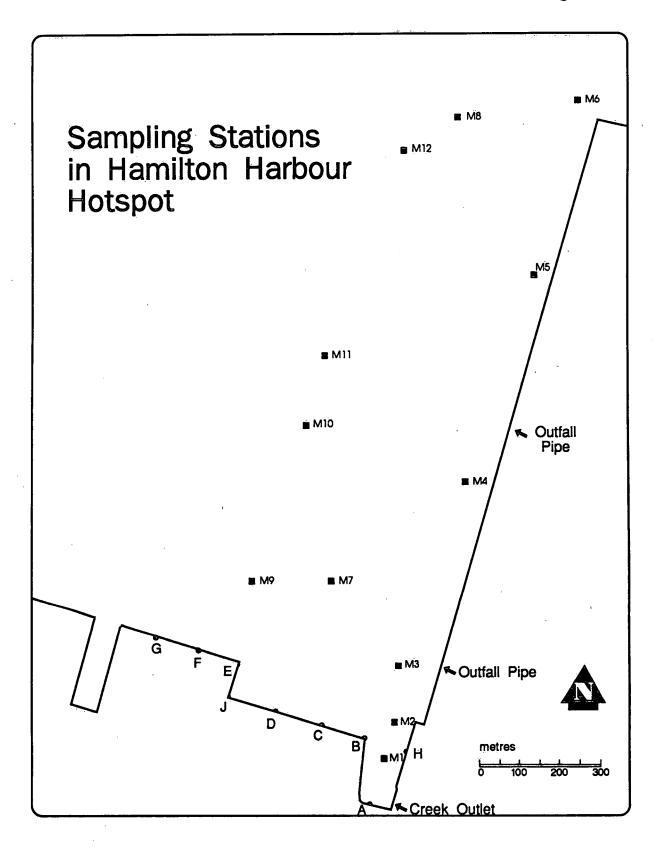
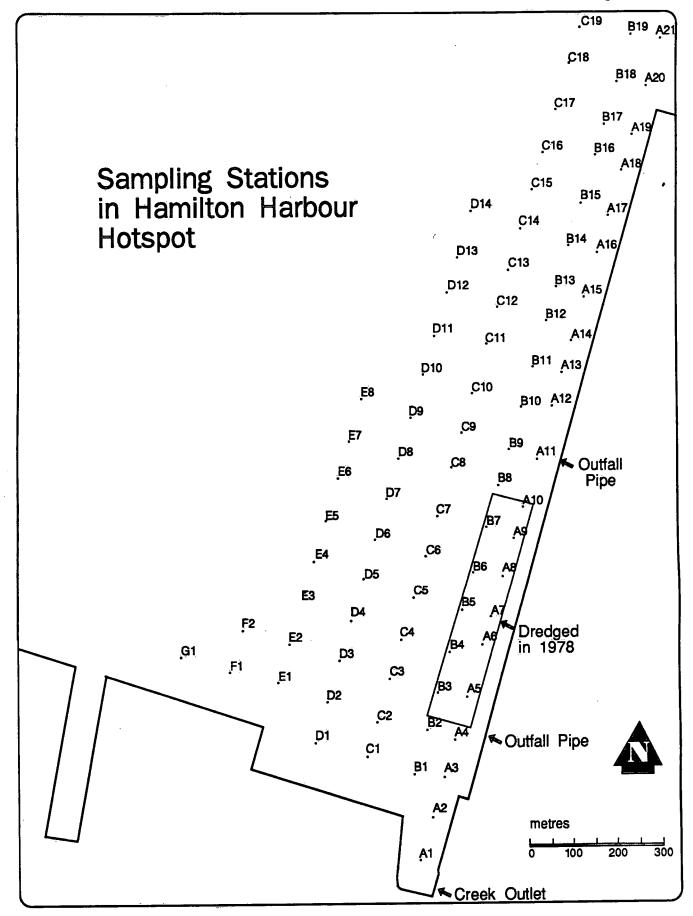
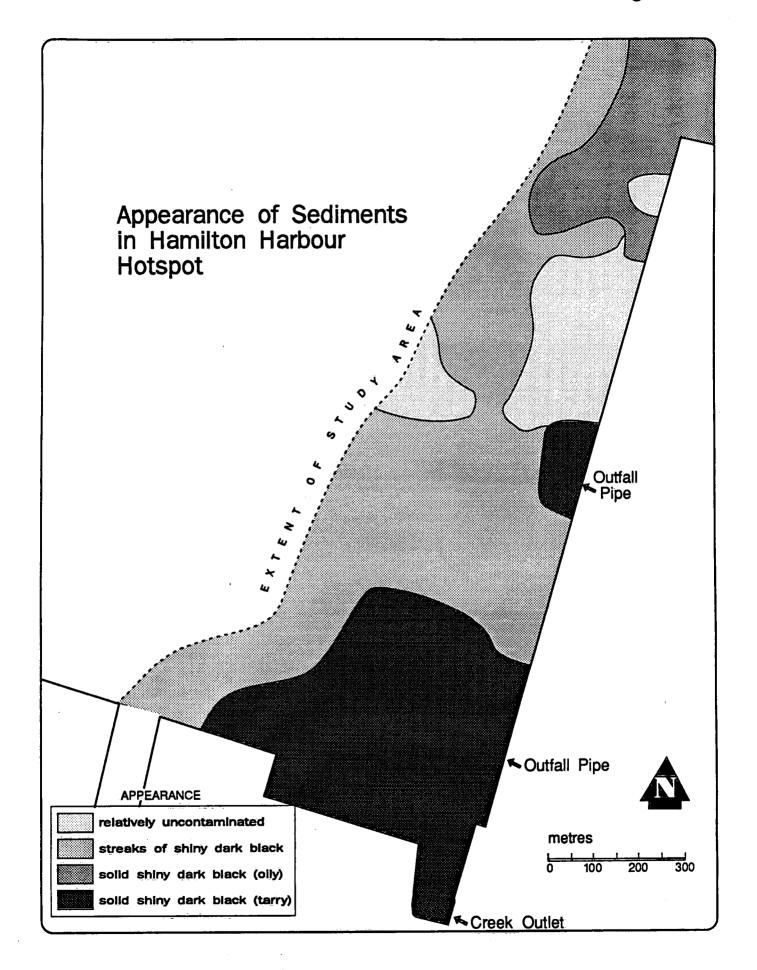
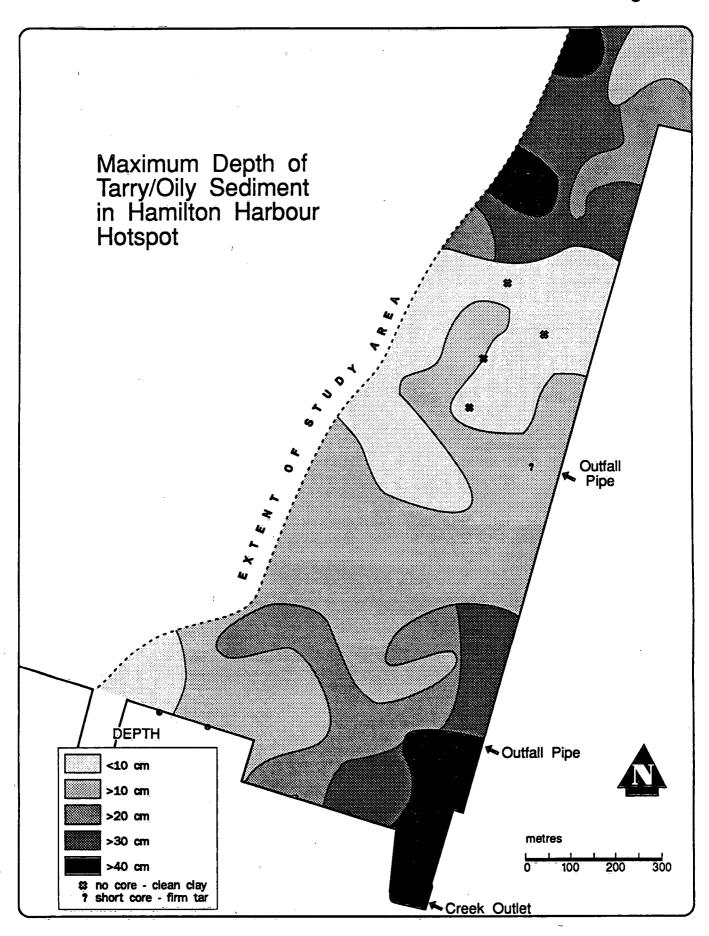


Figure 3







TOTAL POLYAROMATIC HYDROCARBONS (ug/g) IN HAMILTON HARBOUR SEDIMENTS

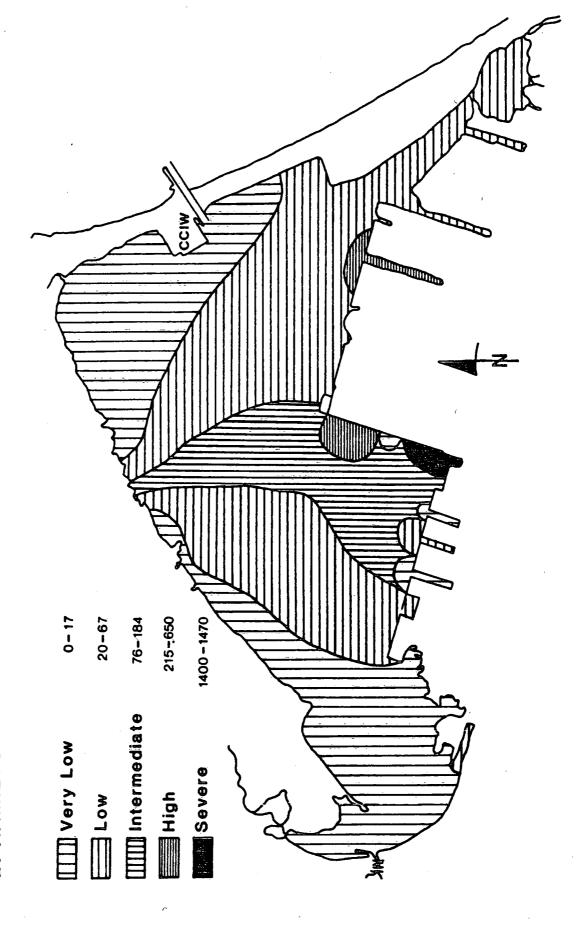


Figure 8 Regression of PAHs on UV Absorption (52 samples) (100) PAHS (ug/g) UV Absorption

Figure 9 Regression of PAHs/UV (16 samples in hotspot)

