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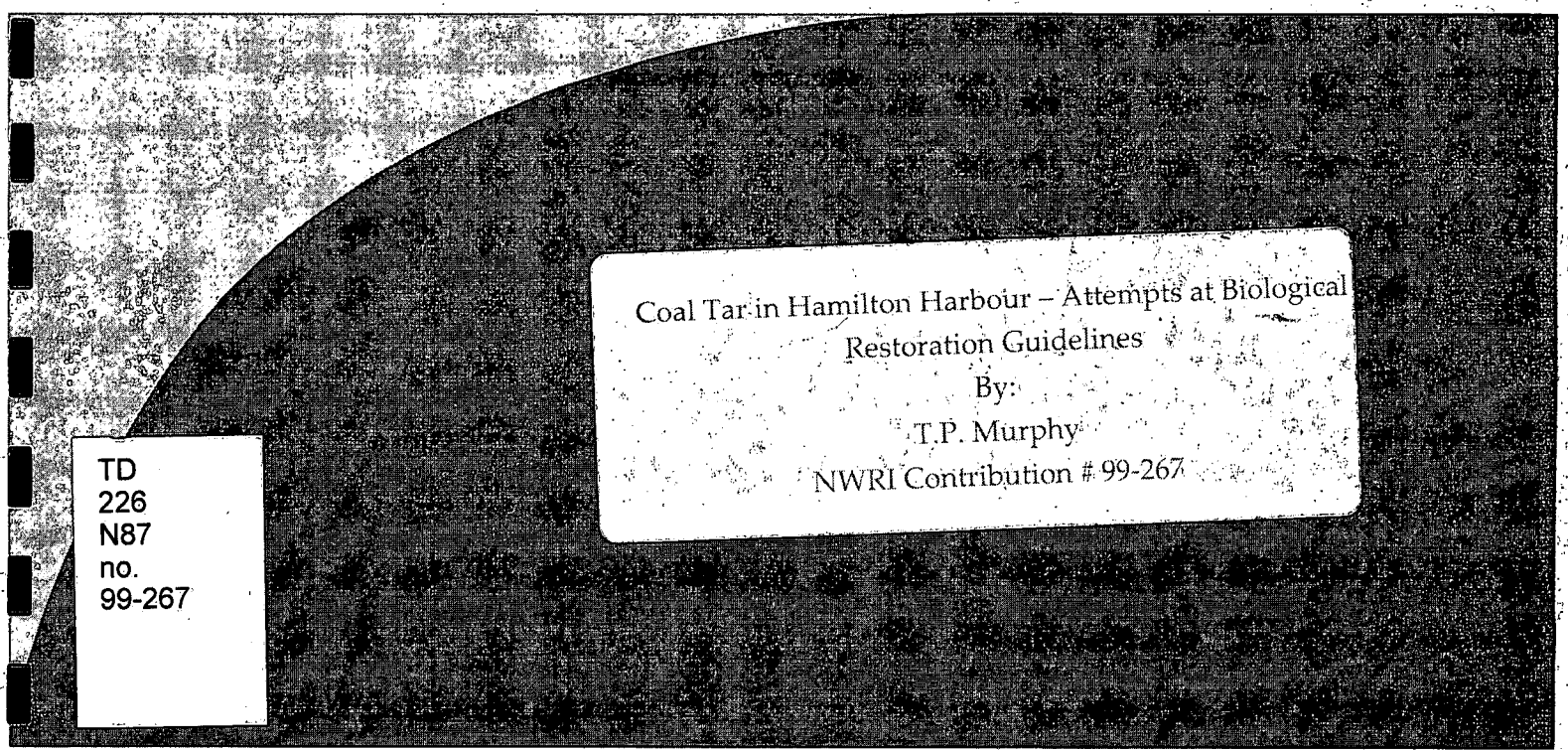

99-267

Coal Tar in Hamilton Harbour - Attempts at Biological Restoration Guidelines

T. P. Murphy

Abstract

Sediments in Hamilton Harbour contain extremely high concentrations of PAHs and other contaminants. Two bioassays were used initially to find hotspots. Three bioassays were used to develop a criteria for cleanup. The bioassays in these sediments yielded the following LC_{50} and EC_{50}'s for PAHs; *Hexagenia* 329 µg/g, *Daphnia* 254 µg/g, and Microtox™ 89 µg/g. The mean bioassay toxicity was rounded down to 200 µg/g and used to define areas in need of treatment. Simple aspects like oil content, ship traffic, and water depth were also used to priorize PAH cleanup.

Manuscript Perspective

Guidelines for sediment cleanup continue to change. In general, early standards used chemical analyses. However, these guideline chemical concentrations were all based upon bioassays. Site specific guidelines are usually developed to address current action plans and realities of the site. In Hamilton Harbour, the development of a standard included chemical, biological and site-specific physical criteria. This standard has been attacked as being ultraconservative, i.e. a surgical strike; however, the cost of the smallest scientifically based cleanup is still very large.

Key Words: PAHs, cleanup guidelines, bioassays, sediments, toxicity

Élimination du goudron de houille dans le port de Hamilton –Lignes directrices provisoires pour les méthodes biologiques de remise en état

T. P. Murphy

Résumé

Les sédiments du port de Hamilton contiennent des concentrations extrêmement élevées de HAP et d'autres contaminants. Au début de l'étude, on a utilisé deux épreuves biologiques pour trouver les points chauds. Par la suite, on a utilisé trois épreuves biologiques pour l'élaboration de critères d'assainissement. Pour les HAP dans ces sédiments, les épreuves biologiques ont donné les valeurs suivantes de CL_{50} et de CE_{50} : *Hexagenia*, 329 µg/g; *Daphnia*, 254 µg/g; et Microtox^{MC}, 89 µg/g. On a arrondi à 200 µg/g la valeur moyenne de toxicité des épreuves biologiques et on l'a utilisée pour définir les zones qui avaient besoin de traitement. On a également utilisé de simples facteurs comme la teneur en hydrocarbures, l'intensité du trafic maritime et la profondeur de l'eau afin d'établir des priorités pour l'assainissement des zones contaminées par les HAP.

Sommaire à l'intention de la direction

Les lignes directrices pour l'assainissement des sédiments continuent à évoluer. En général, les normes antérieures étaient basées sur des analyses chimiques, mais les concentrations de substances chimiques des lignes directrices étaient aussi fondées sur des épreuves biologiques. On élabore habituellement des lignes directrices propres à un site pour répondre aux besoins des plans d'action en cours, ainsi que pour tenir compte des conditions réelles des sites. Lors de l'élaboration de lignes directrices pour le port de Hamilton, on a utilisé des critères chimiques et biologiques, ainsi que des critères physiques propres au site. Certain ont critiqué ces lignes directrices en alléguant qu'elles étaient beaucoup trop conservatrices, c.-à-d. qu'elles avaient l'allure d'une intervention chirurgicale. Toutefois, le coût des travaux d'assainissement basés sur des principes scientifiques, même à petite échelle, sont encore très élevés.

