LABORATORY SEDIMENT

BIOASSAY REPORT

ON ST. MARYS RIVER SEDIMENTS

1992 & 1995

OCTOBER 1997

Ontario

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1992 & 1995

Prepared by:

D. Bedard and S. Petro
Standards Development Branch
Ontario Ministry of Environment and Energy

Prepared for:

P. Kauss
Environmental Monitoring and Reporting Branch
Ontario Ministry of Environment and Energy

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EXECUTIVE SUMMARY

Sediments in the St. Marys River were sampled in the Summer of 1992 and the Fall of 1995, as part of an assessment in characterizing the potential ecological impacts of contaminated sediments for this Area of Concern. In 1992, test sediment was sampled from eight sites extending from Algoma Slip and as far downstream as Lake George. The 1995 survey focused solely on Bellevue Marine park where 14 samples were collected.

An objective of this study was to assess the spatial pattern of sediment toxicity and chemical bioaccumulation using static, laboratory sediment toxicity tests. Three independent toxicity tests were performed on whole-sediment samples. Mortality, growth and avoidance behaviour of the burrowing mayfly, *Hexagenia limbata*, was measured in 21-day tests. Chironomid (*Chironomus tentans*) growth and mortality was measured in 10-day tests. Mortality and chemical uptake by the fathead minnow, *Pimephales promelas*, was examined by a standard 21-day test.

The outcome of the toxicity test results performed in 1992 indicated sediment from Algoma Slip (station 183) to be acutely toxic to both benthic invertebrates, resulting in at least 95% mortality. In addition, mayflies exhibited a strong avoidance behaviour which was not observed in the minnow exposures. For the remaining test exposures, Bellevue Marine park (station 165) sediment yielded the poorest midge and mayfly growth relative to all other test sediments. A dose-response relationship was found between sediment total polycyclic aromatic hydrocarbon (PAH) concentration and benthic growth. The sublethal or IC50 sediment concentrations were 11 μg/g and 25 μg/g for the 10-day midge and 21-day mayfly tests, respectively. These values agreed favourably with the Provincial Sediment Quality Guideline - Severe Effect Level criteria using an acute to chronic application factor of 0.10.

Sublethal effects were the most sensitive response in the 1995 sediment toxicity tests which were observed in the midge, *Chironomus tentans*, followed by the mayfly, *Hexagenia limbata*. Midge body weights were 48% to 91% lower than the control animals at 11 of 13 test sites. Correlation analysis suggested physical attributes of the sediment such as the quantity of woody debris, along with total petroleum hydrocarbon sediment concentrations, as contributing to the poor benthic growth. Most of the sediments associated with reduced growth were collected from the nearshore region. Among the 16 PAH compounds analyzed in surviving fathead minnows, naphthalene was the most biologically available at three sites, where the compound also was measured in the highest concentration in the sediment.

In summary, the examination of biological effects at the sublethal level was critical in ranking sediments collected from the St. Marys river, either on a broad (1992 survey) or narrow (1995 survey) scale. Petroleum-based substances best explained the observed effects in both the midge and mayfly sediment toxicity tests. In the Bellevue Marine park study, substrate type was also considered an important factor. Varying amounts of extraneous material including wood fibres and detritus contributed both directly, as unsuitable habitat, and indirectly, as a reservoir of oil-based substances.

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1.0 INTRODUCTION

In August 1992, the Environmental Monitoring and Reporting Branch (EMRB) of the Ontario Ministry of Environment and Energy (OMOEE) carried out an extensive study of the St. Marys River sediment covering a geographical area from Point aux Pins Bay in the upper portion of the river, at several points along Lake George Channel, and as far downstream as Lake George. The purpose of the investigation was to determine the extent of sediment contamination and effects on benthic community structure, chemical bioaccumulation and laboratory toxicity as outlined in the project description by Kauss (1992).

The study built upon data obtained from prior surveys (UGLCCS, 1988; Burt *et al.*, 1988; Jaagumagi *et al.*, 1991) and was expanded to include the fate and effect of other groups of chemicals that were not previously considered. The purpose of the work was to advise the St. Marys River RAP Cleanup and Restoration Task team of potential areas of sediment impairment and provide information further to the Stage I Remedial Action Plan (OMOE/MDNR, 1992). The 1992 sampling sites were situated at or near municipal and industrial point sources, including the former Northwestern Tannery plant, the existing Algoma Steel Corporation, St. Mary's Paper and the Sault Ste Marie East End and West End sewage treatment plants.

Additional work was carried out in the Fall of 1995 based on the outcome of the 1992 survey (OMOEE, 1995a; this report, 1997). A number of areas were identified for further 1delineation of contamination zones based on field and laboratory studies. Some of the chemicals measured in the sediment are persistent and were shown to be related to a degradation of the benthos, exceeded Severe Effect Level concentrations of the Provincial Sediment Quality Guidelines (Persaud *et al.*, 1992) and were either lethal or sublethal to benthic invertebrates in toxicity tests. One of the areas recommended for additional environmental assessment was Bellevue Marine park (Kauss, 1995a). Ontario Ministry of Environment and Energy, Standards Development Branch (SDB) assisted in both studies of surficial sediment quality by examining the association between inorganic and organic contamination and biological effects using documented laboratory sediment toxicity test procedures (Bedard *et al.*, 1992).

Whole-sediment toxicity tests were conducted for eight field locations in 1992 and at 14 locations in 1995, using the mayfly nymph, *Hexagenia limbata* (21-day exposure, survival and growth), the midge larvae, *Chironomus tentans* (10-day exposure, survival and growth) and the juvenile fathead minnow, *Pimephales promelas* (21-day exposure, survival and chemical bioaccumulation). The battery of sediment toxicity tests provides a number of endpoints using organisms representing different trophic levels in order to measure differences in sediment quality. The laboratory toxicity tests provide a cost-effective technique for determining if sediment-associated contaminants are harmful to benthic organisms or are being released into the water-column. In conjunction with appropriate control sediments, spatial differences in sediment quality, the relative availability of contaminants and their potential impacts can be ascertained. Sediment contaminant concentrations were based on field samples for the 1995 study and in 1992, chemical analysis was based on samples prepared for laboratory toxicity testing, as well as concurrent field-collected sediment with respect to sediment PAH concentrations. The sediment was analyzed for particle size, nutrients, metals,

polychlorinated biphenyls (PCBs), organochlorine pesticides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs), chlorinated benzenes, total petroleum hydrocarbons (TPHs) and solvent extractables. Surviving fathead minnows were submitted for tissue analysis of trace metals in 1992 and total PAHs in 1995.