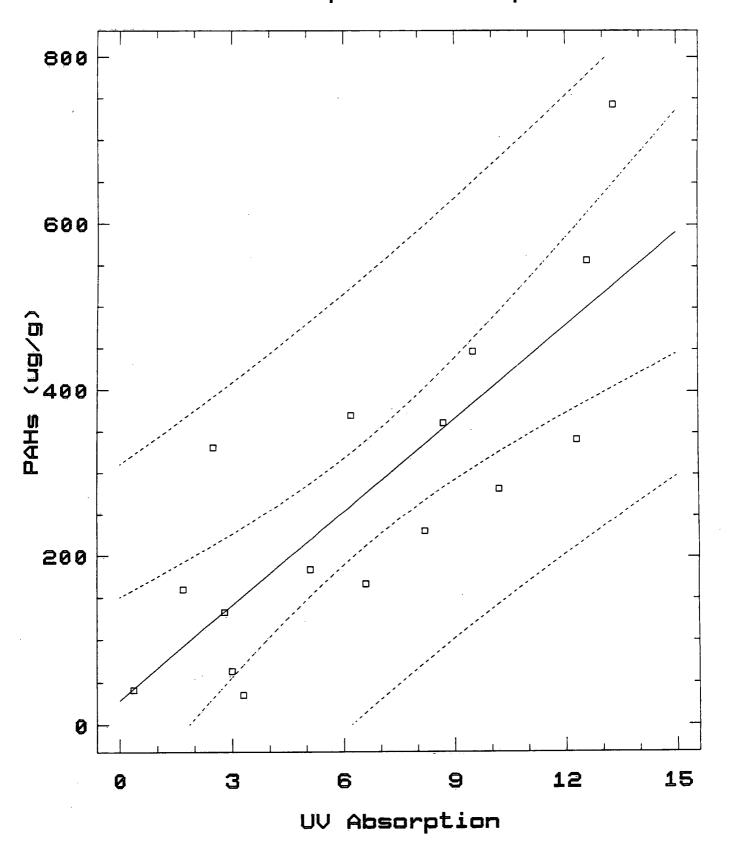
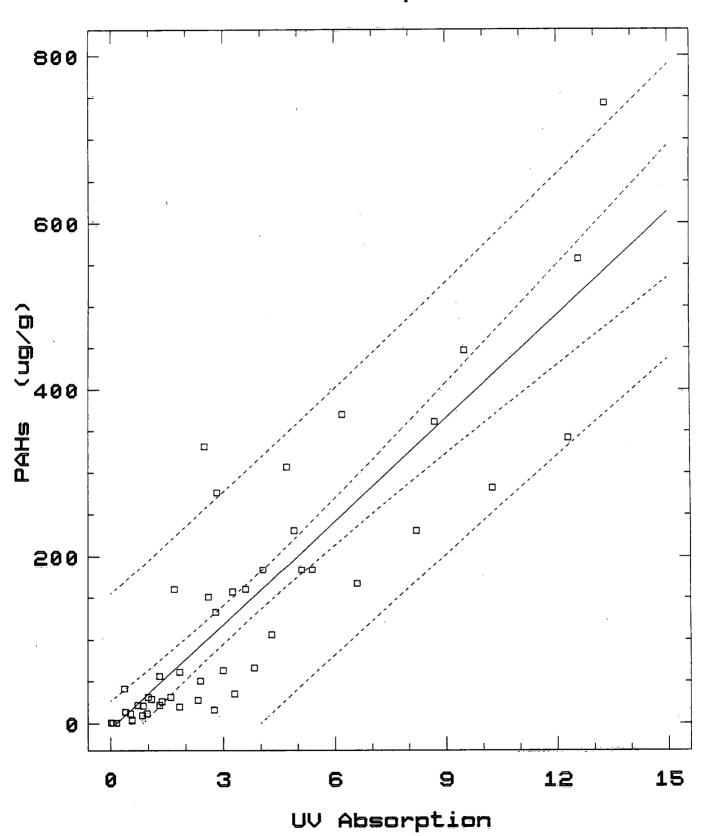
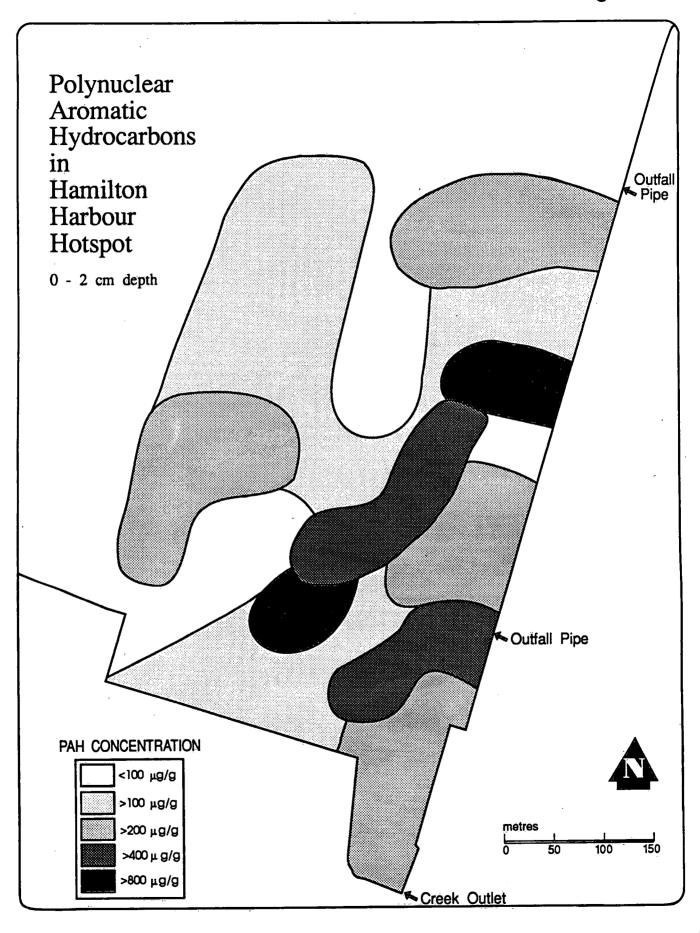
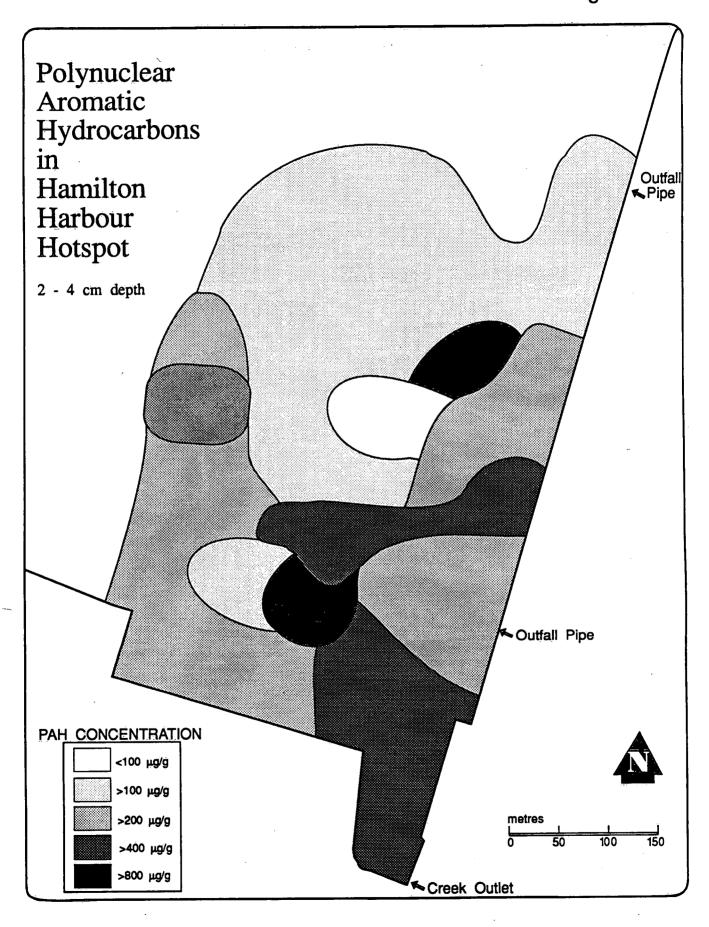


Figure 10 Regression of PAH/UV 48 samples