Mots clés : HAP, lignes directrices d'assainissement, épreuves biologiques, sédiments, toxicité

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Coal Tar in Hamilton Harbour—Attempts at Biological Restoration Guidelines

Tom Murphy

National Water Research Institute, 867 Lakeshore Road, Burlington, Ontario, Canada L7R 4A6

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ABSTRACT: Sediments in Hamilton Harbour contain extremely high concentrations of polycyclic aromatic hydrocarbons (PAHs) and other contaminants. Two bioassays were used initially to find areas with the worst contamination. Three bioassays were used to develop criteria for cleanup. The bioassays in these sediments yielded the following 50% lethal and 50% effective concentrations for PAHs; *Hexagenia* 329 μg/g, *Daphnia* 254 μg/g, and Microtox™ 89 μg/g. The mean bioassay toxicity was rounded down to 200 μg/g and used to define areas in need of treatment. Simple aspects like oil content, ship traffic, and water depth were also used to prioritize PAH cleanup. Environ Toxicol 15: 484–495, 2000

Keywords: PAHs; cleanup guidelines; bioassays; sediments; toxicity

INTRODUCTION

Hamilton Harbour has Canada's highest concentration of heavy industry. Two steel mills, related industries, and neighboring cities once discharged wastes with little treatment into the harbor. An extensive remedial action plan (RAP) has made considerable progress in restoring the area. Notable highlights include greatly improved public access with swimming beaches, substantial new wildlife habitat, and better water quality. However, certain legacies of the past such as contaminated sediments are difficult to remediate. Sediments near outfall pipes from steel mills have concentrations of polynuclear aromatic hydrocarbons (PAHs) exceeding 800 μg/g (Fig. 1; Murphy et al., 1990). Sediments from other sites with lower PAH concentrations than the Hamilton Harbour hotspots have been linked to the induction of fish lesions and tumors; Eagle Harbor, Washington (Swartz et al., 1989), Black River, Ohio (Fabacher et al., 1988), and Vancouver Harbour, British Columbia (Brand and Goyette, 1989). The concentration of papillomas on white suckers from Hamilton Harbour is high (35%, Hamilton Harbour Stage 1 RAP 1992, Hamilton Harbour Stage 2 RAP 1992). A main goal for the Hamilton Harbour remedial action plan is a healthy fishery (Rodgers et al., 1989). This goal cannot be achieved without treatment of these carcinogenic substances.

PAHs are a public concern and must be a focal point of remediation. However, the complexities that should be associated with PAH cleanup, such as bioavailability, are probably beyond the requirements of the first cleanup standards. Unfortunately nonpoint sources of metal and PAH contamination have not been controlled (Irvine et al., 1999; Curran, 2000) so initial sediment remediation must focus on only the most toxic coal tar hotspots. These coal tar sediments burn skin tissue, so acute toxicity is a justified parameter for initial remediation guidance. Another activity influencing sediment management is navigation. Large ships servicing the steel mill frequently resuspend contaminated sediments (Irvine et al., 1997). An aqueous elutriate bioassay with *Daphnia magna* was used to

Correspondence to: T. Murphy; e-mail: tom.murphy@cciw.ca.

detect areas prone to sediment toxin release from shipping. The choice of a second bioassay, Microtox™ reflects the history of the contamination. Areas with high concentrations of acid volatile sulfide (AVS) are found adjacent to steel mills (Brouwer and Murphy, 1994). At one time the steel mills released sulfur balls that are waste products of coking. Sulfur balls are rich in PAHs and form sediments rich in sulfide. Microtox™ responds readily to sulfide (Brouwer and Murphy, 1995). A third bioassay, *Hexagenia* was added to reflect the public objective of a healthy fishery and a desire for this organism to recolonize these sediments. The use of three bioassays to measure the worst of acute sediment toxicity provides a technical framework for a cleanup. To satisfy the public concern over PAHs, the bioassays were standardized on PAH chemistry, but certainly other toxicants including sulfides and metals influenced these bioassays. This paper reviews the procedures used to delineate contamination and attempts to develop a restoration guideline for sediments of Hamilton Harbour.

METHODS

Sample Collection

In the summer of 1987 and 1988, 91 sediment Shipek grab samples were collected across all the harbor for bioassays and chemical analysis (Murphy et al., 1990; Murphy et al., 1991). Sediment cores were collected with gravity corers and 7 cm diameter polycarbonate liners (Mudroch and MacKnight, 1991). On April 11, and July 11, 1989, 81 gravity sediment cores were collected in an area north of pier 15 and west of Stelco (a large steel maker). In 1992, 17 sediment cores were collected from around the harbor for analysis of the surface sediments; global positioning system (GPS) positioning was used for these stations. On Nov. 7, 1994 31 sediment cores were collected from the area near Stelco. Positioning in the Stelco area used a T2 theodolite with a DI3000 distomat. On September 19 and 20, 1994, 45 sediment cores were collected from the Dofasco boatslip. The sample locations were approximately 26 m apart (north to south), extending from the southern tip of the boatslip to the mouth and separated by 20 m in the east to west direction. The launch Pintail was tied up to each bollard and was moved perpendicularly from the dock, taking a sample at 20 m and another at 40 m from the dock. At the mouth of the boatslip, samples were taken at 60, 80, 100, and 120 m from the dock where possible. All cores were divided at 2 cm intervals with a hydraulic extruder and visual observations were recorded. The samples were immediately stored at 4°C.

Chemical Analysis

Hydrocarbon (Oil and Grease) Analysis using Infrared Spectrometry

Wet sediment (1.0 mL), 2.0 mL distilled water, and 4.0 mL carbon tetrachloride (Caledon, analytical grade) were added to preweighed 20 mL glass vials. The vials were sealed and placed on a shaker for 18 h at 300 rpm. At this time, a portion of the extract was removed with a pipet and filtered through a cotton plug into a 0.1 mm NaCl infrared (IR) cell. Five hydrocarbon standards were prepared by dissolving known quantities of bunker oil in carbon tetrachloride. The transmittance of the samples and standards were measured from 3100 to 2600 cm^{-1} on a PYE-Unicam SP3-200 spectrometer. After the samples were measured on the IR, the excess solvent was decanted from the vials, the vials were heated to remove any remaining solvent, then they were dried in an oven to determine the dry mass of the sediment. The peak height at 2950 cm^{-1} was measured and absorbance was determined according to the equation,

$$\text{Abs} = -\log\frac{(1 - \text{peakheight} \times \text{expansion factor})}{150}.$$

A calibration curve and regression analysis were tabulated for the hydrocarbon standards. The mass of hydrocarbon in the samples was calculated according to the equation,

$$\text{mass HC} = \frac{(\text{absorption}-\text{constant})}{(x\text{-coefficient}) \times 4}.$$

Acid Volatile Sulfide

Triplicate wet fresh sediment samples were analyzed for acid volatile sulfide (AVS) using a sulfide electrode technique (Brouwer and Murphy, 1994).

Polycyclic Aromatic Hydrocarbon (PAH) Analysis

Classically, the PAH concentration of sediments is determined by gas chromatography/mass spectrometry (GC/MS) procedure. The cost of this procedure precluded conducting a detailed mapping study using this method alone. Other surrogate assays were used (UV absorption, UV fluorescence, and immunoassay) to map the distribution of PAHs and form comparisons between samples. A smaller subset of samples was analyzed by GC/MS to standardize the methods and quantify the results.