2.0 MATERIALS AND METHODS

2.1 Sample Collection and Site Description

During late August 1992, surficial sediment was collected at eight study locations throughout the St. Marys River corridor. The sampling locations were designated by OMOEE, EMRB for sediment chemistry, field benthic community analysis and laboratory sediment toxicity testing (Kauss, 1992; Table 1). Sediments from these locations have previously been shown to have an impact on in-situ benthos to varying degrees (Burt *et al.*, 1988). The 1995 sediment survey focused on an area adjacent to Bellevue Marine park, situated along the Canadian shore, downstream of the St. Marys rapids (Table 1A). This site was considered a high priority area requiring intensive sampling to aid in delineating zones of sediment contamination. Test sediment was collected in late September 1995 at 14 of 19 study locations (Kauss, 1995a). For each study, depositional material was selected to represent areas of higher potential contamination and facilitate intercomparisons among sites.

Sampling was done by diver using a 9" X 9" stainless-steel Ekman dredge. At each station, approximately 6-10 L of composited surficial sediment (top 5 to 10 cm) was collected from several grabs. The composited sediment was placed into 20 L plastic buckets lined with food-grade polyethylene bags and transported to the Toronto, Ontario laboratory where they were stored at 4°C until required.

In 1992, test sediment was collected in the following locations: an area extending just west of Ashmun Bay (stn 35) and situated near the former Northwestern Leather company along the Michigan border; in Algoma Slip (stn 183) adjacent to Algoma Steel corporation; along the Ontario shoreline in Bellevue Marine park (stn 165); in Lake George Channel downstream of the East End STP (stn 172) and near Bell Point (Stn 169); in Little Lake George (stn 87); and Lake George (stn 102) (Figure 1).

The 1995 sample locations in Bellevue Marine park are indicated in Figure 2. Station 214 was located furthest upstream, nearshore to the Ontario Ministry of Natural Resources property. Station 223 was situated opposite the marina entrance and stn 224 was located furthest downstream, near the Marine museum. The remaining sites were clustered within the embayment, north of Bayfield Dike light, at varying distances offshore. Bottom topography of the collection area showed a range of habitat types such as cobble, bottom vegetation, etc. Detailed field notes revealed several test sites contained surficial sediments varying in texture from soft, black ooze to hard-packed sand (Kauss, 1995b) Petroleum-like odor, oily sheen and wood fibres and chips were characteristic of many of the samples.

In both studies, an appropriate reference control sediment was sampled in a relatively, low-level contaminated area. In 1992, an upstream sample was collected in Point aux Pins

TABLE 1. 1992 St. Marys River Sampling Station Locations (Kauss, 1992)

Station Number	Station Location	Latitude	Longitude
52	Point aux Pins Bay; Reference site	46°29'49"	84°28'06"
183	Algoma Slip; near Bennett Creek	46°31'16"	84°22'48"
35	Northwestern Leather Company dump site; upstream of Ashmun Bay	46°29'28"	84°23'45"
165	Bellevue Marine Park	46°29'55"	84°18'15"
172	Lake George Channel; 500 m downstream of East End WWTP	46°30'31"	84°15'12"
169	Lake George Channel; 1190 m downstream of Partridge Point	46°29'44"	84°13'53"
87	Little Lake George	46°32'26"	84°11'36"
102	Lake George, middle top	46°29'29"	84°07'44"

TABLE 1A. 1995 St. Marys River Sampling Station Locations (Kauss, 1995a)

Station Number	Station Location	UTM Northing	UTM Easting
213	Bellevue Marine Park; Reference site; water depth 6.5 m	5152957.2	705595.0
214	Bellevue Marine Park; water depth 1.0 m	5153245.7	705264.2
226	Bellevue Marine Park; water depth 3.3 m	5153085.5	705826.9
215	Bellevue Marine Park; water depth 5.9 m	5152886.3	705904.1
219	Bellevue Marine Park; water depth 4.0 m	5153183.7	706022.5
227	Bellevue Marine Park; water depth 6.0 m	5153059.1	706310.6
225	Bellevue Marine Park; water depth 5.3 m	5153151.1	706273.9
221	Bellevue Marine Park; water depth 5.5 m	5153021.0	706051.3
217	Bellevue Marine Park; water depth 2.0 m	5152685.6	706186.4
222	Bellevue Marine Park; water depth 4.5 m	5153096.6	706427.1
210	Bellevue Marine Park; water depth 6.9 m	5153026.2	706368.4
211	Bellevue Marine Park; water depth 5.9 m	5152707.5	706408.2
223	Bellevue Marine Park; water depth 3.4 m	5152669.9	706670.8
224	Bellevue Marine Park; water depth 6.1 m	5152574.1	707091.4