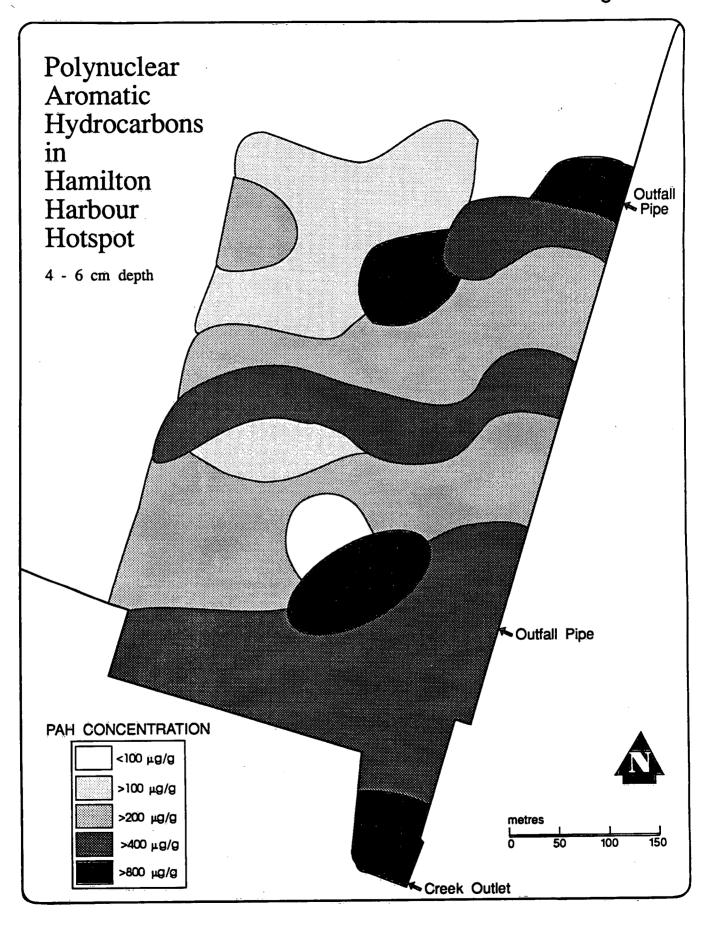
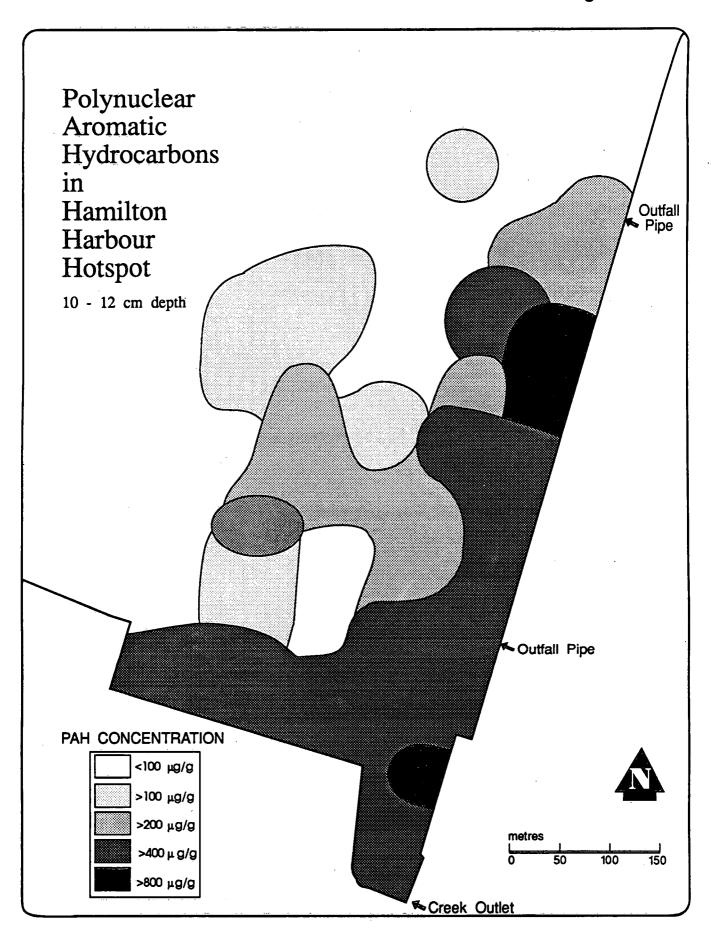
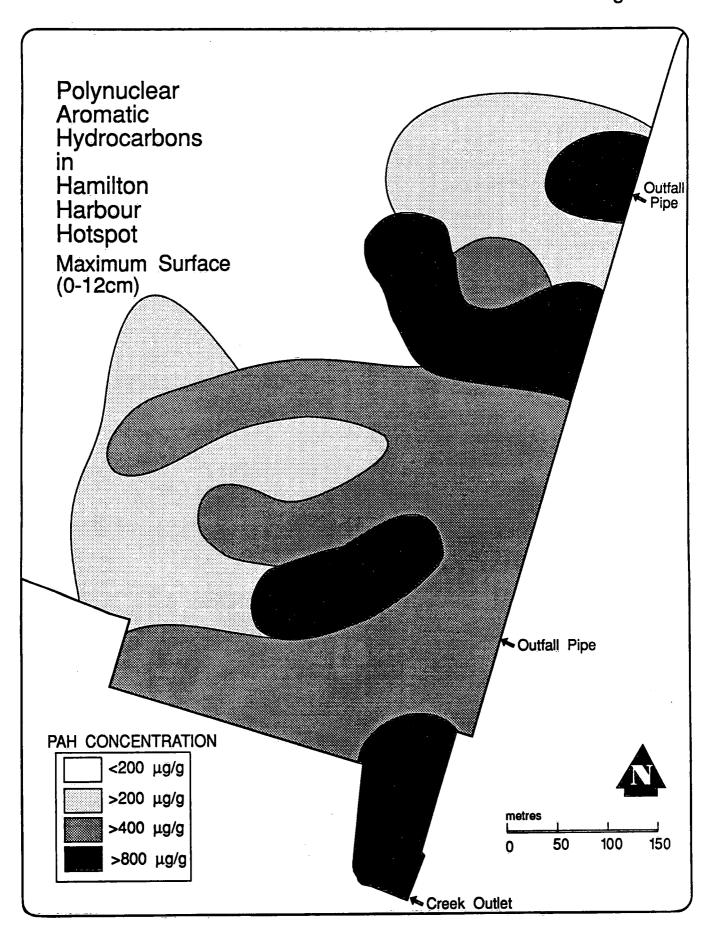
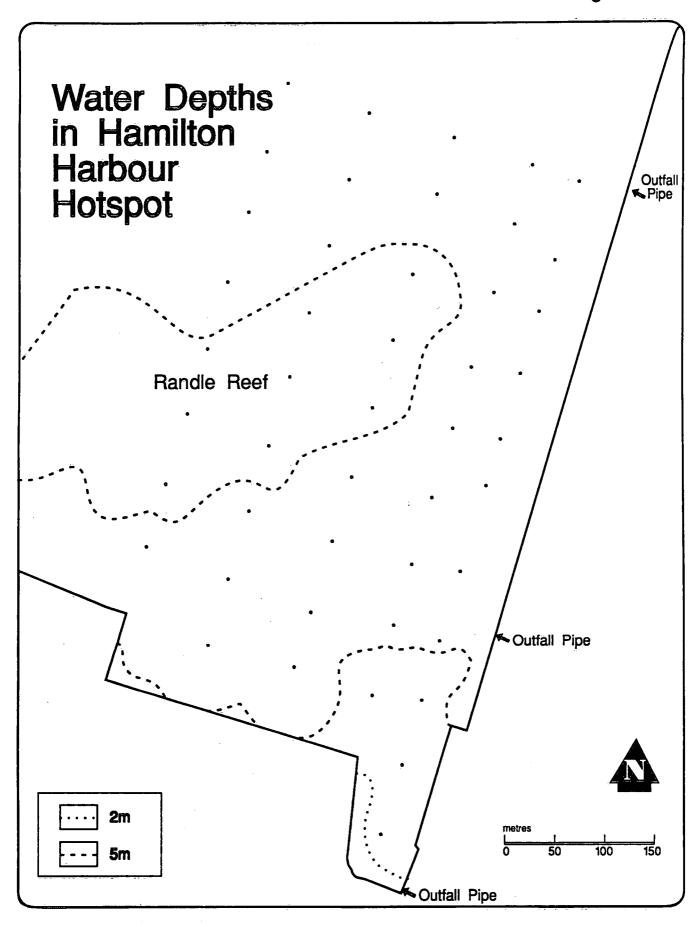
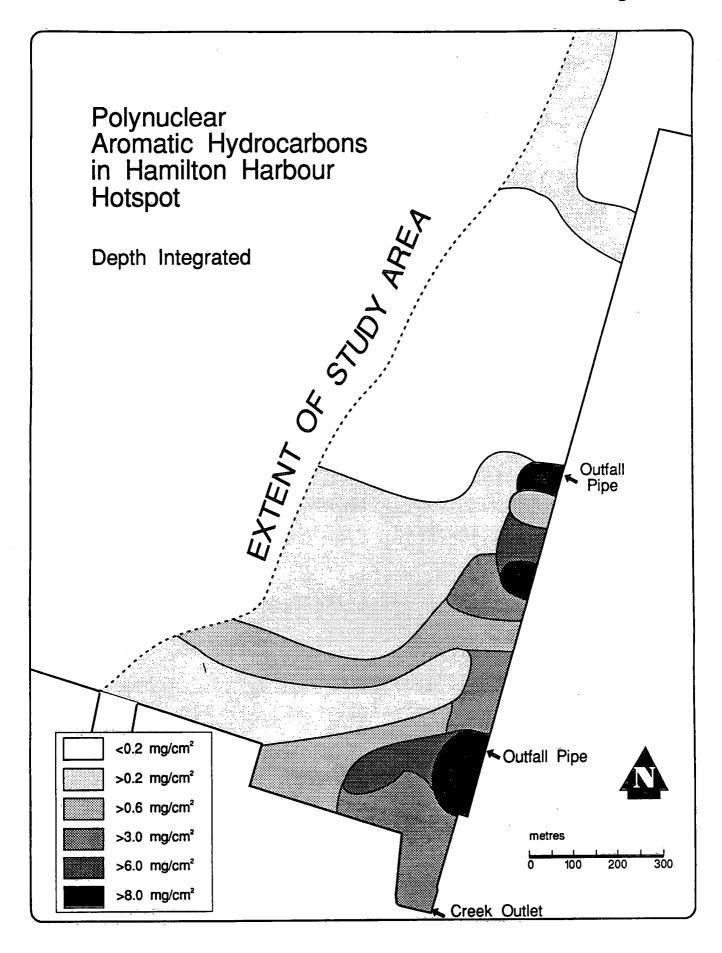