Gas Chromatographic/Mass Spectrographic (GC/MS) Procedure

The sediment sample (10 g) was spiked with a known amount of a surrogate mixture of deuterated PAHs, then extracted in a Soxhlet apparatus with an acetone-hexane (59:41, both Caledon, analytical grade) solvent mixture. The organic extract was base-partitioned with 2% potassium bicarbonate (Baker, reagent grade) solution to separate the acidic compounds from the PAHs and other neutral compounds. The aqueous medium was back-extracted with 50 mL of hexane. The organic fractions were combined, dried through sodium sulfate (Fisher, reagent grade) and concentrated to ca. 3–5 mL. The resulting solutions were analyzed for 16 selected PAHs by GC/MS under the conditions described below:

GC: Hewlett-Packard model 5890
Split splitless injection
30 m fused silica capillary column, DB-5
Injection temperature 300°C
Program: 30°C held for 1 min, 30°C to 285°C at 6°C/min, hold 16.5 min

MS: Hewlett-Packard series 5970 mass spectrometer
Source Temperature 200°C
Electron ionization 70 eV
Select ion monitoring (SIM) mode

Ultraviolet Fluorescence Analysis

In triplicate, 0.25–0.4 g of wet sediment and 4 mL deionized water were added to 20 mL screw cap glass vials and mixed gently to form a suspension. Five mL of *n*-hexane (Caledon, analytical grade) were then added and the vials were placed on a shaker for 20 hours at 300 rpm. After 20 h, 3.0 mL *n*-hexane and 50 mL of the extract were transferred into a quartz cell and mixed well. The quartz cell was placed in a Perkin Elmer LS 50 fluorescence spectrometer; the emissions for wavelengths 250 to 500 nm were recorded. The area under the curve per gram of dry sediment per mL extract was compared between samples. A statistical correlation was made between the GC/MS analysis of a small subset of samples (12) and the UV fluorescence. The results were standardized daily with a chrysene standard.

Spectrophotometric PAH Analysis

In 1994, wet sediments (equivalent of 100 mg dry mass) were placed into 20 mL screw cap glass vials with 5.0 mL of hexane. Samples were sonicated for 30 s, capped and placed on a shaker at 250 rpm for 17 h. Samples were then decanted into centrifuge tubes and centrifuged at setting 5 on an ion-exchange chromatography (IEC) centrifuge for 5 min (1200 g). Very yellow solutions were diluted with hexane and pale yellow extracts were analyzed directly. Absorption was measured at the wavelengths 210, 220, 230, 240, 250, 260, 280, and 300 nm using a baseline 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. A statistical correlation was made between the GC/MS analysis of a small subset of samples (12) and the UV absorption. In similar studies in 1989, iso-octane was used instead of hexane (Murphy et al., 1991); hexane is more compatible for fluorescence studies.

Immunoassay Protocol for PAH Determination

The Quantix PAH 50 laboratory immunoassay kit was used to detect phenanthrene, 2-methyl naphthalene, acenaphthylene, 1-methyl naphthalene, fluorene, acenaphthene, naphthalene, dimethyl naphthalene, and pyrene. Every test was validated with known PAH standards ranging from 5 to 500 ppb.

A mass of 8.4 g sediment was transferred to a 20 mL screw top glass vial with 8.4 mL isopropanol (Caledon, analytical grade). The vial was capped and shaken vigorously for 1 min, then allowed to settle. An aliquot of the solvent phase was diluted 100 fold in isopropanol, then diluted an additional 100 fold in distilled water.

Into each of the 96 wells of the microplate (except blanks) was added 200 μL of standards or sample and 50 μL of PAH conjugate. The microplate was shaken for 10 s then left to incubate without shaking for 10 min. After 10 min, the contents of the microplate were discarded and the wells were rinsed five times with a wash solution and emptied. Substrate solution (200 μL) was added to each well and the microplate was placed on a shaker for 10 min at high speed. After 10 min, 50 μL of stop solution was added to each well and the plate was shaken for 30 s. The color development was measured on a Hyperion Micro-reader III at 650 nm. A calibration curve and regression analysis were tabulated for the PAH standards from which the PAH concentration of the samples was determined.

Biological Analysis

All *D. magna*, *Hexagenia*, and *Photobacterium* bioassays were conducted in the National Water Research Institute (NWRI) laboratories. To calculate 50% lethal concentration (LC_{50}) or 50% effective concentration (EC_{50}), a dilution series was made in each bioassay by mixing varying amounts of one large sediment sample from near Stelco (station "B") with relatively clean sediment from the far west end of the harbor (station

"C"). Sediments from "C" were used as a control in all bioassays.

Photobacterium Bioassays

For the 1991 study, a sediment contact bioassay was developed using *Photobacterium phosphoreum*. 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 ^{14}C-labelled bacteria was used to determine the proportion of bacteria removed by centrifugation. The photoactivity of the *Photobacterium* was compared in each set of analyses to that of *Photobacterium* in sediments from station "C"; a relatively uncontaminated site in the northwest corner of Hamilton Harbour. Sediment dilutions were also used for the *Photobacterium* bioassay. Sediments were collected from five stations spanning the southern hotspot near Stelco at depths of 0–1, 2–4, and 10–12 cm. Full details of this new method can be found in Brouwer et al. (1990). The 1994 study used the Microtox™ direct contact bioassay procedure.

Daphnia magna 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. The samples were not aerated during the extraction. After extraction, the sediment extracts were centrifuged for 20 min at 1000 g. We chose to 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. The source water had good quality, was further purified in Canada Centre for Inland Waters (CCIW), and was routinely used in CCIW's fisheries research. Prior to all experiments, the sediment extracts were oxygenated by bubbling with purified air for 16 h.

Hexagenia Bioassay

Hexagenia (mayflies) eggs were obtained from Windsor University (Elizabeth Hanes) after collection at Riverside Drive 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, and 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 B with a Ponar dredge sampler. The nymphs were 123 days old at the start of the 21-day bioassay. Repetitions were performed in triplicate for the mayfly bioassays. Wide-mouth 2 L jars were filled with 3 cm of sediment (300 cm^3) 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.

RESULTS

The first studies of sediment grab samples discovered hotspots with extremely high concentrations of PAHs (Fig. 1). Some of the hotspots are associated with old outfall pipes from the steel mills and some probably represent old spills of coal tar. A smaller evaluation of the surface of sediment cores indicated much less PAH than was observed in the grab samples (Fig. 2). In many of the surface cores, the PAH concentration had decreased to a tenth of the grab samples. This decrease is not so obvious in the hotspots near Stelco and Dofasco, but it is also present there. The *Daphnia* bioassay maps indicate a similar large difference in surface sediments from grab samples (Figs. 3 and 4). The grab samples were most toxic near the steel mills, but the surface core sediments were most toxic near the outfall of the Burlington sewage treatment plant. The distribution of ammonia matched the latter response (Fig. 5). Ammonia toxicity seems important near the sewage outfall. The comparison of toxicity between the grab samples and the surface sediments to Microtox is also interesting (Figs. 6 and 7). The sample size is different so only a few simple observations are appropriate. The sediments near the steel mills and the deep depositional basin were the most toxic. These sediments were very reducing and sulfide toxicity is suspected. Sediments near the sewage outfall had little toxicity to Microtox. The differences in the grab samples and the surface samples reflects that the harbor sediments are recovering.