FIGURE 1: 1992 St. Marys River Sediment Sampling Stations

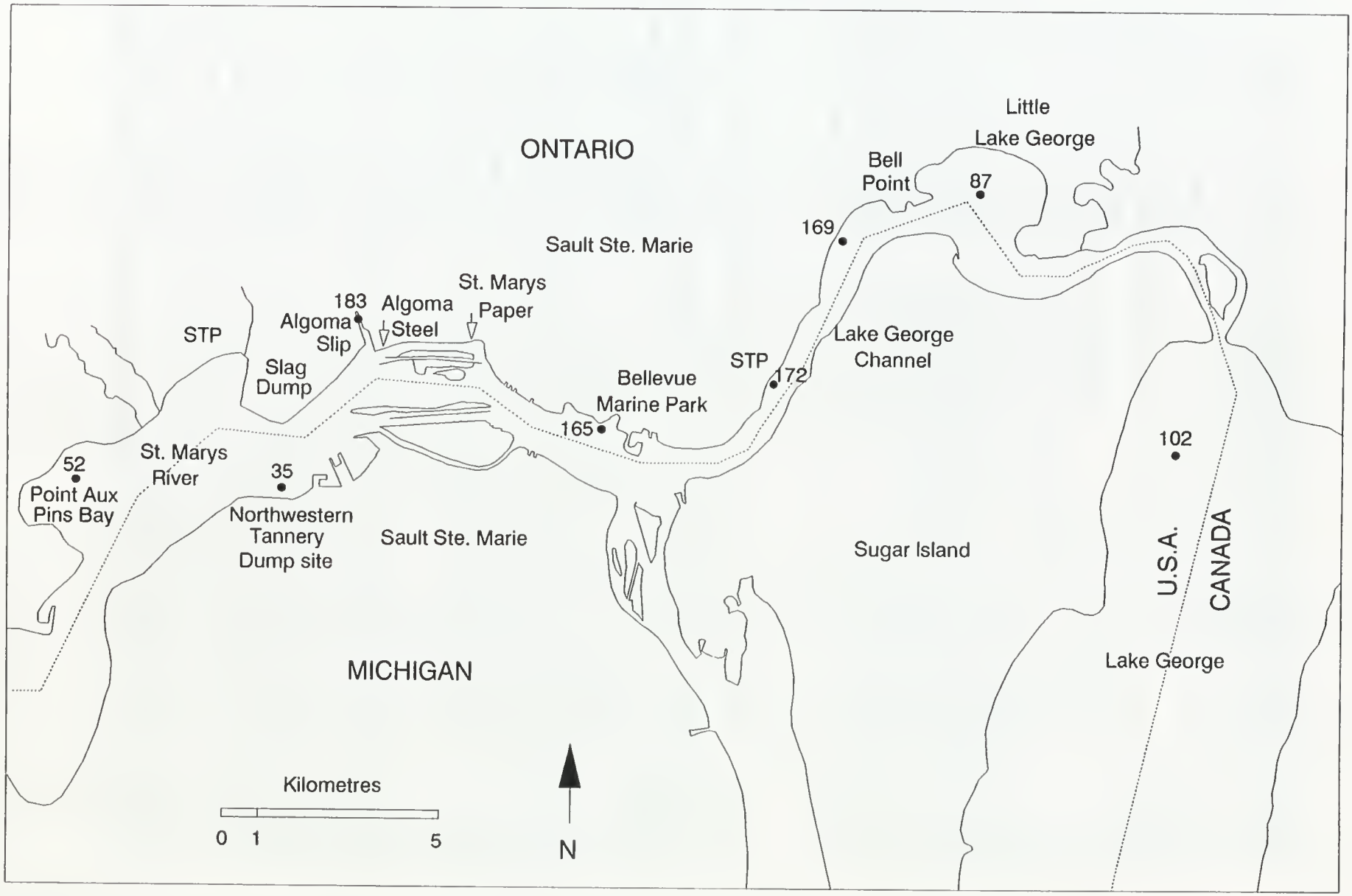
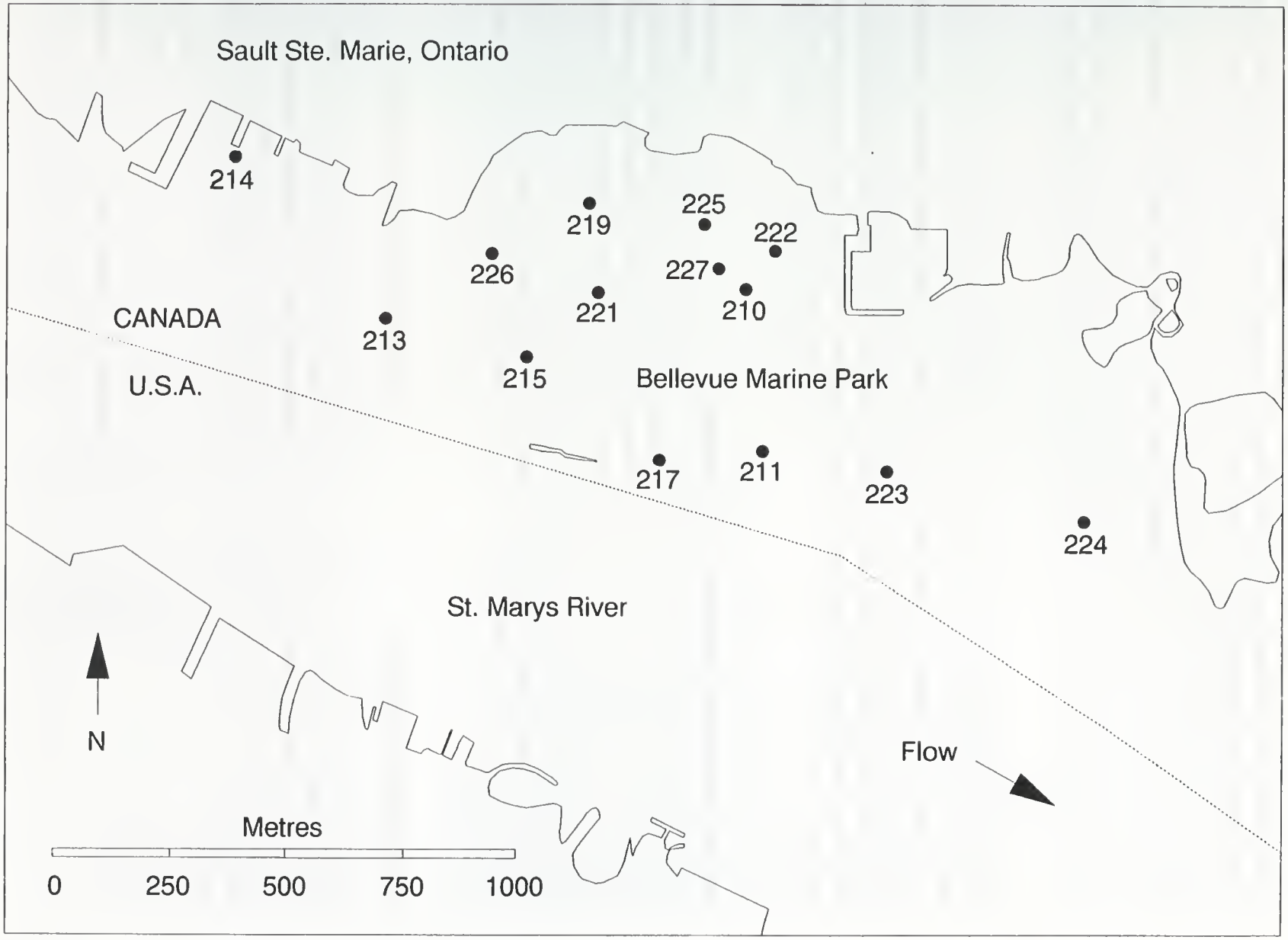