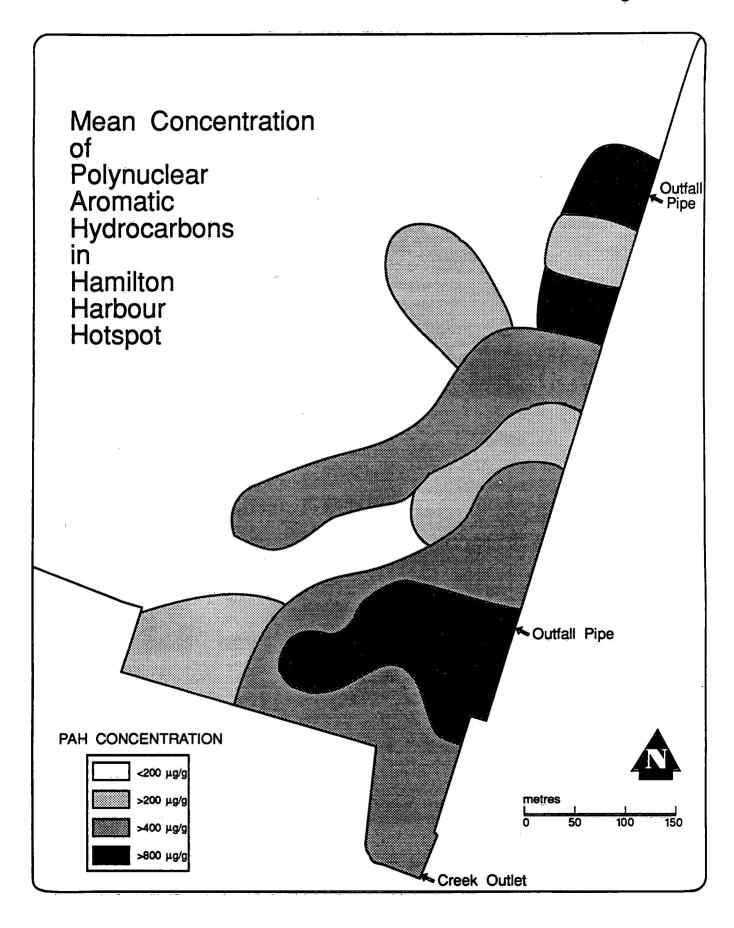
Figure 14



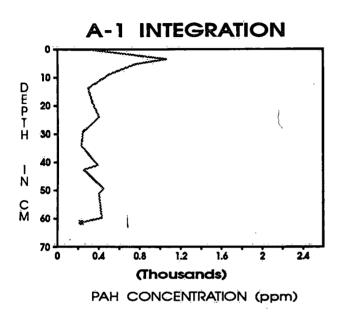


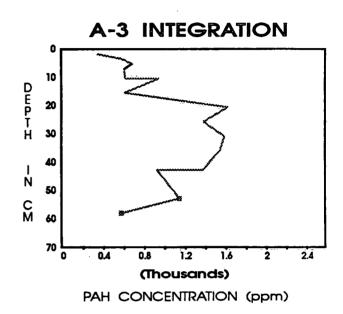


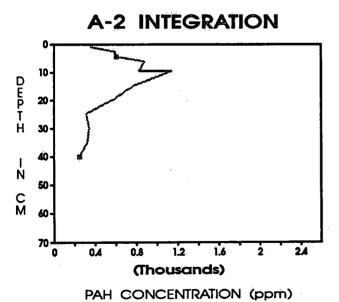


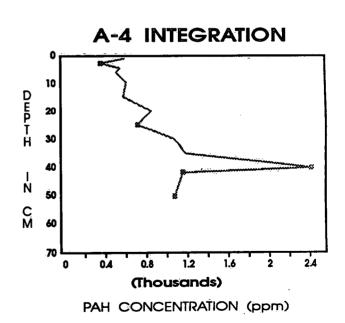


DEPTH PAH PROFILES

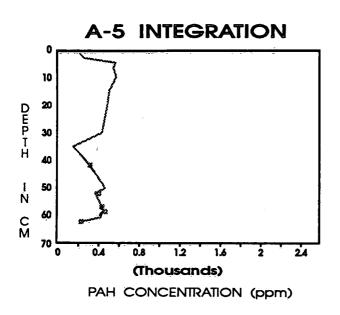


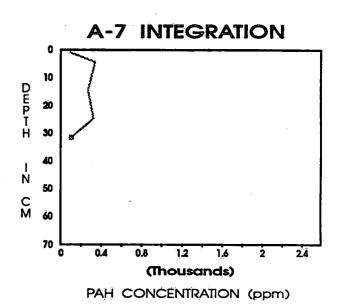


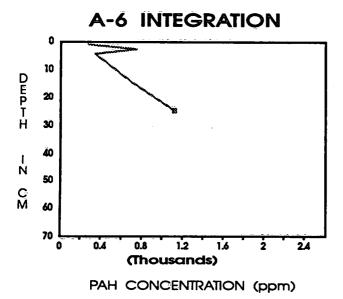


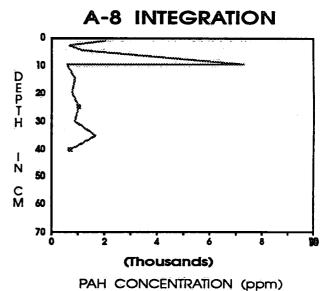


DEPTH PAH PROFILES



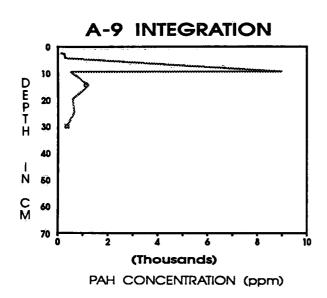


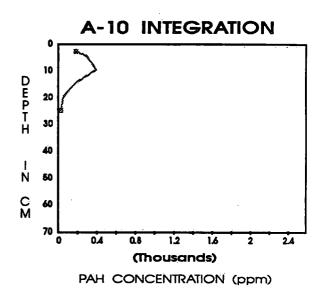


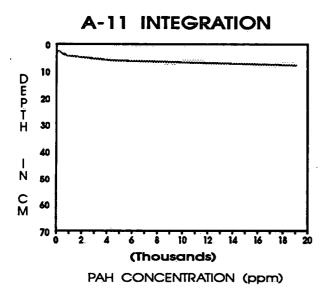


^{*} Note the different scale for the graph of A-8 integration

DEPTH PAH PROFILES







* Note the difference in scales among the three graphs

Figure 19 Regression of 1 Minute PAH Extraction on 17 Hour Extraction

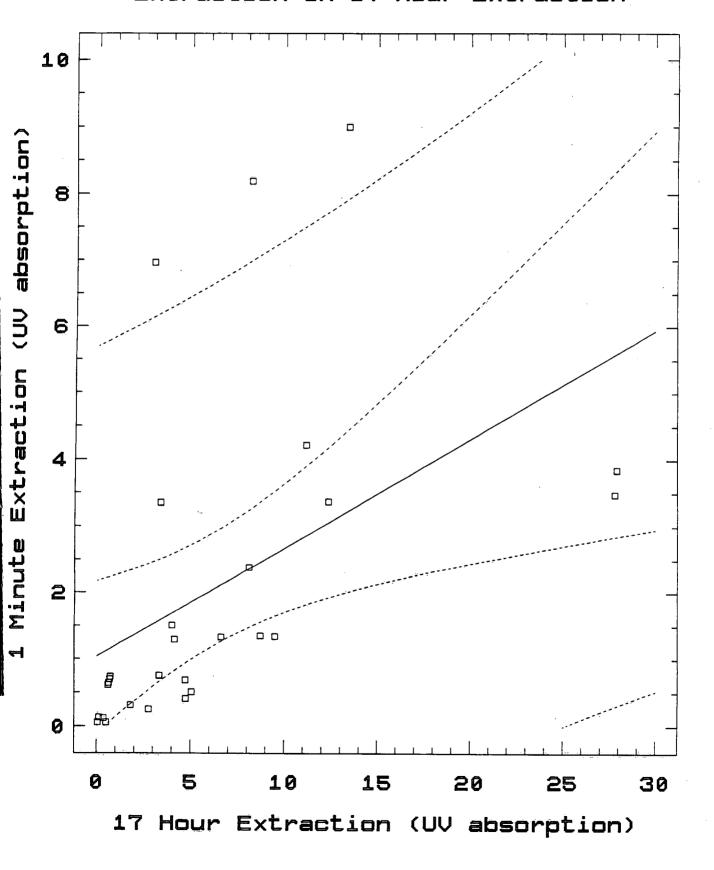


Figure 20 Regression of Photobacterium bioassay on PAHs (33 samples)

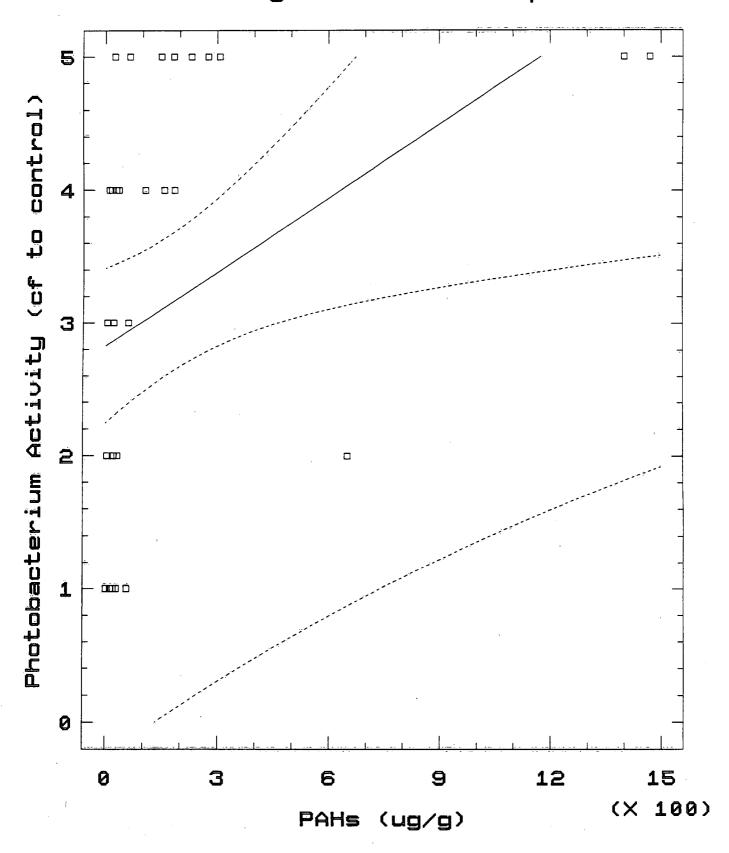
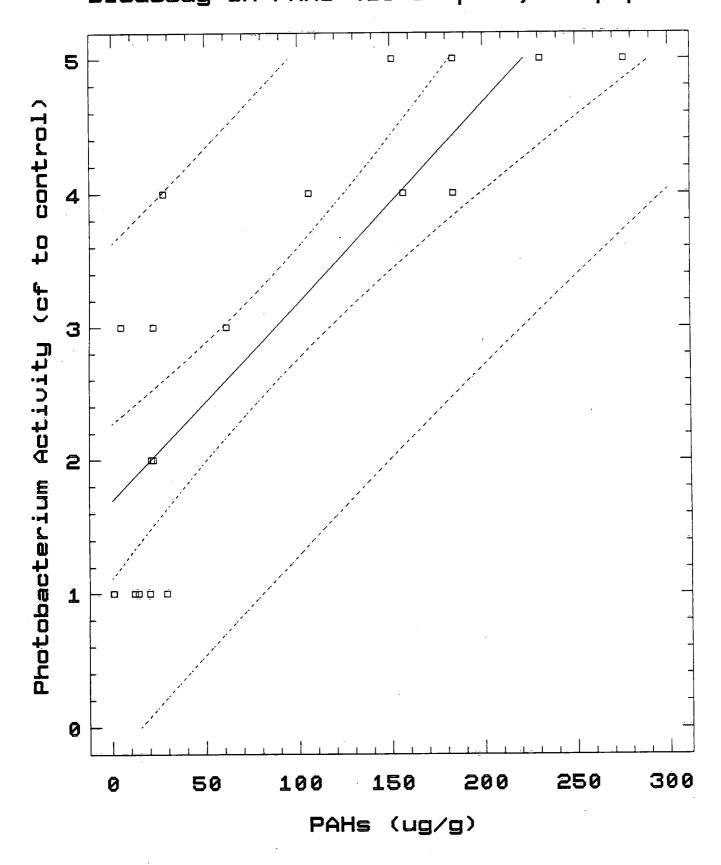
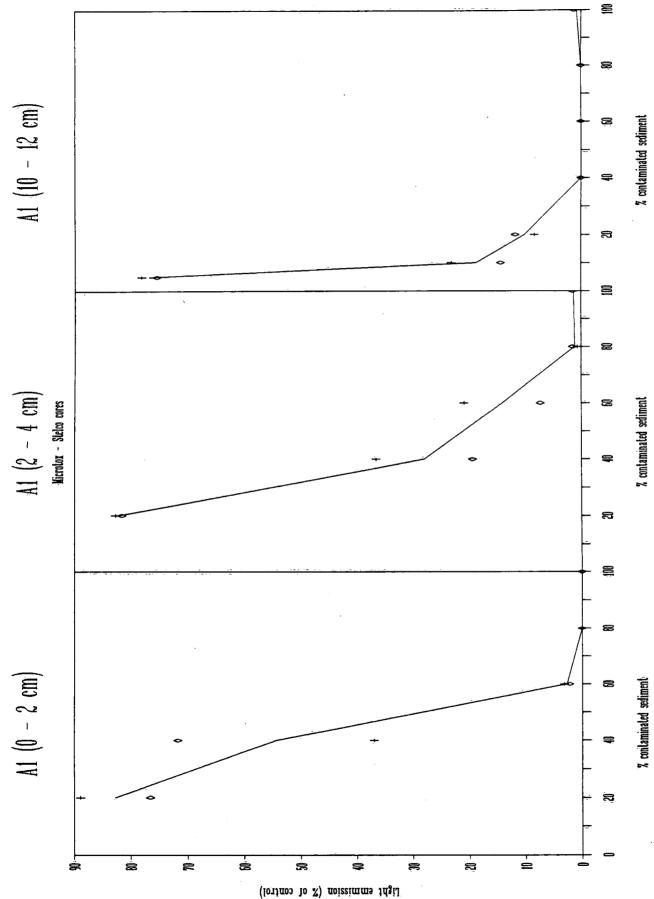


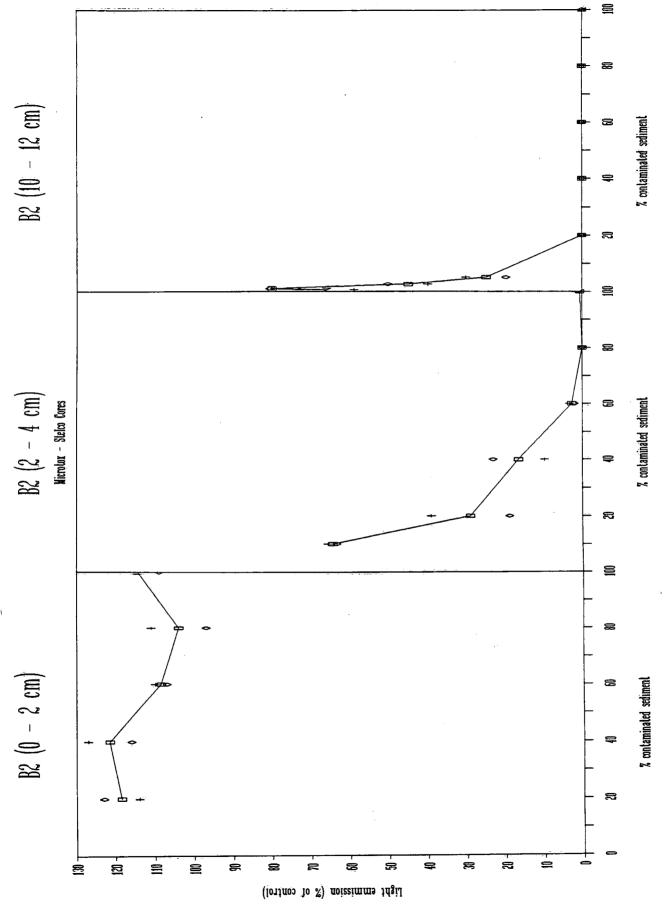
Figure 21 Regression of Photobacterium Bioassay on PAHs (19 samples, no pipes)