The hotspots were studied in more detail. Two simple measurements of the sediments in the Stelco area are useful. First, the water content of the sediments in the southern part of the site is much higher than the northern part (Fig. 8). This reflects changes in water depth and shipping activity. The sediments in the southern shallow water column (2–8 m) are more readily resuspended by ships than the northern sediments in deeper water (>15 m). Second, the southern sedi-

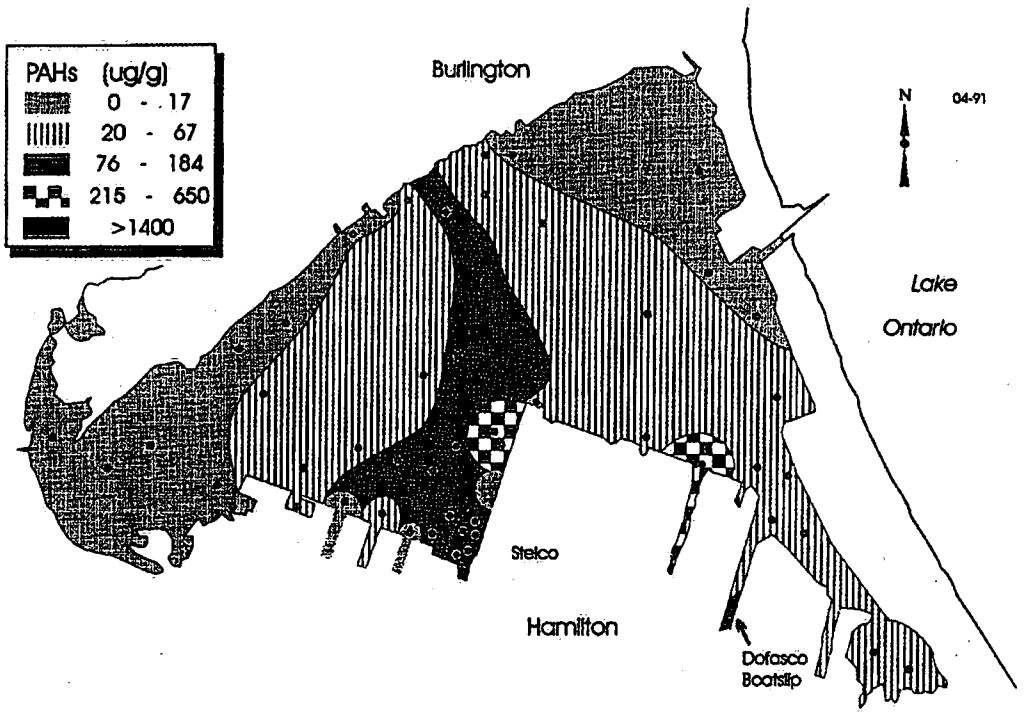

Fig. 1. PAHs in surface sediments, grab samples.

ments have much more oil than the northern sediments (Fig. 9). Probably PAHs in oil are more bioavailable (Hughes et al., 1997). This second aspect is less certain than the first, but collectively both arguments were used to prioritize action on the southern sediments first. A third point of utility is the coefficient of variation of analyses in the contaminated sediments with a high water content and frequent ship resuspension was less than 10%. The sediments further to the north in deeper water were much more variable.

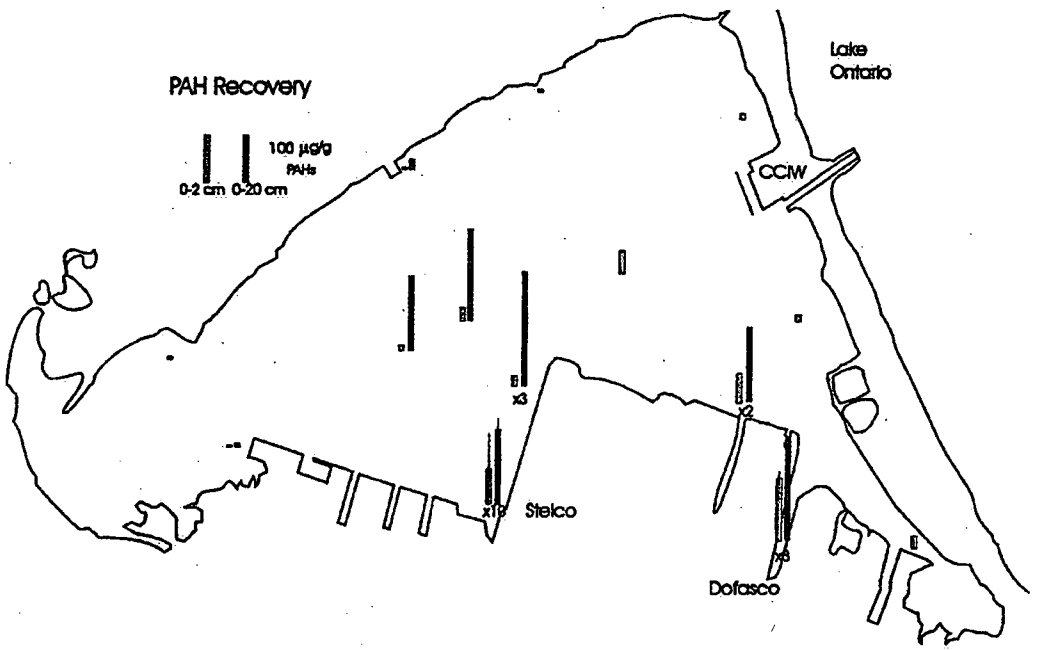

Fig. 2. PAHs in surface 0–2 cm of sediments vs. grab samples.

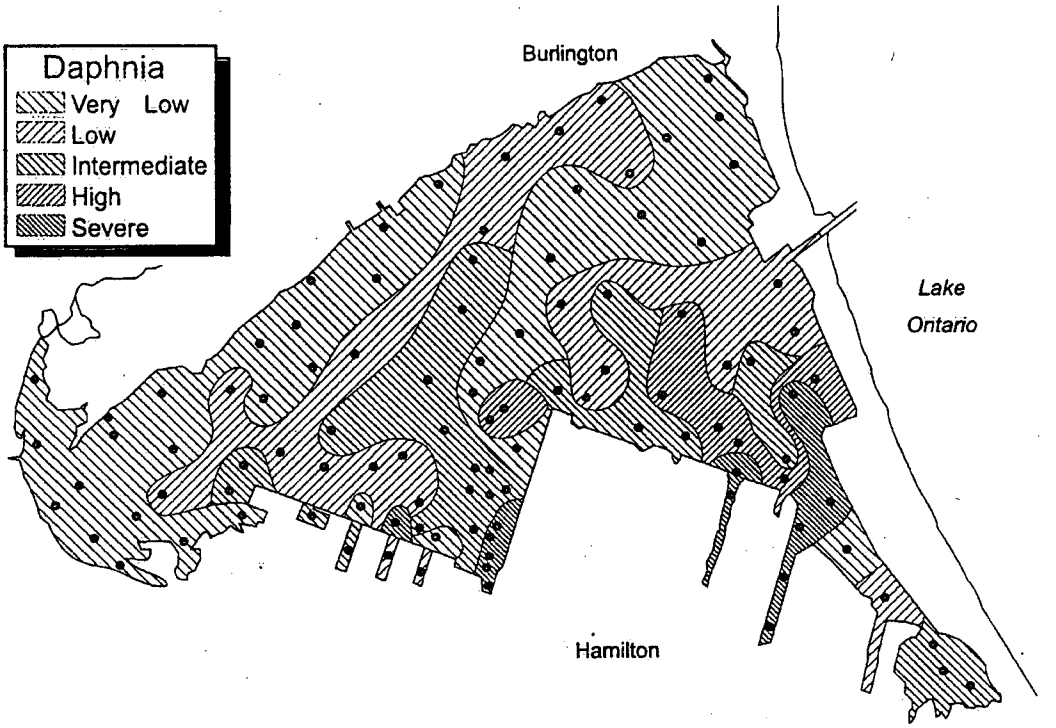

Fig. 3. Toxicity of grab sediments to *Daphnia*.