FIGURE 2: 1995 Bellevue Marine Park Sediment Sampling Stations



(stn 52), an area not subjected to point source inputs. For the Bellevue Marine park study, sediment from stn 213 was collected offshore in an area exposed to fast-flow conditions and consisted of fine-grained sand and low amounts of woody debris. The reference control sediment should be representative of naturally occurring background contamination levels for the study area and be physically similar to the test sediments to discriminate effects due to physical or chemical causes. Sediment collected from Honey Harbour in Georgian Bay, Ontario, served as a negative control for each bioassay. The negative control sediment is a relatively uncontaminated sediment that provides a measure of test acceptability (ASTM, 1997). Both control sediments are a basis for comparing the biological responses from the test sediments.

2.2 Analytical Methods

Chemical analysis of sediment and biota samples was carried out by the OMOEE, Laboratory Services Branch, located in Toronto. Routine test methods are described in the *OMOE Handbook of Analytical Methods for Environmental Samples* (OMOE, 1983). Quality assurance procedures included method blanks, spikes, duplicates and standard reference materials. Analytical detection limits for each of the sediment and tissue parameters are listed in Table A1.

Sediment Nutrients and Particle Size Characterization

Homogenized bulk sediment (< 2 mm fraction) was measured for total phosphorus (TP), total Kjeldahl nitrogen (TKN) and percent weight loss on ignition (LOI) which measured approximate organic content. Sediment total organic carbon (TOC) was determined with a LECO carbon analyzer using a dry combustion technique which oxidized carbon to CO_2. Particle size was measured on 50 g, air-dried samples using a Microtrac particle size analyzer for the size range 1.0 mm to 0.1 μm. This was to provide data for %sand (2mm -62 μm), %silt (62- 3.7 μm) and %clay (3.7 - 0.1 μm) size classes. Detailed test methodology is described in OMOEE (1995b; 1995c).

Trace Metals in Sediment

Prepared sediment samples were digested using a concentrated aqua-regia acid mixture (1 part HNO_3 to 3 parts HCl). The dissolved trace metals including As, Cd, Cr, Cu, Fe, Pb, Mn, Ni and Zn in the digestates were detected by inductively coupled argon plasma atomic emission spectroscopy (ICP-AES), and Hg by flow injection vapour generated flameless atomic absorption spectroscopy (AAS). Detailed test methodology is described in OMOEE (1994a).

Organic Chemicals in Sediment

Moist sediment samples were extracted with acetone and dichloromethane. The extract was transferred to a rotary evaporator, concentrated and fractionated on a Florisil column. Different solvent combinations were used to elute the extracts into three groups: fraction A1

contained total PCBs, five Aroclor groups, hexachlorobenzene, heptachlor, aldrin, octachlorostyrene, pp-DDE and mirex; fraction A2 contained a- & b-BHC, a- & b-chlordane, op-DDT, pp-DDD, pp-DDT; and fraction A3 included heptachlor epoxide, oxychlordane, dieldrin, endosulfan I & II, endosulfan sulphate, endrin and methoxyclor. Analytes were identified and quantified using capillary gas chromatography equipped with a Ni^{63} electron capture detector (GLC-ECD). Detailed test methodology is described in OMOEE (1994b; 1994c).

Trace Metals in Biota

Pooled whole fish samples (~2.5g) were thawed, homogenized and acid digested using a concentrated mixture of nitric acid (HNO3) and perchloric acid (HClO4) on triplicate samples per station for the 1992 samples. The digestate was allowed to concentrate by solvent evaporation on a heat block. The dissolved trace metals including Al, Cd, Cu, Pb, Mn, Ni and Zn in the digestates were detected by flow injection vapour generated flameless atomic absorption spectroscopy (AAS). Detailed test methodology is described in OMOEE (1996).

Organic Chemicals and Percent Lipid in Biota

Pooled whole fish samples (~5 g) were thawed, homogenized and acid digested using concentrated hydrochloric acid (HCl) on single samples per station for the 1995 samples. The digestate was reacted with a mixture of 25% dichloromethane in hexane. The extract was treated with sodium bicarbonate to ensure neutralization and dried with anhydrous sodium sulphate. Dichloromethane-cyclohexane was added to the evaporated samples, followed by clean-up and detected by capillary gas chromatography equipped with a mass selective detector. Final results are reported on a wet weight basis for 16 PAH compounds, 14 chlorinated organic compounds and 14 pesticides. Percent lipid was determined on an aliquot (25 mL) of the final extract obtained prior to clean-up. The solvent was allowed to evaporate by air-drying in a fumehood for 24 hours and lipid residues were measured. Detailed test methodology is described in OMOE (1990).

2.3 Laboratory Biological Testing Methods

Basic Experimental Design

Sediment biological tests were conducted according to OMOEE standardized procedures (Bedard *et al.*, 1992) and are briefly described below. The bioassays were static, single-species tests using whole-sediment. The experimental unit was a 1.8 L test chamber containing prepared sediment and dechlorinated municipal tap water (1:4, v:v). The chambers were randomly placed into a holding tank at ambient room temperature and maintained under a 16:8 hour, light:dark photoperiod and continuous aeration. Station 217 sediment obtained in the 1995 study was tested under ventilation given the strong sewage-like odour associated with this material and the test was conducted without a controlled photoperiod.