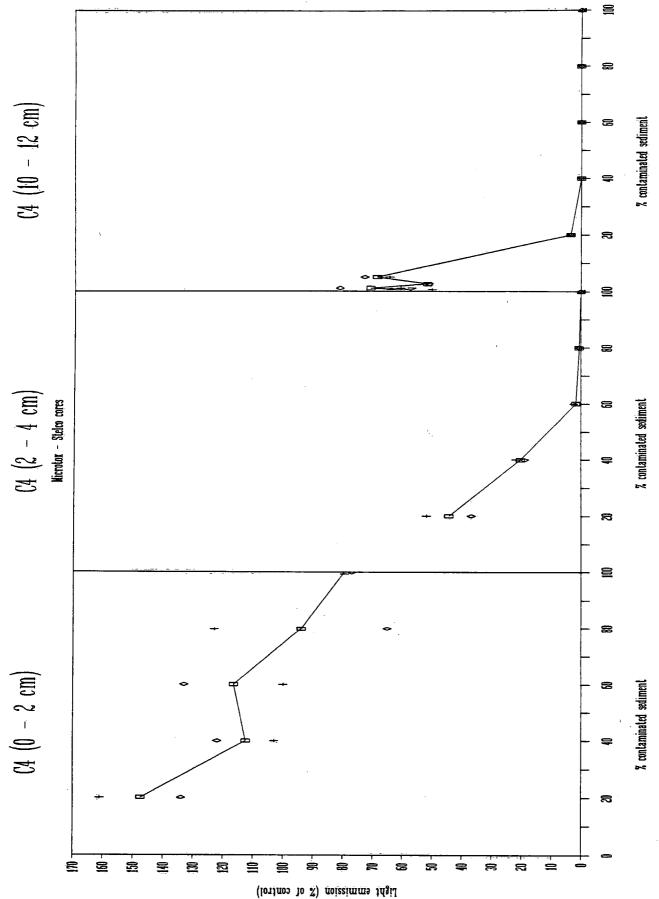


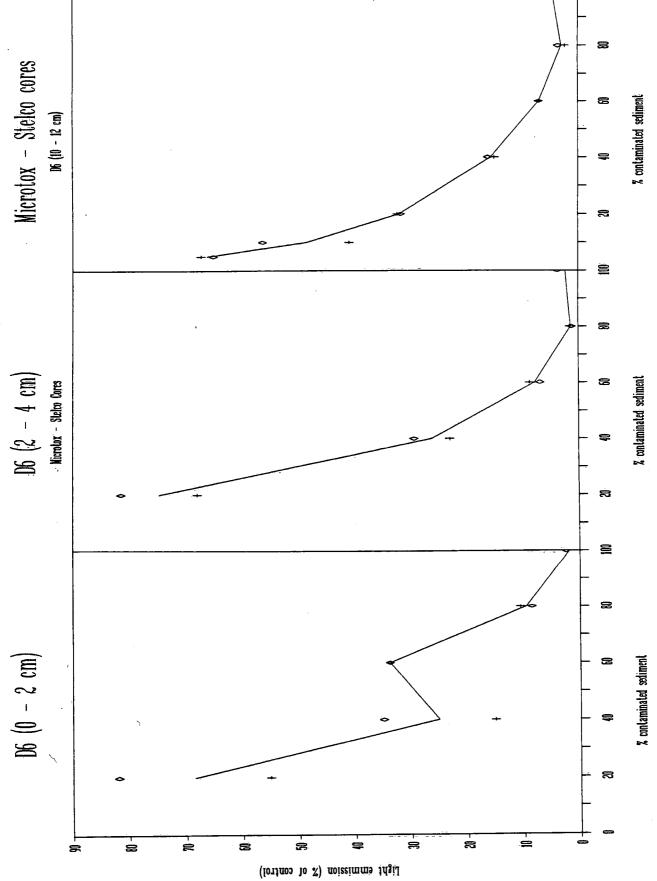
Microtox 100% Diluted Hamilton Harbour Sediment **\$** 80% 60% % toxic sediment Daphnia outlier 40% 20% % Daphnia 06 80 7 2 50 -20 | **4** ← 30 10 -10 100 - 09

% of control (Micro.), % live Daphnia









8

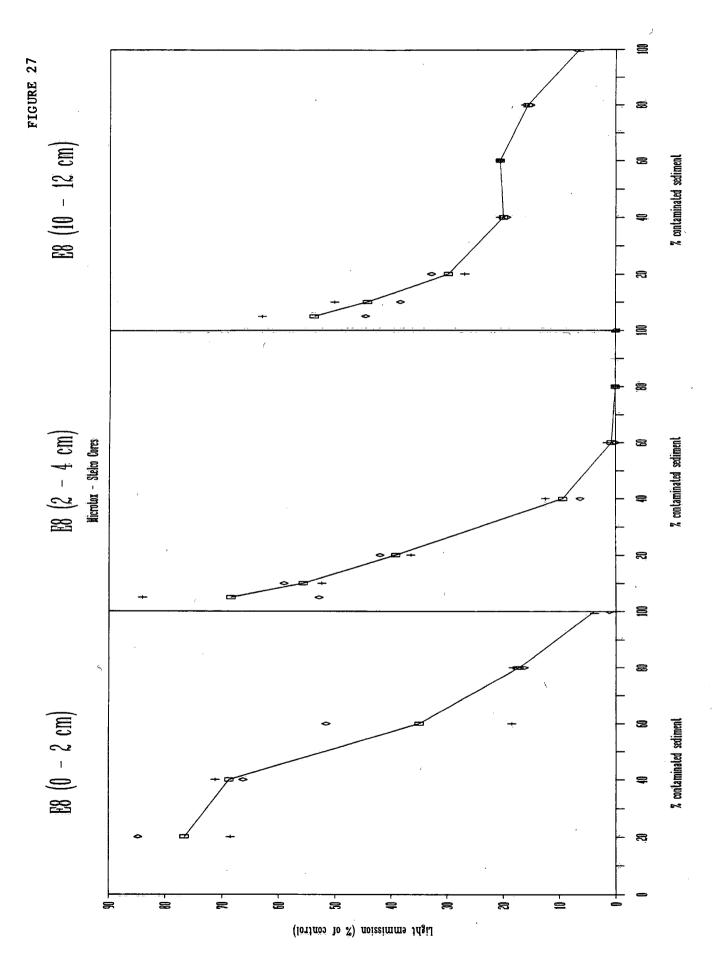


Figure 28 Regression of Hexagenia Survival on PAH Concentration

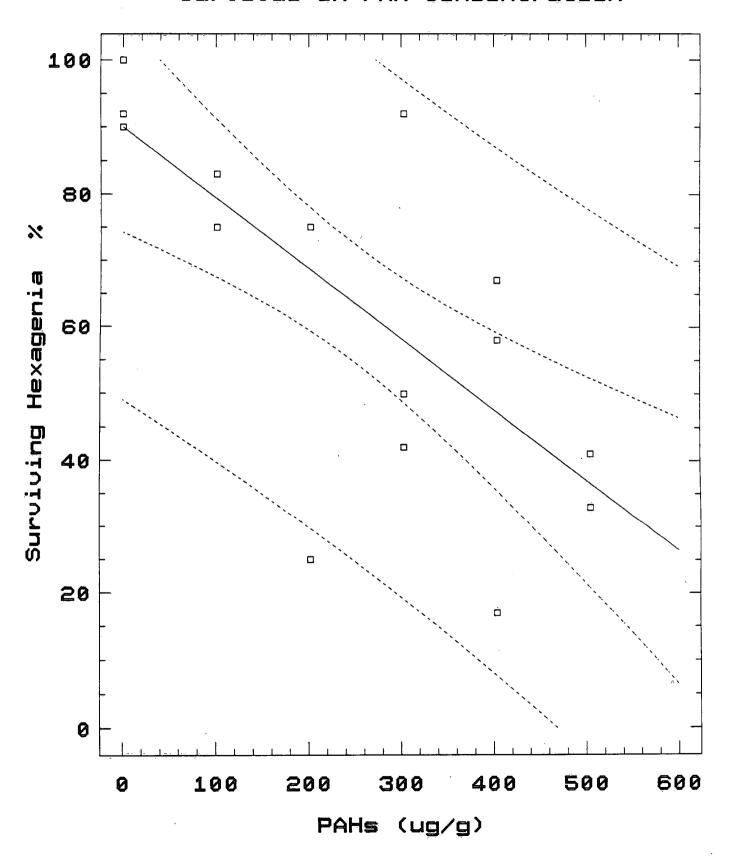


Table 1

Instrument Position	Distance	Core Number
A	65.67	A-1
A	149.66	A-2
A	232.16	A-3
A	307.96	A-4
A	396.33	A- 5
A	506.29	A-6
A	563.02	A-7
A	545.29	A-8
A	731.33	A-9
A	790.55	A-10
A	890.45	A-11
A	1005.17	A-12
A	1074.49	A-13
Ä	1142.35	A-14
A	1229.31	A-15
A	1324.97	A-16
A	1402.93	A-17
A	1492.75	A-18
A	1572.89	A-19
A	1671.65	A-20
. A	1768.83	A-21
В	83.90	B-1
В	175.13	B-2
В	250.76	B-3
В	334.87	B-4
В	423.46	B−5
В	504.35	B-6
В	599.27	B-7
В	684.76	B-8
В	760.97	B-9
B	846.88	B-10
B	928.92	B-11
В	1030.44	B-12 No core
B	1099.52	B-13
В	1183.48	B-14
В	1276.70	B-15
В	1377.20	B-16
B	1438.30	B-17
B	1525.87	B-18
В	1624.18	B-19

Table 1 continued Instrument Position	Distance	Core
С	89.04	C-1
Ċ	160.57	C-2
Ċ	246.00	C-3
Č	332.18	C-4
Č	422.10	C-5
C	506.06	C-6
0		C-7
		C-8
Ċ	692.23	
C	763.82	C-9
C	843.22	C-10 No core
С	948.46	C-11 No core
Ç	1024.91	C-12
C	1104.48	C-13 No core
С	1188.53	C-14
С	1267.73	C-15
С	1349.96	C-16
С	1432.41	C-17
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	1533.07	C-18
C	1606.46	C-19
D	85.33	D-1
D	168.46	D-2
D	253.40	D-3
D	337.15	D-4
D	426.23	D-5
D		D-6
	508.00	•
D	593.17	D-7
D	674,95	D-8
D	761.98	D-9
D	852.03	D-10
D	933.28	D-11
D	1020.73	D-12
D	1097.20	D-13
D	1190.81	D-14
E	87.82	E-1
E	170.58	Ē-2
E	258.71	E-3
E	342.81	E-4
— F:	425.88	E-5
F	513.16	E-6
五 正	595.59	Ē-7
E E E E E E	678.97	E-8
-	05 00	F-1
F F	85.00	
F	185.00	F-2
G	85.00	G-1

Table 1 continued

Distances between survey points in Figure 3

Survey points	Distance	(m)
A-I	49.8	
в-н	102.2	
I-H	149.7	
В-С	103.9	
C-D	108.7	
D-J	102.2	
E-J	86.9	
E-F	100	
F-G	100	

Table 2 Loss on Ignition - Sediment Organic Content

Core Samples A1 0-2 2-4 10-12 B1 0-2 2-4 10-12 C4 0-2 2-4 10-12 D6 0-2 2-4 10-12 E8 0-2 2-4 10-12	(Fig. 2)	Loss on Ignition 13.8 16.1 14.6 12.5 13.8 13.9 11.2 10.2 13.1 7.2 6.1 8.3 3.6 3.8 2.5	(%)
Grab Samples M1 M3 M4 M5 M6 M8 M11	(Fig. 3)	Loss on Ignition 14.8 10.4 6.5 6.4 12.9 13.2 9.5	(%)
Grab Samples 13 25 26 29A 34 41 42 52 55 59 60A 61 62 63 67 69 74 75 76 80 86 87	(Fig. 4)	Loss on Ignition 10.9 10.7 8.5 1.8 3.6 14.8 10.7 12.7 10.7 5.1 8.1 9.4 12.0 7.3 12.8 3.8 7.8 10.1 4.6 3.0 7.9 3.2	(%)

Table 3

PAHs IN HAMILTON HARBOUR SEDIMENTS - Subset of 52 GC/MS Analyses

		GRAB SA	MPLES	GRAB SAMPLES (FROM FIG. 3)	G. 3)			GRAB SA	MPLES (GRAB SAMPLES (FROM FIG.1)
COMPOUND	Σ.	M2	M 2*	M3	A	M5(1)	M5(2)	We We	6 W	M11
ln na/a:						:			:	
NAPHTHALENE	19.8	91.9	13.5	53.2	0.27	8.2	16.2	12.4	18.2	7.7
ACENAPHTHYLENE	8.2	49.0	24.4	43.1	0.00	11.8	20.9	8.9	3.9	4.4
ACENAPHTHENE	3.3	61.4	8.8	105.0	0.00	11.2	8.6	2.6	0.0	0.0
FLUORENE	3.5	72.0	39.1	120.0	0.00	14.6	19.8	6.3	1.9	2.4
PHENANTHRENE	20.6	171.0	33.8	189.0	0.26	85.5	116.0	39.4	10.7	20.1
ANTHRACENE	6.7	64.6	29.5	88.1	0.00	26.8	39.2	13.1	3.9	9.9
FLUORANTHENE	31.4	108.0	34.2	134.0	0.31	93.9	129.0	51.7	18.2	31.1
PYRENE	22.8	234.0	34.8	280.0	0.24	126.0	184.0	40.3	17.3	31.3
BENZOAANTHRACENE	16.1	102.0	51.1	86.0	0.14	30.5	46.3	18.8	6.4	9.3
CHRYSENE	18.3	2.06	48.3	78.2	0.17	29.0	44.0	18.2	7.1	10.9
BBFLUORANTHENE	20.5	96.3	36.7	85.3	0.08	22.3	35.1	15.4	6.4	10.1
BKFLUORANTHENE	11.1	36.0	30.3	27.4	0.00	11.4	15.8	8.0	3.5	5.3
BapyRene	15.4	69.2	38.7	61.6	0.12	22.3	32.9	15,6	4.6	8.1
INDENOPYRENE	13.9	86.3	39.0	67.4	0.00	23.5	33.4	15.7	4.0	5.9
DIBENZOANTHRACENE	4.4	11.4	6.9	8.0	0.00	2.7	4.3	2.0	0.0	0.0
BENZOPERYLENE	15.0	57.6	38.2	43.7	0.00	14.9	21.4	6.6	0.0	4.6
TOTAL (ug/g)	231.1	231.1 1401.4	507.3	507.3 1470.0	1.59	534.7	767.0	276.2	105.9	157.9

*1989 samples, all other samples were collected in 1988.