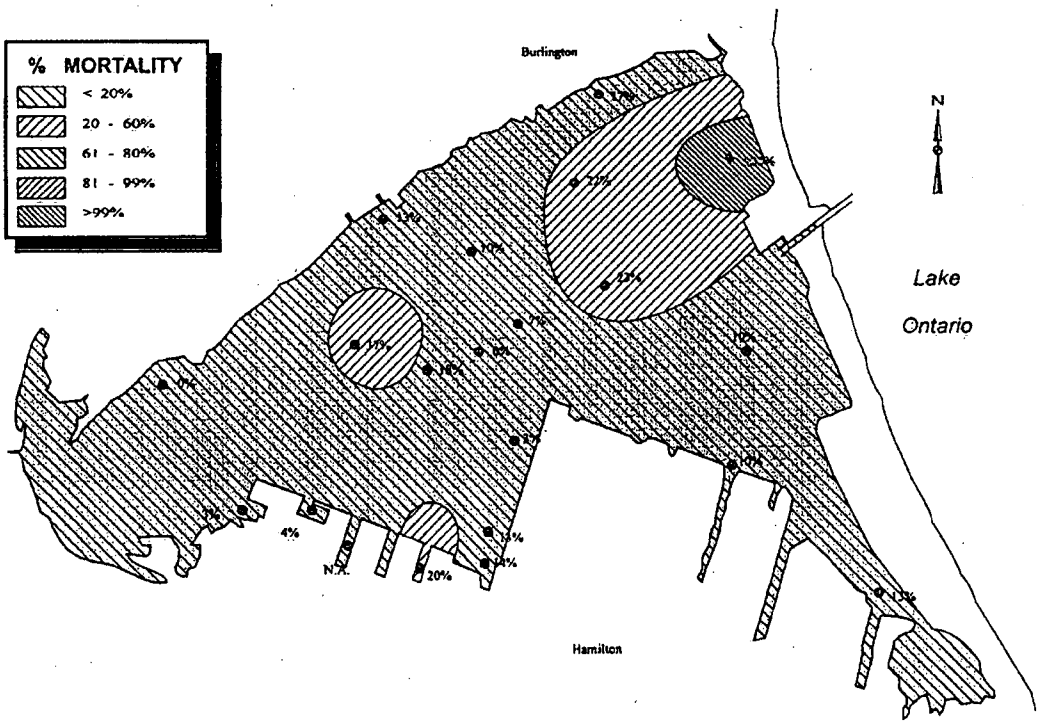

Fig. 4. Toxicity of surface 0–2 cm sediments to *Daphnia*.

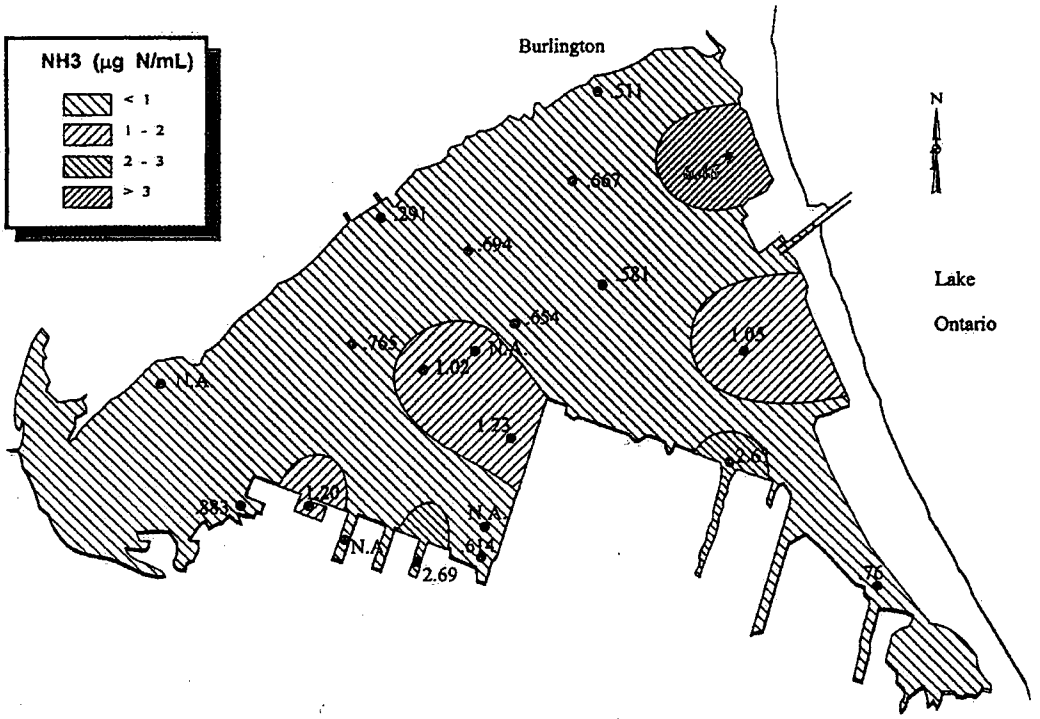

Fig. 5. Ammonia concentration in surface sediments.

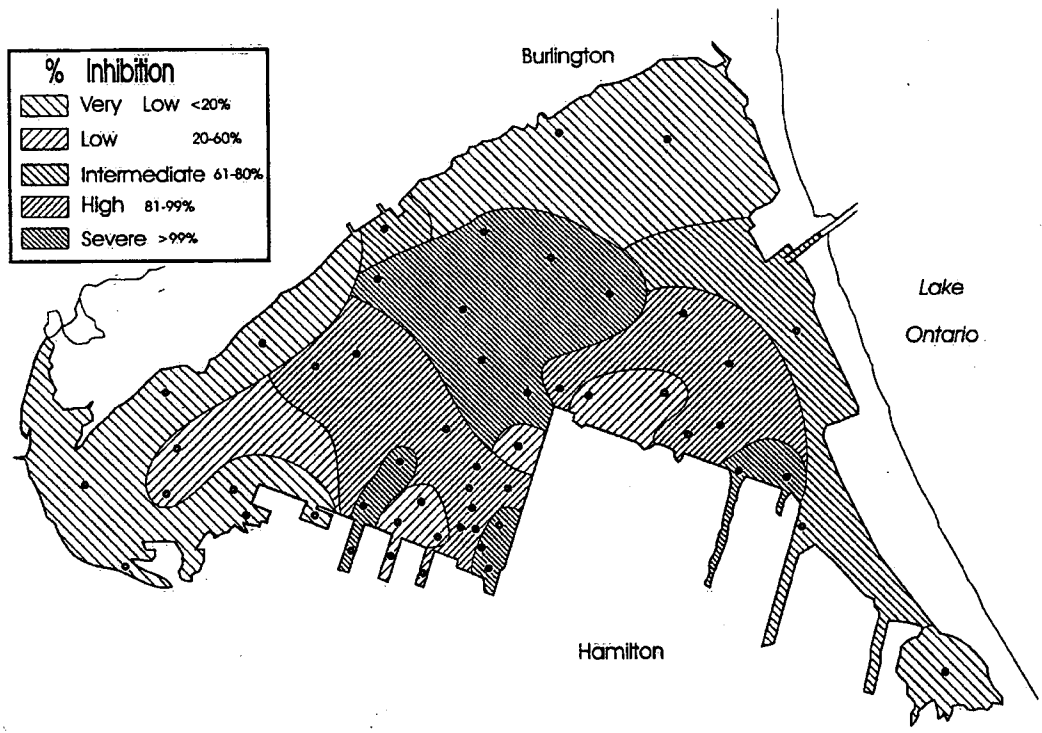

Fig. 6. Microtox toxicity of grab sediments.