Moist field-collected bottom sediment was pressed through a 2-mm stainless-steel sieve

to remove existing large biota and debris prior to use. Subsamples of this homogenized sediment were submitted for chemical and physical characterization according to standard OMOEE procedures for the 1992 samples only (OMOE, 1989). In 1995, sediment chemistry was based on the field 0 - 10 cm section of core samples that were collected concurrently with the sediment used in the laboratory toxicity tests. The sieved sediment was homogenized with a spatula and stored in 4 L acid-rinsed glass jars until required. Three hundred and twenty-five millilitre aliquots of homogenized sediment were placed into the test chamber and overlaid with the test water. After settling overnight, the chambers were aerated continuously until the termination of the test. A clean, negative control sediment that was collected from Honey Harbour, Georgian Bay, was used for each bioassay. Negative control mortality must not exceed 15% for mayflies and fathead minnows and 25% for chironomids or the test is declared invalid.

Water in the exposure chambers was regularly monitored for pH, conductivity, total ammonia, un-ionized ammonia and dissolved oxygen. The 1992 exposures were not measured for ammonia. Dead organisms were removed and the numbers recorded on a daily basis. Any signs of abnormal behaviour of the test organisms or changes in appearance of the test chambers were noted. Water loss due to evaporation was replenished as needed.

Hexagenia limbata Lethality and Growth Assay

The 1992 toxicity test used 3 month old laboratory-reared mayfly nymphs with an average wet weight of 5.71 mg ± 0.45 (s.e.) (n = 50). The 1995 toxicity test used 4.5 month old nymphs that weighed 6.69 mg ± 0.41 (s.e.) (n = 44). The nymphs were raised from eggs collected by Dr. J. Ciborowski at the University of Windsor, Windsor, Ontario. Mayflies were reared according to OMOEE procedures (Bedard *et al.*, 1992) and methods described in the literature (Friesen, 1981).

The rearing procedure involved the transfer of 600 newly-hatched nymphs to a 6.5 L aquarium which contained 2 cm of autoclaved sediment and 5.6 L dechlorinated tap water. Animals were maintained at ambient room temperature, 16:8 hour, light:dark photoperiod, constant aeration and fed a vegetable diet.

Test organisms were retrieved from the rearing aquaria by sieving small portions of sediment in a 500-μm mesh brass sieve. The nymphs were washed into an enamelled tray which held a fine mesh sieve and aerated, dechlorinated water. A Pasteur pipette (5-mm opening) was used to transfer the mayflies into 100 mL beakers of water and the contents were gently poured into the test chambers. Three laboratory replicates were run for each station in the 1992 sediment bioassay. The 1995 toxicity test was conducted without laboratory replication except for three randomly selected stations (219, 227, 210), as well as the two control sediments. In each study, ten nymphs were added per jar, for a period of 21 days. Animals were not fed during the length of the test.

At the end of the test, the contents of each test chamber were emptied and rinsed in a sieve bucket. Surviving animals were counted and transferred to 150 mL beakers holding 100 mL dechlorinated water. The nymphs were immobilized with Alka-Seltzer®, blotted dry and individuals weighed to the nearest 0.01 mg, placed in vials and stored in a freezer.

Chironomus tentans Lethality and Growth Assay

Each toxicity test used 10-12 day old, cultured chironomid larvae weighing an average wet weight less than 1 mg. The OMOEE continuously cultures *C. tentans* larvae from egg to adult following standard methods (Bedard *et al.*, 1992, Mosher *et al.*, 1982, Townsend *et al.*, 1981). Egg masses were acquired from Dr. J. Giesy at Michigan State University, Lansing, Michigan and have been cultured for several generations in our laboratory.

Initially, the midges were reared in enamelled trays for a period of 10 to 12 days and then maintained in a 21 L aquarium containing 1.6 L of silica sand. The cultures were held at ambient room temperature with continuous aeration and under a 16:8 hour, light:dark photoperiod. The larvae were provided a vegetable diet *ad libitum*.

Second instar larvae were directly transferred from the enamelled rearing pans into the test chamber using the 5-mm opening of a Pasteur pipette. A total of 15 animals were added per chamber to each of the three replicates in the 1992 study and single test chambers were employed for the 1995 study. The latter study did include replication at three test (stn 227, 225, 210) and two control exposures. Animals were fed daily 30 mg of a Cerophyll®:Tetra Conditioning Vegetable® (3:2, w:w) diet.

After 10 days, the contents of the test chambers were emptied and washed in a sieve bucket. Surviving animals were sorted, removed and placed into 150 mL beakers holding 100 mL dechlorinated water and 15 mL silica sand. The larvae were counted, blotted dry and individuals weighed to the nearest 0.01 mg.

Pimephales promelas Lethality and Bioaccumulation Assay

The tests used cultured, juvenile fathead minnows with an average wet weight of 273 mg ± 23 (s.e.) (n=40) and 367 mg ± 17 (s.e.) (n=30), for the 1992 and 1995 toxicity tests, respectively. The minnows were cultured at the OMOEE laboratory and followed techniques which for the most part are US EPA procedures (USEPA, 1987) with minor revisions (Bedard *et al.*, 1992).

Cultures were maintained at 20°C in a flow-through dechlorinated water system and under a 16:8 hour, light:dark photoperiod. Breeders were kept in 60 L glass aquaria and eggs were laid on spawning tiles. The tiles were incubated in a 25°C water-bath and the developing larvae were transferred to 400 L fibreglass holding tanks. Larval fish were fed 48-hour old live brine shrimp while juveniles and breeders were provided frozen brine shrimp. Each size class was fed *ad libitum*.

Each test chamber received 10 juvenile minnows for triplicate jars in 1992 and single jars per sample for the 1995 study. The minnows were sorted into 250 mL glass beakers in groups of five. The contents of the beakers were emptied into a small net and the minnows released into the test chamber.

The minnows were exposed for 21 days and fed Tetra Conditioning Vegetable® diet in an amount equivalent to 1% of the average starting wet weight, on a daily basis. After 21

days the surviving fathead minnows were pooled from each replicate, counted, immobilized with Alka-Seltzer® and placed into 30 mL glass vials and frozen pending chemical analysis.