Table 3 (continued)

PAHS IN HAMILTON HARBOUR SEDIMENTS

			S	AMPLE ST	ATIONS (C	SAMPLE STATIONS (CORES FROM FIG. 2)	M FIG. 2)		
	¥	¥	¥	B 2	B2	B 2	2	2	2
COMPOUND	0-2 cm	2-4 cm	10-12 cm	0-2 cm	2-4 cm	10-12 cm	0-2cm	2-4cm	10-12c
in ug/g:									
NAPHTHALENE	102.0	115.0	160.0	154.0	193.0	192.0	55.20	75.30	83.20
ACENAPHTHYLENE	9.1	11.7	6.6	14.2	15.2	25.6	9.28	15.40	4.67
ACENAPHTHENE	3.5	3.4	12.5	6.9	11.7	24.8	3.81	7.53	5.38
FLUORENE	5.9	27.1	107.0	2.7	12.0	30.7	2.12	14.10	5.02
PHENANTHRENE	25.8	28.9	87.3	31.8	54.0	118.0	19.40	43.90	19.40
ANTHRACENE	15.8	16.3	30.9	10.9	15.2	33.0	7.42	18.30	7.49
FLUORANTHENE	26.1	35.5	52.9	35.3	45.6	96.3	23.10	50.00	16.10
PYRENE	20.8	28.0	39.7	27.2	34.3	72.7	18.20	39.60	11.50
BENZOAANTHRACENE	5.4	7.4	9.3	0.9	8.0	16.6	4.00	8.82	2.35
CHRYSENE	5.9	7.4	6.3	7.4	9.1	17.6	5.00	9.52	2.67
BDFLUORANTHENE	2.7	9.6	7.6	2.3	14.5	31.1	10.30	20.70	4.36
BKFLUORANTHENE	5.8	2.7	4.6	9.6	0.0	0.0	0.00	0.00	0.00
Bapyrene	8.2	8. 9.	7.3	12.5	9.5	22.1	7.30	15.90	2.23
INDENOPYRENE	18.9	19.0	8.9	23.6	12.9	32.7	10.80	22.50	2.67
DIBENZOANTHRACENE	6.9	3.6	2.5	6.8	2.3	3.9	0.00	2.21	0.00
BENZOPERYLENE	16.6	14.9	8.5	19.1	9.6	25.5	8.10	18.30	0.00
TOTAL (ug/g)	282.5	342.3	558.4	370.2	447.0	742.8	184.0	362.0	167.0

Table 3 (continued)

PAHS IN HAMILTON HARBOUR SEDIMENTS

		SAMPLE	SAMPLE STATIONS (CORES FROM FIG. 2)	CORES FF	NOM FIG. 2	5
	90	D 6	90	E8	E8	<u>8</u>
COMPOUND	0-2cm	2-4cm	10-12cm	0-2cm	2-4cm	10-12c
ln ug/g:						
NAPHTHALENE	6.88	4.05	19.84	8.32	7.30	0.00
ACENAPHTHYLENE	2.94	1.74	3.68	3.22	1.63	0.00
ACENAPHTHENE	1.95	0.97	11.93	1.47	1.15	0.00
FLUORENE	10.10	6.9	12.55	2.28	1.30	0.51
PHENANTHRENE	10.20	5.26	33.88	12.30	7.62	0.76
ANTHRACENE	4.85	3.51	8.04	4.93	3.23	0.00
FLUORANTHENE	11.10	6.34	16.76	17.71	10.80	1.29
PYRENE	8.94	5.12	11.59	16.10	9.58	1.20
BENZOAANTHRACENE	1.68	0.64	2.41	9.91	6.71	1.17
CHRYSENE	1.53	0.00	2.81	11.20	5.91	1.49
BDFLUORANTHENE	2.64	0.00	4.58	21.60	13.70	2.69
BKFLUORANTHENE	0.00	0.00	00.0	27.80	11.40	3.56
Bapyrene	0.00	0.00	2.46	40.90	19.20	4.86
INDENOPYRENE	0.00	0.00	2.51	68.50	30.50	11.00
DIBENZOANTHRACENE	0.00	0.00	00.00	24.30	8.16	3.78
BENZOPERYLENE	0.00	0.00	0.00	09.09	22.30	8.77
· · · · · · · · · · · · · · · · · · ·	•				9	3
TOTAL (ug/g)	62.8	34.6	133.0	331.20	160.49	41.09

Table 4 Area and Volume of PAH contaminated sediments

Depth	PAH Concentration#	Area	Volume*
(cm)	(µg/g)	(ha)	(M^3)
0-2	800	1.24	3,260
	400	2.98	8,540
	200	<u>5.04</u>	18,300
	total	9.26	30,100
2-4	800	1.65	2,300
	400	4.88	16,000
	200	<u>8.68</u>	<u>19,800</u>
	total	15.21	38,100
4-6	800	3.06	6,700
	400	9.59	26,800
	200	<u>8.59</u>	14,800
	total	21.24	48,300
10-12	800	1.72	2,600
	400	8.17	25,600
	200	4.49	3,400
	total	14.38	31,600
Mean**	800	3.60	11,100
	400	6.43	20,000
	200	<u>2.77</u>	6,600
	total	12.80	37,700
Max/surface	800	5.58	20,000
-	400	10.1	25,000
	200	6.56	10,400
•	total	22.25	55,400

^{*}Sediment containing 200-400, 400-800 and more than 800 μ g/g of PAHs.

^{*}Assumes dredging is done until uncontaminated sediment is reached.

**Arithmetic mean of PAH concentration from surface to deepest sediment with an undetectable PAH concentration.

As per above except that the contour isopleths are the maximum concentration of PAHs in the sediment from 0-2 to 10-12 cm.

METALS IN HAMILTON HARBOUR HOTSPOT SEDIMENT

i) Acid Extractable Metals

Sampling Station:	(ng/g)	Co (ng/g)	Cr (ug/g)	Cu (úg/g)	Fe (mg/g)	Mn (mg/g)	Hg (ng/g)	Ni (09/6n)	Pb (ug/g)
M3 (1)	7.8	25.0	NO	159.0	46.3	1.91	N.D.	55.0	429.0
M3 (2)	10.0	15.0	55.9	119.0	64.1	1.66	0.666	N.D.	N.O.
M4 ·	6.0	19.9	70.7	88.7	29.8	1.36	140.0	N.D.	N.D.
M5	6.0	20.0	19.0	61.0	25.8	1.08	90.1	N.D.	N. O.

* N.D. = Not determined

Table 5 (continued)

METALS IN HAMILTON HARBOUR HOTSPOT SEDIMENT

i) Acid Extractable Metals

Sampling Station:	Depth (cm)	(6/6n) Cq	Co (ng/g)	(ng/g)	Fe (mg/g)	Hg (ng/g)	Mn (mg/g)	(6/6n)	Pb (ug/g)	Zn (mg/g)
	0-2	4.3	8.5	117.0	89.8	9.7	1.62	31.2	399	2.74
	2-4	5.1	8.0	111.0	94.0	19.2	1.66	34.4	208	4.00
	10-12	6.6	12.4	77.4	267.0	36.3	4.56	21.4	982	4.28
	0-5	3.3	9.4	83.6	59.7	8.4	1.58	31.8	215	1.76
	2-4	4.2	9.5	86.0	9.79	19.0	1.67	37.7	303	2.19
	10-12	5.8	7.2	81.0	83.6	.	1.94	28.2	521	4.08
	0-2	3.2	7.2	77.9	0.09	6.1	1.52	29.8	203	1.53
	2-4	4.0	6.5	67.0	63.9	10.9	1.55	26.9	308	2.44
	10-12	5.8	7.0	77.0	93.5	15.9	1.91	32.5	492	4.16
	0-2	1.8	6.9	43.8	49.2	4.8	1.04	21.7	136	0.99
	2-4	2.2	0.9	36.9	44.8	10.0	0.87	17.5	137	0.91
	10-12	0.1 2	7.2	31.6	52.7	4.0	0.94	25.6	97	0.35
	0-2	1.7	6.5	37.0	33.3	4.1	1.00	18.1	94	0.64
	2-4	1.7	6.2	38.4	36.8	5.6	1,11	16.2	109	0.61
	10-12	<1.0 <1.0	7.2	25.7	28.3	0.3	0.75	13.0	307	0.22

Table 5 (continued)

METALS IN HAMILTON HARBOUR HOTSPOT SEDIMENT

ii) Water Extractable Metals (1:1)

Sampling Station:	AI (ug/L)	(ng/L)	Co (ng/L)	Cu (ng/L)	Fe (mg/L)	Mn (mg/Ŀ)	Hg (ng/L)	Ni (ug/L)	Pb (ug/L)	Zn (ng/L)
M2	508.0	3.4	6 .	70.2	2.68	0.58	520.0	හ. ස	370.0	2560.0
M3 (1)	635.0	6.0	3.0	16.3	5.88	1.63	N.D.	9.6	65.7	382.0
M3 (2)	1270.0	2.4	9.6	81.2	7.56	18.20	160.0	8.09	114.0	1:150.0
4Μ	188.0	V	1.0	7.4	0.25	0.73	N. O.	2.2	 6	11.8
M5	619.0	0.5	9. 1.	3.4	3.19	2.13	Z. Ö.	11.2	50.2	264.0
M6	490.0	1.2	1.4	53.2	1.68	1.20	140.0	10.4	50.6	284.0
6W	684.0	2.2	1.2	44.8	9.38	1.96	160.0	11.6	132.0	1030.0
M1.1	786.0	4.4	1.6	65.8	12.50	1.72	260.0	17.4	191.0	1500.0

^{*} N.D. = Not determined

Table 6

Sam	ple	РАН	(µg/g) [^]	EC ₅₀
A1	0-2	282		121
	2-4	342		120
	10-12	557		84: "
B2	0-2	370		(370)*
	2-4	447		67
	10-12	743		37
C4	0-2	184		220*
	2-4	361		65
	10-12	167)	17
	0-2	63		25
	2-4	35		11
	10-12	133		13
	0-2	331		165
	2-4	160		29
	10-12	_54		5
mea	.'n	282		90

Polynuclear aromatic hydrocarbons determined by GC/MC *Sample was not toxic.
*Extrapolated value.