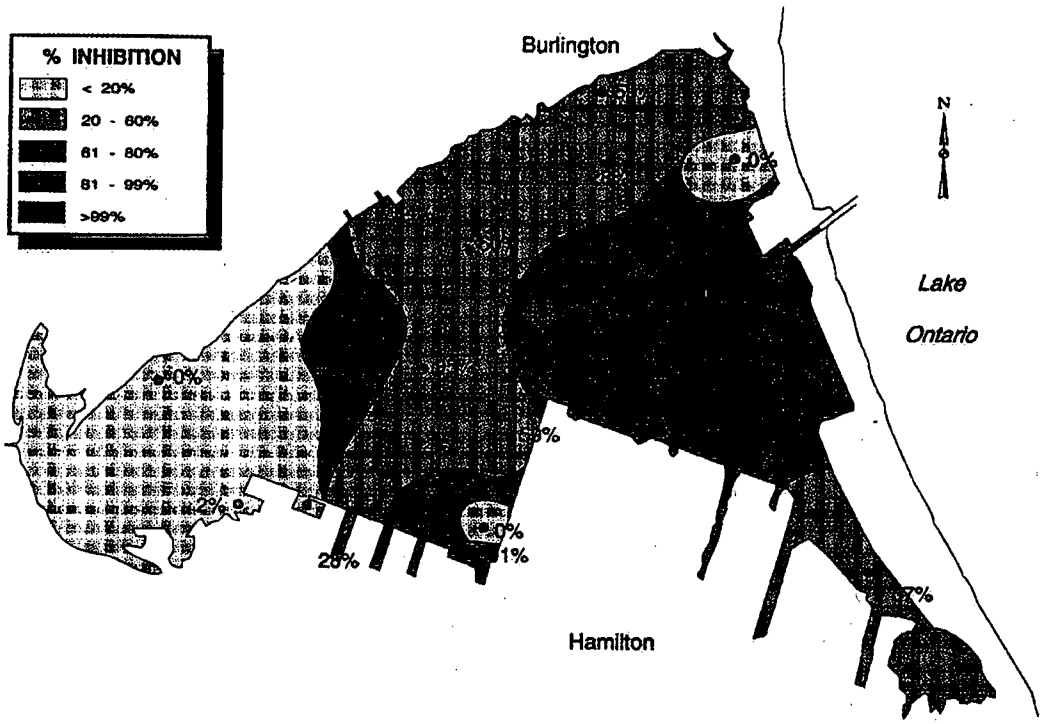

Fig. 7. Microtox toxicity of surface core samples.

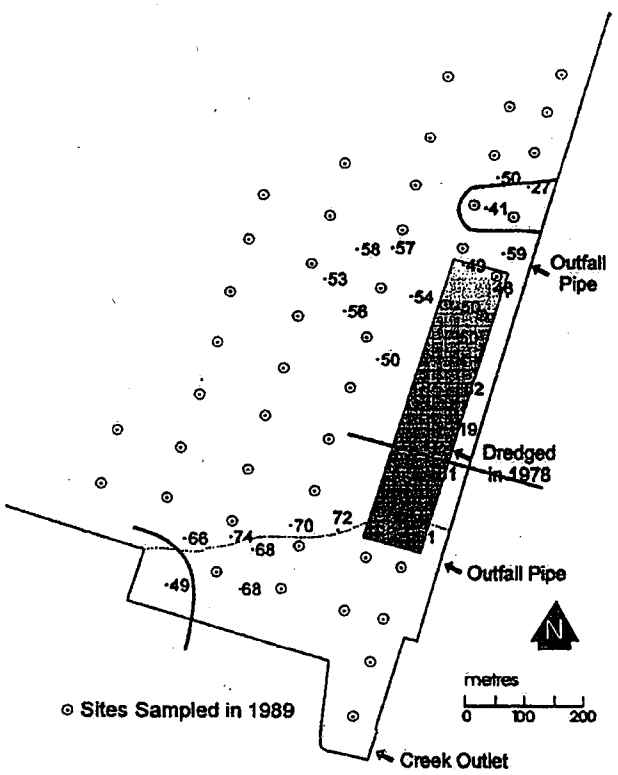

Fig. 8. Percent moisture in sediments.

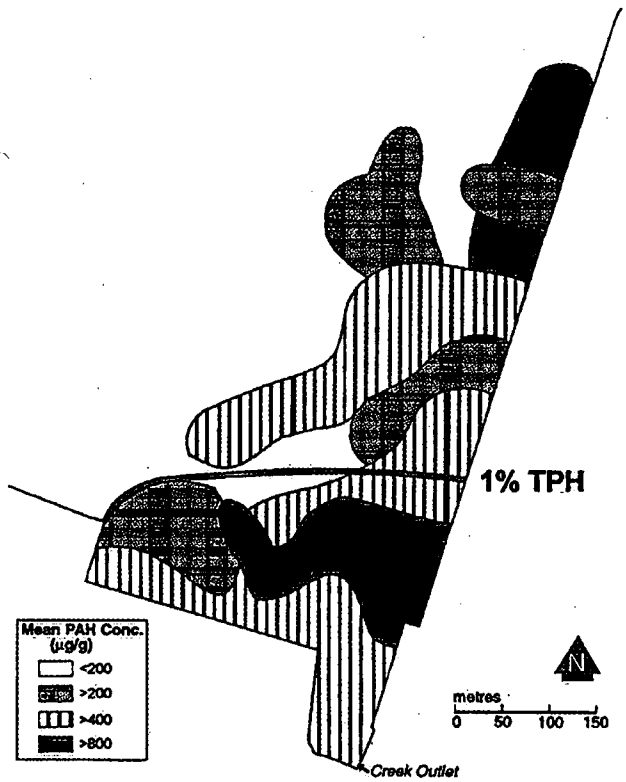

Fig. 9. Mean PAH concentration in Randle reef hotspot.

The three bioassays used in this study yielded the following LC_{50} and EC_{50}s; *Hexagenia* ($329 \pm 30 \mu g$), *Daphnia* (254 ± 50 $\mu g/g$), and Microtox (89 ± 15 $\mu g/g$). The arithmetic mean was rounded down to 200 $\mu g/g$. To represent the toxicity in terms of the PAHs the chemical surrogate analyses (mainly Stelco area) were used to provide rough maps that were adjusted and confirmed with GC/MS analyses. Outliers in the UV absorption were found that required resolution with GC/MS. The UV absorption was a good surrogate tool to help estimate PAHs in >2000 samples.