Reference Toxicant Testing

A water-only reference toxicity ($CuSO_4$) test was conducted with *H. limbata* and *C. tentans* for 48-hours and LC50s were calculated for the 1995 study only. The static tests consisted of four test concentrations and a control. The nominal copper concentrations were 0.05, 0.25, 0.5, 1.0 and 3.0 mg/L. Ten mayfly nymphs or midge larvae were placed into each of four replicate 250 mL beakers. To help reduce stress, five glass tubes were placed into the mayfly test beakers and a fine layer of silica sand was added to the midge test containers. Mortality was monitored every 24 hours and water quality parameters were taken at 0 and 48 hours. The mayfly test used 4.5 month old laboratory-reared mayfly nymphs with an average wet weight of 5.4 mg ± 0.5 (s.e.). The midge larvae were 10-12 day post-hatch with an average wet weight < 1 mg in each set of tests.

Bioassay Schedule for St. Marys River 1992 Sediment Samples

Test Organism	Species	Starting Date ('92)	Completion Date ('92)	Test Duration
Mayfly	*Hexagenia limbata*	Fri. September 11	Fri. October 2	21 days
Chironomid	*Chironomus tentans*	Sat. September 5	Tue. September 15	10 days
Minnow	*Pimephales promelas*	Fri. September 11	Fri. October 2	21 days

Bioassay Schedule for St. Marys River 1995 Sediment Samples

Test Organism	Species	Starting Date ('94/'95)	Completion Date ('94/'95)	Test Duration
Mayfly	*Hexagenia limbata*	Thur. October 12	Thur. November 3	21 days
Chironomid	*Chironomus tentans*	Fri. October 6	Mon. October 16	10 days
Minnow	*Pimephales promelas*	Wed. January 10	Wed. January 31	21 days

2.4 Statistical Methods

Statistical analyses were performed using the SAS® software package (SAS, 1985). Comparisons were made among the test and control sediments using One-Way Analysis of Variance (ANOVA) and Tukey's studentized range test (HSD) and planned comparisons (Steel and Torrie, 1960). Dunnett's one-tailed *t*-test was used solely to compare mortality between the control and test sediments and the associated minimum significant difference (MSD) was described as a measure of test sensitivity. Analysis was made on arc-sine transformed mortality data. Homogeneity of variance across groups was tested using Bartlett's test. Coefficients of variation (C.V. %) were calculated for each endpoint as a measure of test precision. Spearman rank correlation analysis was used to investigate the correlation among the different biological endpoints for each species and sediment characteristics. Simple linear regression was used to measure the strength of the relationship between chemical and biological variables. LC50's (including the associated 95% confidence limits) were calculated using software developed by Stephan (1977) and were derived by probit analysis. Differences in whole-body tissue residues for metals among the 1992 sites were determined using Tukey's studentized range test (HSD) and statistical analyses were carried out on log-transformed data. All contaminant residues are converted to a dry weight basis using a dry weight ratio of 0.15.

3.0 RESULTS

3.1 Water Quality Test Parameters

Conductivity, pH and dissolved oxygen parameters were periodically measured on the overlying water for each test species in each of the two studies and are summarized in Tables 2; 2A. Values are reported as mean ± standard deviation. Test chambers holding stn 217 sediment were omitted from any routine water chemistry measurement in order to prevent cross-contamination by bacterial organisms associated with faecal matter that may have been present in the sample.

Similar pH water quality measurements were recorded among the test sites, regardless of test species or study. For the reference control and test sites, pH averaged from 7.6 to 8.3. Conductivity readings for most test sites fell between 272 and 367 umho/cm. Slightly higher conductivity was noted at stns 183 and 35 for the 1992 study and averaged 426, 434 and 453 umho/cm in the mayfly, midge and minnow assays, respectively. Dissolved oxygen within the test jars remained above acceptable levels (>4 mg/l) throughout the test (OMOEE, 1994d). Test temperature was at or near 20°C for each bioassay.

The amount of total ammonia present in the overlying test water was analyzed for the 1995 study only. After correction for temperature and pH, the converted un-ionized ammonia readings were also recorded in Table 2A. Each of the test and reference sediments resulted in un-ionized ammonia above the PWQO of 0.02 mgNH_3/L in the midge and minnow toxicity tests. Average values ranged from a low of 0.02 mgNH_3/L in the mayfly exposures, a moderate level of 0.08 mgNH_3/L in the midge tests and the highest readings occurred in the fish exposures (0.22 mgNH_3/L). The latter value is likely a reflection of ammonia loadings from both the sediment and the test organism.

TABLE 2. Mean (± s.d.) water quality characteristics in 1992 sediment bioassays.

Test Organism: Mayfly (Hexagenia limbata)[a]		Test Temperature: 19.7°C (0.7)	
Station	*pH*	*D.O.* mg/L	*Conductivity* umho/cm
Control	8.21 (.22)	8.8 (0.1)	338 (20)
Reference (52)	8.22 (.17)	8.9 (0.1)	256 (25)
Stn 183	8.34 (.07)	8.8 (0.1)	448 (70)
Stn 35	8.21 (.21)	8.9 (0.0)	404 (20)
Stn 165	8.13 (.16)	8.8 (0.0)	297 (31)
Stn 172	8.07 (.14)	8.8 (0.1)	286 (30)
Stn 169	8.26 (.25)	8.9 (0.1)	263 (21)
Stn 87	8.13 (.04)	8.9 (0.0)	283 (28)
Stn 102	8.10 (.28)	8.8 (0.1)	247 (18)
Test Organism: Midge (Chironomus tentans)[b]		Test Temperature: 20.7°C (0.9)	
Station	*pH*	*D.O.* mg/L	*Conductivity* umho/cm
Control	8.10 (.16)	8.8 (0.1)	349 (19)
Reference (52)	7.85 (.36)	8.8 (0.2)	296 (5)
Stn 183	8.31 (.20)	8.8 (0.2)	452 (54)
Stn 35	8.30 (.21)	8.8 (0.1)	417 (15)
Stn 165	7.88 (.09)	8.9 (0.3)	314 (17)
Stn 172	8.16 (.26)	8.7 (0.2)	341 (16)
Stn 169	8.16 (.28)	8.8 (0.1)	287 (5)
Stn 87	7.93 (.33)	8.7 (0.2)	323 (3)
Stn 102	8.19 (.03)	8.8 (0.3)	255 (1)
Test Organism: Minnow (Pimephales promelas)[a]		Test Temperature: 19.7°C (0.7)	
Station	*pH*	*D.O.* mg/L	*Conductivity* umho/cm
Control	7.52 (.72)	9.0 (0.1)	361 (32)
Reference (52)	7.96 (.22)	8.8 (0.1)	299 (4)
Stn 183	7.93 (.28)	8.9 (0.1)	465 (68)
Stn 35	7.59 (.33)	9.0 (0.1)	442 (117)
Stn 165	7.93 (.27)	8.8 (0.1)	330 (21)
Stn 172	7.77 (.35)	8.9 (0.1)	369 (65)
Stn 169	7.43 (.59)	8.9 (0.0)	284 (9)
Stn 87	7.86 (.04)	8.9 (0.1)	330 (16)
Stn 102	7.48 (.33)	8.9 (0.1)	272 (21)