Appendix 1		Description of Sediment Cores (numbers in brackets represent odor	ediment Cores ets represent odor o	on a scale of 1 to 10	Description of Sediment Cores (numbers in brackets represent odor on a scale of 1 to 10, 10 being the worst)	
Depth	A-1	A-2	A-3	A-4	A-5	Ą-6
0-1.7 cm 1.7-3.4 3.4-5.1	-oil smeil -pitch black	-very smelly & shiny pitch black	-"clean", dead worm -sticks &	-brown surf. -black	-viscous, colloidal oxidized layer	-brown skim -black and smelly
5.1-6.8 6.8-8.5 8.5-10.2	and streaky with a sheen		blacker than above	-FOUL oily smell	-black shiny smelly, like other cores	COTES
11.9-13.6 13.6-15.3 15.3-17	= 2 >	->	-stinkier and blacker	>		
17-18.7 18.7-20.4 20.4-22.1	-lighter marbling &		>	-gravelly		
22.1-23.8 23.8-25.5 25.5-27.2	selddid -		-small bits of hard, porous	-purple oily film		-never hit granular
27.2-28.9 28.9-30.6	- -			-gritty iron ore pellets? (rusty)	,	
32.3-34 32.3-34 34-35.7			-gravelly			
35.7–37.4 37.4–39.1 39.1–40.8	> <u></u>	-shiny milk chocolate colour (oily sheen),	-sewage.smell (still black)		-gritty layer starts	
42.5-44.2 44.2-45.9 45.9-47.6 47.6-49.3		very surriv		-very gritty, smelly & oily		
49.3-51 51-52.7			-mud turns to brown		,	
54.4–56.1 56.1–57.8 57.8–59.5 59.5–61.2			1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1		-drier and not gritty	
61.2-62.9 62.9-64.6 64,6-66.3						

A-11	-smooth mud -gravelly (7) -chunky -pure COAL TAR? -very stlcky tar
A-10	-light brown surflittle shells & gravel, not much smell harbled with black
6-A	-live worms, smell not bad -old snail shells -gravelly, marbled stinky stinky
A-8	-brown layer, live worms, still smells -very gravelly (fron ore) -smell stronger than at surfgets less gravelly here
A-7	-clay layer starts, still smells a bit
Depth	0-1.7 cm 1.7-3.4 3.4-5.1 5.1-6.8 6.8-8.5 8.5-10.2 10.2-11.9 11.9-13.6 11.9-13.6 13.6-15.3 15.3-17 17-18.7 17-18.7 17-18.7 17-18.7 17-18.7 18.7-20.4 20.4-22.1 22.1-23.8 23.8-25.5 27.2-28.9 28.9-30.6 30.6-32.3 32.3-34 34.2-45.9 44.2-45.9 45.9-47.6 45.9-47.6 45.9-47.6 52.7-54.4 54.4-56.1 56.1-57.8 56.1-57.8 56.1-62.9 66.9-64.6

A-16	-brown sand, pebbles -sand, black streaks	-brown sand, specks of black	->	-no more black	_>	-some plant matter	-little bit of clay																		
A-15	-sandy, shells, detritus -drier	-sand, light clay streaks -no shells, "tobacco"	-just sand -sand streaked with clav	-even more clay	-few shells	-lots of "tobacco",	NO BLACK IN CORE	-1/4 is shells														-			
Ą-14	-sandy, light brown -patches of gravel -hlackish metal flakes2	-darker, shells, clay streak -shells & black detritus	-clay & snail shells	-light clay & snail	süeits —	V -darker clav drier	-"tobacco"-like bits	dry, sandy clay, shells	-dark clay/sand, still shells	-lots of organic matter,	dark sand, bit of clay														-
A-13	-crumbly gravel, silty -clay, gravelly, grey -still no black	small dark streak	l tiny snail	Shells	-drier, brown	organic material	-lots of yellowy brown	like tobacco					·												
A-12	-sandy, light & dark patches, snail shells, detritus																								
Depth	0-1.7 cm 1.7-3.4 3.4-5.1	5.1-6.8 6.8-8.5	8.5-10.2 10.2-11.9	11.9-13.6 13.6-15.3	15.3-17	17-18.7 18.7-20.4	20.4-22.1 22.1-23.8	23.8-25.5	25.5-27.2 27.2-28.9	28.9-30.6	30.6-32.3 32.3-34	34-35.7	35.7-37.4	37.4-39.1 39.1-40.8	40.8-42.5	42.5-44.2	45.9-47.6	47.6-49.3	51-52.7	52.7-54.4	54.4-56.1 56.1-57.8	57.8-59.5	59.5-61.2 61.2-62.9	62.9-64.6	64.6-66.3

A-21	-wet, black, shiny -clay in shiny black -more clay -gelatinous, pitch black -more clay streaks -brown sand, light clay, black streaks -no black in sand
A-20	-light surf, then dark -gelatin. oily black -as above, air pockets - more black & oily, strong oily smell -clay starts -sandy, more clay -more sand -black still in sand - sand - v
A-19	-green, fluffy surfbrown/black, shiny -shiny black streaks -brown, black globs -clay, globs of pitch black oily sheen v -black, no clay
A-18	-light sand, detritus -black streaks -clay streaked into light black -cracks from air spaces -black & shiny -black, clay streaks, air spaces -black, moist, shiny, clay streaks
A-17	-light brown & black -pitch black in dark brown sand, TARRY -pitch black, gravel, shells, clay -shiny, no clay -dark brown sand, no shells or gravel -oily smell, darker (almost black) -shells, air pockets -black/brown clay starts -black goo, abrupt start to dry clay layer -light clay, no streaks -light clay, no streaks
Depth	0-1.7 cm 1.7-3.4 3.4-5.1 6.8-8.5 6.8-8.5 10.2-11.9 11.9-13.6 13.6-15.3 15.3-17 17-18.7 17-18.7 17-18.7 18.7-20.4 20.4-22.1 22.1-23.8 23.8-25.5 25.5-27.2 27.2-28.9 28.9-30.6 30.6-32.3 32.3-34 34-35.7 35.7-37.4 39.1-40.8 40.8-42.5 44.2-45.9 45.9-47.6 47.6-49.3 49.3-51 55.7-54.4 54.4-56.1 56.1-57.8 55.9-61.2

Description of Sediment Cores (numbers in brackets represent odor on a scale of 1 to 10, 10 being the worst)

B-5	-very wet, brown skim -black mottled (6) -dark but not pitch black (7-8) -pitch black mottled with light black, looks "rich" -consistently black -mottled again	-clay plug
B-4	-light brown skim (5) - (7) -streaked black with brown-gray -clay plug	
B-3	-light brown skim (4) -brown with shiny, pitch black material(7) -thick pitch black (8) many gas bubbles bubbles v -pitch black and sticky -streaked but not as black as at 18 cm -piece of wood takes up	rost of slice
B-2	-fhin brown skim -(3) -foul smelling, black: -less smell than above -smell gets worse again	>
B-1	-brown skim (4) -very shiny black (8) -still very foul, shiny, tarry & viscous -chocolate brown, consistency as	above (7) -mottled iron ore, brown & clay (3) -no longer mottled black-brown (no sheen) (4)
Depth (cm)	0-1.7 cm 1.7-3.4 3.4-5.1 5.1-6.8 6.8-8.5 8.5-10.2 10.2-11.9 11.9-13.6 13.6-15.3 15.3-17 17-18.7 18.7-20.4 20.4-22.1 22.1-23.8 23.8-25.5 27.2-28.9	28.9-30.6 32.3-34 34-35.7 35.7-37.4 37.4-39.1 39.1-40.8 47.6-49.3 47.6-49.3 49.3-51 57.4-56.1 57.8-59.5 67.8-59.5 67.8-59.5 67.9-64.6

B-10	-sand & clay -streaky clay -clay, shells, black		v v v v "tobacco", shells in sandy light grey clay			->					· ·									
B-9	-light brown, very firm & gritty (3)	-still sandy, light brown (1)										·								
B-8	-brown & blackish -chunks of metal	(9) -	-clay plug																	
B-7	-thin brown skim (5)		-sandy bottom (0)																	
B-6	-(4) -more smelly		-mottiled but not really black		-mostly grey with	much drier than	above 	>												
Depth (cm)	0-1.7 cm 1.7-3.4 3.4-5.1	5.1-5.8 6.8-8.5 8.5-10.2 10.2-11.9	11.9-13.6 13.6-15.3 15.3-17 17-18.7 18.7-20.4 20.4-22.1	22.1-23.8 23.8-25.5 25.5	27.2-28.9	30.6-32.3	32.3-34 34-35.7	35.7-37.4	39.1-40.8	42.5-44.2	44.2-45.9 45.9-47.6	47.6-49.3	51-52.7	52.7-54.4	54.4-56.1 56.1-57.8	57.8-59.5	59.5-61.2	61.2-62.9	62.9-64.6	64.6-66.3

B-15	-runny black below brown -streaky dark brown -dry sand, dark brown	-gelatinous brown & black, olly	-brown, tarry, olly	-gelatin, clay & dark brown -hlack olly nelations	-brown sand, no black	-sand brown, clay on bottom	-light grey clay								
B-14.	-brown moist sand -drier, bit of "tobacco"	dry pure sand, dark brown													
B-13	-algae, fine sand, grey -fine sand, shades of grey V	-bit lighter, shells	-fewer shells, uniform fawn colour	-lighter sand	-dark brown sand & lighter patches, shells, "tobacco", no smell	-v. dry.sand, detritus									
B-12	NO CORE												ì		
B-11	-sandy, shells & stones -dry, shells, brown sand -drier, fewer shells, looks clean	>													
Depth (cm)	0-1.7 cm 1.7-3.4 3.4-5.1 5.1-6.8 6.8-8.5	8.5-10.2 10.2-11.9 11.9-13.6	13.6-15.3 15.3-17 17-18.7	18.7-20.4 20.4-22.1 22.1-23.8	23.8-25.5 25.5-27.2 27.2-28.9	28.9-30.6 30.6-32.3	35.7-37.4	37.4-39.1 39.1-40.8 40.8-42.5	42.5-44.2 44.2-45.9 45.0-47.6	47.6-49.3 49.3-51	51-52.7 52.7-54.4	54.4-56.1	57.8-59.5 59.5-61.2	61.2-62.9 62.9-64.6 64.6-66.3	1

B-19	-black & watery dark brown -dark black shiny gelatin -dark brown, black streaks -TAR pitch black, lighter streals, gelatinous
B-18	-black under light brown -gelatinous, black ooze -stinky, black streaks -lighter black streaks
B-17	-wet, v.black, light surfpitch black, patchy brown-pitch black gelatinous material, air pockets, shiny, stinky V -light grey, wet, pitch black shiny globules sandy dark brown, drier, smelly, oily sheen dark brown sand, black clay streaks, oily sheen
B-16	-green on top -black, shiny, air spaces -pitch black, lighter streaks -pitch, oily black, light brown patches, stinky -VERY TARRY, sticky, very light grey clay streaks
Depth (cm)	0-1.7 cm 1.7-3.4 3.4-5.1 5.1-6.8 6.8-8.5 6.8-8.5 10.2-11.9 11.9-13.6 13.6-15.3 15.3-17 17-18.7 17-18.7 17-18.7 17-18.7 17-18.7 17-18.7 17-18.7 17-18.7 17-18.7 17-18.7 17-18.7 17-18.7 17-18.7 17-18.7 17-18.7 17-18.7 17-18.7 18-18.9 18-19.7

Description of Sediment Cores (numbers in brackets represent odor on a scale of 1 to 10, 10 being the worst)

C-5	-brown layer (6) -streaks of black -shiny pitch black (8)	sand starts sand firm, grayish black	-pure sand, (1), no black		· !
G-4:	-slight smell, it brown -black, fine & gooey	-(5) nastier smell & gooey	- >	less bad smell from here down -clay starts -lighter brown (4)	-very dry; fine sand (3)
C-3	-light brown surf (5) -mottled black (8) -sand, no black, dry			·	
C-2	-black & nasty below surface -mottled black, no shininess -very firm sand, few black streaks	; 6	>		į
L-0	-thin skim, watery (6) -streaked with black (8)	<u></u> >	-nasty, thick shiny grayish black (9)	(not inclined) V	-black but not shiny as above (5)
Depth (cm)	0-1.7 1.7-3.4 3.4-5.1 5.1-6.8 6.8-8.5 8.5-10.2	10.2-11.9 11.9-43.6 13.6-15.3	15.3-17 17-18.7 18.7-20.4	22.1-23.8 23.8-25.5 27.2-28.9 28.9-30.6 30.6-32.3 34-35.7	35.7-37.4 37.4-39.1 39.1-40.8 40.8-42.5 42.5-44.2 44.2-45.9

C-10	NO CORE
6-O	-brown (streaky) sand: - (4) -sandy, blacker than above (7) -very firm clay, dark brown (50%) with black - (5) -black streaked with clay (7)
8-J	-sandy brown & black -(5) -sandy, black streaks & grey clay, steel bits
C-7	-sandy brown skim (3) -streaks of black (5) -(7) black, still sandy -50% sand:black stuff very dry
9-0	-loose brown layer (6) -black, oily smell -black but not pitch (7) -streaks of black -dry sand, streaks of grey -pure sand except few black streaks
Depth (cm)	0-1.7 1.7-3.4 3.4-5.1 5.1-6.8 6.8-8.5 6.8-8.5 8.5-10.2 10.2-11.9 11.9-13.6 13.6-15.3 15.3-17 17-18.7 17-18.7 17-20.4 20.4-22.1 22.1-23.8 23.8-25.5 25.5-27.2 27.2-28.9 28.9-30.6 30.6-32.3 32.3-34 34-35.7 42.5-44.2