The studies in the Dofasco boatslip were surprisingly different. Some of the relationships developed at the Stelco area did not apply well to Dofasco. The switch from iso-octane to hexane might have been partly responsible but there were big differences in the two sites. For example, the Dofasco site has proportionally much less naphthalene (<0.1%) than the sediments near Stelco (up to 2%). Whether this difference reflects a spill of naphthalene or *in situ* biodegradation processes is uncertain. With Dofasco sediments, neither UV fluorescence or UV absorption were as useful as with sediments near Stelco, but it is potentially significant that UV absorption analysis at the stations treated by *in situ* treatment (B1, and C1) indicated >50% less PAHs than GC/MS analysis (Figs. 10 and 11). Results from a PAH immunoassay greatly underestimated PAHs as measured by GC/MS (Fig. 12). The only relationship that was statistically significant was the one between the Microtox assay and the AVS concentrations ($r = 0.527$, $n = 20$, Fig. 13). AVS was usually associated with PAHs but there were enough exceptions that made this statistically insignificant (Fig. 14). As simple screening tools any of these tools were useful, but for this study GC/MS analysis was still required. A comparison of the surface 0–2 and 2–4 cm sections of the cores indicates a recovery is taking place. This response occurs in spite of extremely high concentrations of PAHs at the extreme south end of the boatslip (8423 $\mu g/g$) and ongoing inputs from non-point sources. The standards proposed for the area near Stelco were accepted by Dofasco, but the only ongoing action is related to the containment of dirty non-point effluent. Other potential plans include containment of the worst sediments within a structure on site that could potentially also function as a dock.

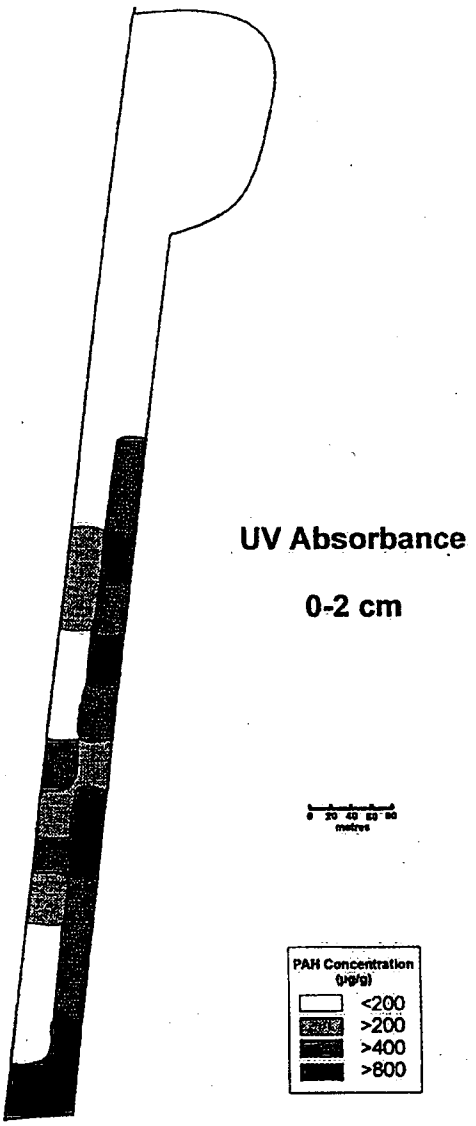

Fig. 10. UV fluorescence of Dofasco sediment extracts.

DISCUSSION

The effort spent mapping the distribution of PAHs is essential to the management of the harbor. Simple factors like location of existing outfalls, water depth, shipping, etc. helped prioritize the planned treatment of hotspots. A hotspot in deep water near an ongoing discharge (Ottawa St. slip) was given a low priority for cleanup. One hotspot (Randle Reef, Stelco area) is deemed as the most important for action. It is in shallow water where sediment resuspension is potentially important. Also it had a high content of oil suggesting that the PAHs in these sediments were likely more bioavailable (Hughes et al., 1997).

The concept of using bioassays for a cleanup standard was well received by the local remedial action plan. Using an acute toxicity bioassay for carcinogenic material may seem odd, but it became a workable endpoint for an initial cleanup guideline. Acute toxicity from these carcinogen containing sediments is readily apparent. Frequent chemical burns have deprived many

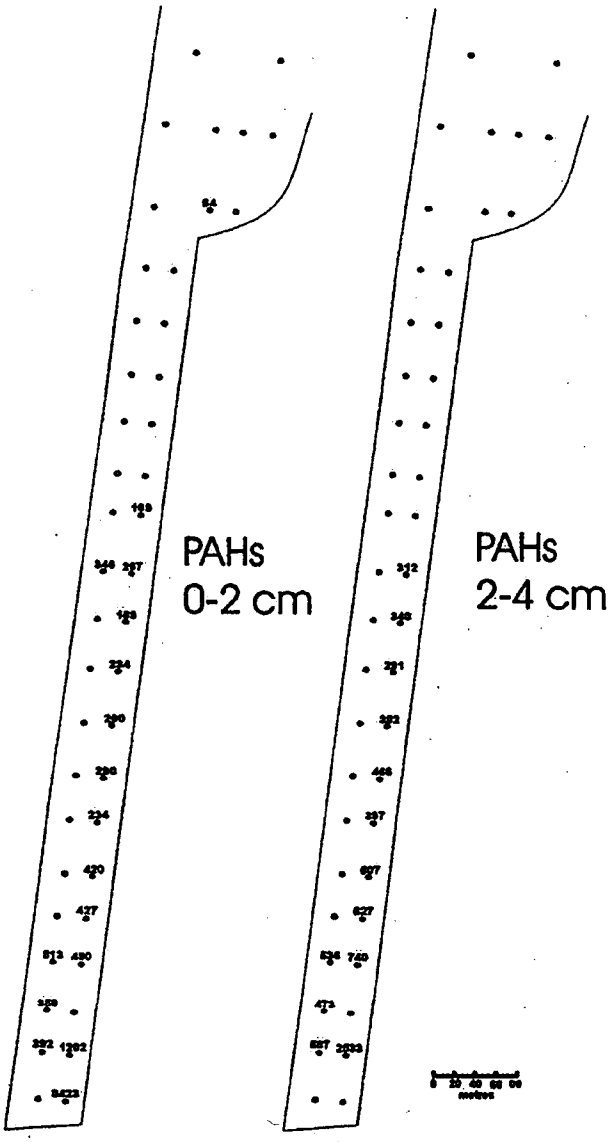

Fig. 11. PAHs in surface sediments of Dofasco boatslip.