a Sample size N=3;

b Sample size N=2;

TABLE 2A. Mean (± s.d.) water quality characteristics in 1995 sediment bioassays.

Test Organism: Mayfly (Hexagenia limbata)[a] Test Temperature: 20.1°C (1.1)

Station	*pH*	*D.O.* mg/L	*Conductivity* umho/cm	*Total Ammonia* mg/L	*Un–ionized Ammonia* mg/L
Control	7.83 (.13)	8.7 (0.3)	335 (12)	<0.10	<0.003
Reference (213)	8.12 (.04)	8.4 (0.4)	320 (14)	0.30 (0.24)	0.011
Stn 214	8.17 (.12)	8.6 (0.2)	328 (14)	0.51 (0.36)	0.024
Stn 226	8.00 (.15)	8.4 (0.7)	289 (26)	0.46 (0.32)	0.017
Stn 215	7.99 (.15)	8.0 (0.6)	373 (25)	2.00 (1.95)	0.075
Stn 219	7.69 (.24)	8.4 (0.8)	268 (18)	0.70 (0.52)	0.021
Stn 227	7.98 (.13)	8.4 (0.6)	284 (10)	0.83 (0.79)	0.031
Stn 225	7.83 (.18)	8.4 (0.5)	257 (23)	1.03 (0.81)	0.037
Stn 221	7.94 (.15)	8.4 (0.5)	272 (16)	0.62 (0.45)	0.019
Stn 217	Not Measured	Not Measured	Not Measured	Not Measured	Not Measured
Stn 222	8.03 (.24)	8.4 (0.1)	299 (24)	0.33 (0.28)	0.012
Stn 210	7.97 (.24)	8.3 (0.6)	280 (21)	1.43 (0.51)	0.049
Stn 211	8.03 (.03)	8.4 (0.2)	298 (15)	0.47 (0.44)	0.017
Stn 223	8.05 (.15)	8.5 (0.4)	310 (29)	0.23 (0.23)	0.010
Stn 224	8.15 (.13)	8.6 (0.3)	301 (27)	0.29 (0.30)	0.012

Test Organism: Midge (Chironomus tentans)[b] Test Temperature: 20.7°C (1.0)

Station	*pH*	*D.O.* mg/L	*Conductivity* umho/cm	*Total Ammonia* mg/L	*Un–ionized Ammonia* mg/L
Control	7.89 (.30)	8.7 (0.1)	343 (17)	0.11 (0.01)	<0.003
Reference (213)	8.22 (.02)	8.5 (0.3)	349 (30)	1.38 (1.01)	0.101
Stn 214	8.06 (.01)	8.7 (0.3)	340 (29)	1.90 (1.55)	0.072
Stn 226	7.83 (.05)	8.6 (0.3)	288 (5)	1.55 (1.20)	0.043
Stn 215	8.07 (.24)	8.4 (0.6)	397 (42)	3.45 (2.89)	0.230
Stn 219	7.94 (.02)	8.7 (0.3)	301 (7)	1.90 (0.84)	0.072
Stn 227	8.10 (.00)	8.7 (0.3)	308 (19)	2.20 (1.41)	0.083
Stn 225	7.88 (.14)	8.7 (0.5)	287 (6)	2.85 (.134)	0.095
Stn 221	8.02 (.05)	8.7 (0.1)	313 (22)	2.45 (1.76)	0.092
Stn 217	Not Measured	Not Measured	Not Measured	Not Measured	Not Measured
Stn 222	8.05 (.04)	8.7 (0.3)	324 (20)	1.49 (1.13)	0.056
Stn 210	8.03 (.07)	8.6 (0.1)	301 (12)	2.60 (1.97)	0.098
Stn 211	8.10 (.01)	8.6 (0.3)	352 (37)	2.25 (1.34)	0.085
Stn 223	8.07 (.09)	8.5 (0.0)	322 (30)	1.03 (0.80)	0.038
Stn 224	8.10 (.00)	8.8 (0.4)	316 (20)	1.02 (0.67)	0.038

a Sample size N=3; b Sample size N=2.

Underlining indicates un–ionized ammonia concentrations that exceed the PWQO of 0.02 mg/L.

TABLE 2A. Continued.