					!
C-15	-shiny black under light surf -wet, dark brown/black shiny -black shiny & brown sand, shells	->	-dark brown, sticky, fine sand, shells -sand, black streaks, shells	-dark brown sand, few black streaks	->
C-14	-light brown surfblack; brown sheen -shells, sandy dark brown -sandy, air pockets, broken snail shells, black streaks		-dark brown sand, few shells	-dark brown, blackish oily sheen, shells, air pockets	
C-13	NO CORE	!			
C-12	-metal hunk, snall shells, woody matter, sandy dark grey -1/4 clay, rest dark brown sand	-v. hard clay, dry, light grey with few dark streaks			
C-1	NO CORE				
Depth (cm)	0-1.7 1.7-3.4 3.4-5.1 5.1-6.8 6.8-8.5	8.5-10.2 10.2-11.9 11.9-13.6	13.6–15.3 15.3–17 17–18.7 18.7–20.4 20.4–22.1	22.1-23.8 23.8-25.5 25.5-27.2	27.2-28.9 28.9-30.6 30.6-32.3 32.3-34 35.7-37.4 37.4-39.1 39.1-40.8 40.8-42.5 44.2-45.9

C-19	-runny, light brown -gelatinous, air pockets, black streaks	-olly sheen -gelatinous light clay & TARRY pitch black	-dark brown clay, black streaks, gelatinous, air pockets -dark brown, black clay streaks	-dry dark grey clay, shells, black streaks	-dark grey, darker streaks, sand, alr pockets -sandy gravel, small shells dark grey, darker streaks
C-18	-light brown surt, black -black gelatinous, lighter streaks	dark brown streaks in gelatinous black, oily, shiny material	- >	-gelatinous dark brown & grey, air pockets	dark grøy, black streaks, sticky
C-17	-light brown surf, black -black shiny, light streaks, very wet	l V -drier, gelatinous, air spaces -as above, olly sheen	-clay streaked into pitch shiny black, all gelatinous -dark brown/black sand starts	,	
C-16	-black speckled with brown shiny, runny, light brown surf -black gelatin, brown streaks	-dark, gelatinous black streaks, TARRY, air pockets I	>	-clay, many streaks of tarry black shiny material	
Depth (cm)	0-1.7 1.7-3.4 3.4-5.1 5.1-6.8	8.5-10.2 10.2-11.9 11.9-13.6 13.6-15.3	17-18.7 18.7-20.4 20.4-22.1 22.1-23.8 23.8-25.5 25.5-27.2	27.2-28.9 28.9-30.6 30.6-32.3	34-35.7 35.7-37.4 37.4-39.1 39.1-40.8 40.8-42.5 42.5-44.2

Description of Sediment Cores

	(numbers in brackets represent odor on a scale of 1 to 10, 10 being the worst)
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D-5	-brown top -sand starts, black (5) -blacker -1/2 ebony, 1/2 lighter -not as bad as above (8) -sandy black (not too dark) (4) v -brown black sand	
.3 D-4	- (6) -sand starts, black streaks -clay starts, 50% ebony, 50% clay -dark brown & black (5) -sandy streaky -dirty sand (4)	
D-3	-light brown (4) -streaks of black (6) -mostly black & sticky (8) -pitch black (9) -black, 50% mottled grey (7) V -pitch black again (8-9) -mottled, 1/3 jet blackdirty sand, brown (5)	-sand bit dirty, (2), dry, black streaks
D-2	-brown on top (5) -very shiny pitch black (9) -black, streaky brown -more dark brown clay than black (5)	
<u>-</u> -0	-oozy, brown layer (3) -bit darker (5) -pitch black (8), 50% sand / V -pitch black, shiny (9) shiny (9) V -less intense black (8) -clay layer begins -VERY sticky & gummy,	dark, streaky clay, mild smell
Depth (cm)	0-1.7 1.7-3.4 3.4-5.1 5.1-6.8 6.8-8.5 6.8-10.2 10.2-11.9 11.9-13.6 13.6-15.3 15.3-17 17-18.7 18.7-20.4 20.4-22.1 22.1-23.8	25.5-27.2 27.2-28.9 28.9-30.6 30.6-32.3 32.3-34 34-35.7 35.7-37.4 39.1-40.8 40.8-42.5 42.5-44.2 42.5-44.2 45.9-47.6 47.6-49.3 51-52.7 51-52.7 52.7-54.4 54.4-56.1 56.1-57.8 57.8-59.5 62.9-64.6 64.6-66.3

Description of Sediment Cores (numbers in brackets represent odor on a scale of 1 to 10, 10 being the worst)

D-10	ry (2) -brown runny sandy gravel riety -light brown sand, no terial black, reddish streaks / / / -black layer in sand, gravel	shells, streaky black sand
	-complex, much clay (2) -some black, very grey bits of unknown material -no smell, no black -still no smell	
D-8 D-9	-darker towards bottom -sandy (4) - (6)	
D-7	-brown -(7) -gritty, streaks of ebony through black (7) -mottled, hard clay with black streaks -very hard sand, dark but not black (1) -black reappears in sand (4)	
D-6	-no brown on top (7) -muddy clay -dry heavy clay -gritty layer (3) -steel chunks and clay	
Depth (cm)	0-1.7 1.7-3.4 3.4-5.1 5.1-6.8 6.8-8.5 6.8-8.5 10.2-11.9 11.9-13.6 13.6-15.3 15.3-17 17-18.7 18.7-20.4	22.8-25.5 25.5-27.2 27.2-28.9 28.9-30.6 30.6-32.3 32.3-34 32.7-37.4 35.7-37.4 47.6-49.3 49.3-51 52.7-54.4 54.4-56.1 56.1-57.8 61.2-62.9 61.2-62.9

Description of Sediment Cores (numbers in brackets represent odor on a scale of 1 to 10, 10 being the worst)

Depth (cm)	D-11	D-12	D-13	D-14
0-1.7 1.7-3.4 3.4-5.1 5.1-6.8	-green & woody on surf. -dry grey clay, stones, black streaks	-sandy dark brown, lighter brown surf.	-it brown surf, dead worm -sandy, light black -dk brown, black streaks	-dark brown -dark brown
6.8-8.5 8.5-10.2 10.2-11.9			-dk brown sand, few shells	
11.9-13.6 13.6-15.3 15.3-17 17-18.7			-same sand, larger shells	-dark brown, black streaks
18.7-20.4				
22.1-23.8 23.8-25.5				
25.5-27.2				
27.2-28.9 28.9-30.6				
30.6-32.3				
34-35.7				·
35.7-37.4				
39.1-40.8				
40.8-42.5 42.5-44.2				
44.2-45.9				
45.9-47.6				
49.3-51				
51-52.7				
52.7-54.4				
54.4-56.1 56.1-57.8			•	
57.8-59.5				
59.5-61.2				
61.2-62.9				
62.9-64.6				
64.6-66.3				

Description of Sediment Cores (numbers in brackets represent odor on a scale of 1 to 10, 10 being the worst)

(ille worst)	E-5	-a bit black under surface -grey streaked with black (7) -mottled greybrown, black streaks, gooey clay (5) -less black (3), sand streaked with clay -mottled, mostly red sand (2) -sand with bits of shells? -mottled, some black, sandy (2)
(HUILIDELS III DIACAGIS LEPIESEII OUGI OII A SCAIG OI 1 (O 10, 10 DEILIG IIIG WOISI)	E-4	-brown on top -(7) -black with shiny ebony streaks (5) -more brownish -dark, lots of metal chunks (3) -very sandy, white metal chunks, no black
nachels lepresent odor o	E-3	-brown layer (7) -sandy, bits of steel -sandy, tar, not as dark as above -dark but not ebony
	E-2	lost core
	7	-black under surt. (5) - (7) - (8) black shiny foul -sandy less fout, lighter (6.5) -clay, sticky light brown with black streaks, gummy
	Depth (cm)	0-1.7 1.7-3.4 3.4-5.1 5.1-6.8 6.8-8.5 8.5-10.2 10.2-11.9 11.9-13.6 13.6-15.3 15.3-17 17-18.7 17-18.7 17-18.7 17-18.7 17-18.7 17-20.4 20.4-22.1 22.1-23.8 23.8-25.5 27.2-28.9 28.9-30.6 30.6-32.3 32.3-3 32.3-3 32.3-3 32.3-4 34-35.7 35.7-37.4 37.4-39.1 39.1-40.8 40.8-42.5 47.6-49.3 49.3-51 55.7-54.4 55.7-54.4 55.7-54.6 66.2-64.6

Description of Sediment Cores (numbers in brackets represent odor on a scale of 1 to 10, 10 being the worst)

8-W	-clay streaks, pellets -grey, black, light brown streaks -very firm sand -gritty /
E-7	- (5) -black & streaked (7) -(6) mottled with some black -(5) -sand still (4) -clay mottled into sand (4)
9- 9-	-brown on top (2) -greybrown sand (3) -darker black (6) -streaks of ebony & clay through sand -brown black sand (4) \frac{1}{V} -sand, streaked with shades of brown (2) -(1)
Depth (cm)	0-1.7 1.7-3.4 3.4-5.1 5.1-6.8 6.8-8.5 6.8-8.5 10.2-11.9 11.9-13.6 13.9-17 17-18.7 17-20.4 20.4-22.1 22.1-23.8 23.8-25.5 27.2-28.9 28.9-30.6 30.6-32.3 32.3-34 34-35.7 37.4-39.1 39.1-40.8 47.6-49.3 47.6-49.3 45.9-47.6 47.6-49.3 57.7-57.4 56.1-57.8 56.1-57.8

Description of Sediment Cores (numbers in brackets represent odor on a scale of 1 to 10, 10 being the worst)

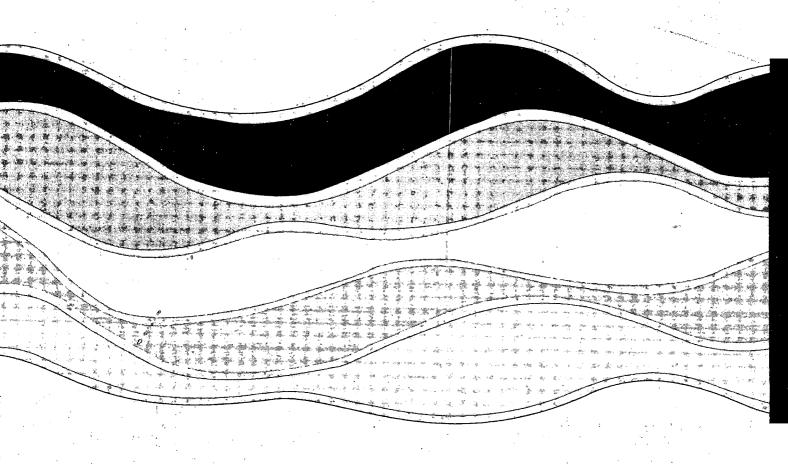
G-1	-light brown surface, black streaks, clay, TAR globs -clay, black streaks -fewer black streaks, drier	-sandy, greyish, very dry, shells -very sandy, no black	-light sand, light black streaks	,				
F-2	-light top, sandy dark brown -dark brown sand, oily, smeily -drier	-stinky, olly film distinct, black brown gelatinous mud, no sand	-black sand	-dry black sand, lighter streaks, broken snail shells				
Ξ.	-green surf, olly film -black brown, olly V	-pitch black gelatinous oily film -sandy brown, oily -brown sand, no black						,
Depth (cm)	0-1,7 1,7-3,4 3,4-5,1 5,1-6,8	8.5-10.2 10.2-11.9 11.9-13.6 13.6-15.3	1/-10.7 18.7-20.4 20.4-22.1	22.1-23.8 23.8-25.5 25.5-27.2	27.2-28.9 28.9-30.6 30.6-32.3	35.7-37.4 35.7-37.4 37.4-39.1 39.1-40.8	42.5-44.2 42.2-45.9 45.9-47.6 47.6-49.3 49.3-51	51-52.7 52.7-54.4 54.4-56.1 56.1-57.8 57.8-59.5 61.2-62.9 62.9-64.6 64.6-66.3



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