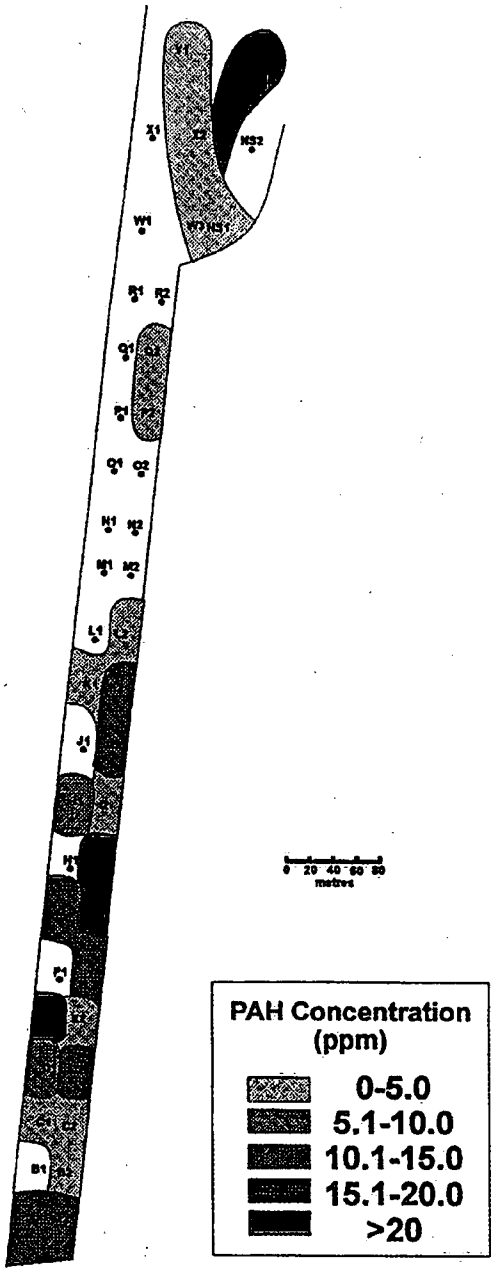

Fig. 12. PAH immunoassay of Dofasco sediments.

catfish of their barbells. Moreover tumors are a difficult endpoint. Cancers can be caused by other factors than PAHs including viri.

Three bioassays are more likely to represent the actual risks in nature better than one bioassay. Several other bioassays were evaluated but the responses were similar. The use of Microtox as part of a battery of bioassays has specific utility. Microtox is very sensitive to reduced sulfur (Jacobs et al., 1992, Brouwer and Murphy, 1995) and the related anoxia restricts biodegradation of PAHs. The steel mill wastes were typically rich in both sulfur and PAHs. Sulfides were generally associated with PAHs (Fig. 14). Attempts to interpret the cause of toxicity with these data are restricted by sample variability and the number of samples collected. In this harbor, Microtox was the most useful bioassay. Attempts to use UV fluorescence and UV absorption of hexane extracts were at times useful but there were spatial exceptions with complexities and the Microtox approach has biological relevance. By reducing the toxicity of the sediments to Microtox, the potential for biodegradation of PAHs is enhanced (Murphy et al., 1995).

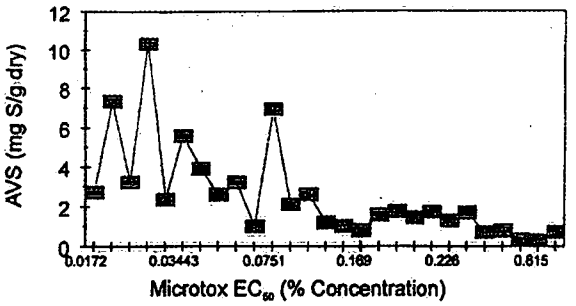

Fig. 13. Microtox–AVS in Dofasco boatslip sediments.

The relationship with anoxia and potential for bioremediation fit well with the desire to treat the large areas with 200–800 μg/g PAHs *in situ*. Locally it was perceived that with sediments containing more than 800 μg/g of PAHs, *in situ* bioremediation could not produce an acceptable residual. We found that bio-oxidation of sulfides by injection of nitrate and nutrients stimulated biodegradation of PAHs and reduced toxicity to Microtox (Murphy et al., 1995). About two-thirds of the PAHs biodegraded in a pilot-scale treatment. Differences in chemical and biological surrogate methods of measuring PAHs might actually represent differences in bioavailability but this study was not designed to resolve this aspect.

We were fortunate to be able to conduct detailed non-point source loading studies coincident with these bioremediation treatments. The discovery of runoff of >60 tonnes/yr. of coal dust and >60 kg/yr. of PAHs from one site (Curran et al., 2000) delayed further sediment remediation projects. The organic contaminants came from a steel mill and could be controlled. However, the loading of metals from the sewershed above the local steel mill was substantial and more difficult to control (Irvine et al., 1999). A comparison of

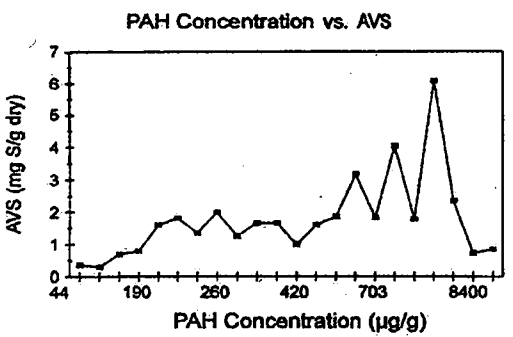

Fig. 14. PAH–AVS in Dofasco boatslip sediments.

the cost-effectiveness of source treatment and sediment treatment is beyond the purpose of this paper. However, these non-point source loading studies clearly show that, at first, sediment cleanup guidelines should only be directed at the very worst sediments.

Not all sediment treatment has to be direct. Indirect methods of enhancing bioremediation, or expediting natural attenuation should be evaluated. Parts of the harbor are anoxic and improved treatment of the sewage could expedite PAH biodegradation in sediments. The natural attenuation of PAHs is partly mediated via biodegradation and partly by physical adsorption (Knaebel et al., 1996, Apitz and Meyers-Schulte, 1996; White and Alexander, 1996). To justify using bioremediation or natural attenuation it is necessary to characterize the bioavailability of the PAHs. Not all PAHs are bioavailable (Paine et al., 1996; Madsen et al., 1996). As a further example, a recent patent in the USA advocates adding coal to soils as part of a bioremediation procedure (Mayfield, 1996). The American patent agents are highly regarded and they accepted coal as a benign material.

While we study the optimal cleanup strategies, the harbor is slowly recovering. The sediments will probably be the last aspect to respond and, even with lots of money, it will take time. The ongoing job of prioritizing sequential cleanups should consider the following objectives for restoration guidelines:

(1) Site specific and realistic.
(2) Hotspots should not act as sources of contamination.
(3) Boatslips should not be more toxic than depositional areas.
(4) 800 μg/g of PAHs should be used as an interim objective.

The fourth point seems to contradict the third, but it is financially realistic. Moreover, the dilution that must occur when sediments are resuspended must be considerable, so for treatment purposes, it is appropriate to focus on only the worst of the worst sediments.

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Canada Centre for Inland Waters
P.O. Box 5050
867 Lakeshore Road
Burlington, Ontario
L7R 4A6 Canada

National Hydrology Research Centre
11 Innovation Boulevard
Saskatoon, Saskatchewan
S7N 3H5 Canada

St. Lawrence Centre
105 McGill Street
Montreal, Quebec
H2Y 2E7 Canada

Place Vincent Massey
351 St. Joseph Boulevard
Gatineau, Quebec
K1A 0H3 Canada

Centre canadien des eaux intérieures
Case postale 5050
867, chemin Lakeshore
Burlington (Ontario)
L7R 4A6 Canada

Centre national de recherche en hydrologie
11, boul. Innovation
Saskatoon (Saskatchewan)
S7N 3H5 Canada

Centre Saint-Laurent
105, rue McGill
Montréal (Québec)
H2Y 2E7 Canada

Place Vincent-Massey
351 boul. St-Joseph
Gatineau (Québec)
K1A 0H3 Canada