Test Organism: Minnow (Pimephales promelas)[a]	Test Temperature: 20.6°C (0.7)				
Station	*pH*	*D.O.* mg/L	*Conductivity* umho/cm	*Total Ammonia* mg/L	*Un–ionized Ammonia* mg/L
Control	7.36 (.51)	8.5 (0.1)	369 (65)	2.60 (0.52)	0.056
Reference (213)	7.67 (.63)	8.2 (0.2)	396 (61)	2.96 (3.59)	0.111
Stn 214	7.80 (.14)	6.6 (1.8)	417 (94)	11.50 (8.04)	0.298
Stn 226	7.76 (.15)	8.1 (0.7)	337 (41)	9.20 (5.73)	0.270
Stn 215	7.44 (1.32)	8.7 (0.5)	424 (61)	6.33 (6.80)	0.396
Stn 219	7.74 (.05)	8.1 (0.3)	352 (58)	7.86 (5.78)	0.189
Stn 227	7.44 (.77)	8.2 (0.3)	342 (41)	5.40 (4.84)	0.162
Stn 225	7.31 (.67)	7.0 (0.8)	329 (26)	6.36 (4.90)	0.074
Stn 221	7.67 (.59)	8.3 (0.4)	376 (53)	5.76 (3.67)	0.174
Stn 217	Not Measured	Not Measured	Not Measured	Not Measured	Not Measured
Stn 222	7.39 (.85)	8.0 (0.4)	369 (56)	5.86 (7.91)	0.145
Stn 210	7.60 (.09)	7.1 (0.7)	361 (49)	10.80 (6.37)	0.572
Stn 211	7.67 (.60)	8.6 (0.2)	351 (40)	2.13 (2.55)	0.239
Stn 223	7.55 (.24)	7.7 (0.5)	368 (51)	6.83 (325)	0.090
Stn 224	7.81 (.06)	7.9 (0.2)	355 (80)	6.76 (4.96)	0.216

a Sample size N=3.

Underlining indicates un–ionized ammonia concentrations that exceed the PWQO of 0.02 mg/L.

3.2 Sediment Characterization

The following sections summarize the sediment physical and chemical parameters to aid in the interpretation of the biological toxicity results. Chemical analysis is based either on field surficial sediment (1995 samples) or on the sediment prepared for toxicity testing (1992 samples). The latter approach is preferred because the data is based on a subsample that is removed from the prepared, sieved sediment samples that was used directly in the laboratory toxicity tests. Given the large number of samples collected in 1995 and the analytical cost involved, it was decided that the field sample chemistry would be used for the interpretation of the 1995 toxicity results. Using this approach, the chemistry results may not accurately reflect the exposure conditions in the laboratory tests, especially given the handling and manipulation of the sediment prior to testing.

Physical and Nutrient Properties

Sediments were characterized for % sand (2mm-62μm), % silt (62-3.7μm), % clay (3.7-0.1μm), % loss on ignition (%LOI), total organic carbon (TOC), total phosphorus (TP) and total Kjeldahl nitrogen (TKN) (Tables 3; 3A).

Sediment samples collected in 1992 encompassed a wide geographical area and represented a diverse group of sediment types (Millar *et al.*, 1965) (Table 3). Several of the test sediments, including stns 165, 172, 169 and 87, were classified as silty loam with at least 75% fine-sized particulates. This group of sediment samples most closely resembled the upstream reference sediment (stn 52) in terms of particle-size composition. Sediment from Lake George (stn 102) was comprised solely of silt and clay. The most coarse-textured sediment was obtained from stn 35 (68% sand) and an intermediate loam sediment was found at stn 183. A wide range of organic matter content was noted, even within a particular substrate type (Range: 14 - 200 mg/g TOC). Those sediments devoid of organic enrichment appear to be found in areas of higher energy conditions (stn 35) or in the deeper, less productive waters of the larger waterbodies (stns 87 and 102). An unusually high amount of TOC was recorded at stn 183 (200 mg/g), which to a certain extent is compounded by the relatively high concentration of oil. Total phosphorus and TKN varied little among locations.

The 1995 field sediments could be described as belonging to two general categories. Soft-textured sediments having less than 50% sand were described as *loose ooze* according to field notes (Kauss, 1995b). The majority of the remaining test sediments had varied proportions of wood fibres and wood chips of different size classes, which may have influenced the particle-size analysis. Similarly, any carbon associated with this detrital material will be reflected in the TOC measurements. Exceedences of the PSQG-SEL of 100 mg/g for TOC were found at stns 227, 222, 210, 211 and 224. Field notes indicate that stations with a water depth greater than 5.9 m, typically had surficial sediment of higher organic content. These areas may be subjected to slower current conditions and a higher deposition rate, as compared to shallower areas within the bay. Overall, the test sediments had moderate to high concentrations of TOC (33 - 160 mg/g) and the lowest amount of TOC was reported in the reference sediment (stn 213) of 23 mg/g. Other nutrient parameters e.g. TP, TKN, were below PSQG-SEL concentrations in all samples.

TABLE 3. Sediment physical and nutrient characteristics in control(s) and St. Marys River 1992 sediment used in sediment bioassays.

Station	*% Sand* (2mm–62um)	*% Silt* (62–3.7um)	*% Clay* (3.7–0.1um)	*% LOI*	*TOC* mg/g	*TP* mg/g	*TKN* mg/g
Control	0.3	64.3	35.5	9.5	39	1.0	3.5
Upstream Reference Station 52	10.3	72.6	17.3	9.2	47	0.3	1.8
Algoma Slip Station 183	43.7	39.7	16.6	12	200	0.3	1.7
Tannery Bay Station 35	68.0	24.4	7.7	3.1	14	0.4	1.0
Bellevue Marine Park Station 165	12.0	66.9	21.2	8.4	28	0.6	2.0
STP – East End Station 172	11.5	71.8	16.7	10	76	0.9	2.6
W of Bell Pt Station 169	23.0	62.3	14.7	11	73	0.6	1.8
Little Lake George Station 87	23.0	57.3	20.0	3.5	19	0.5	1.3
Lake George Station 102	0.0	65.6	34.5	5.4	18	0.7	1.7
PSQG SEL Conc. (mg/g dry weight)					100	2.0	4.8

Shading indicate sediment nutrient concentrations that exceed PSQG–SELs.

TABLE 3A. Sediment physical and nutrient characteristics in control(s) and St. Marys River 1995 field sediment.

Station	*% Sand* (2mm–62um)	*% Silt* (62–3.7um)	*% Clay* (3.7–0.1um)	*% LOI*	*TOC* mg/g	*TP* mg/g	*TKN* mg/g
Georgian Bay Control	20.5	68.8	10.7	6.9	43	1.3	4.1
Upstream Reference Station 213	88.6	18.1	2.1	2.0	23	0.2	0.3 <T
Bellevue Marine Park Station 214	74.0	23.4	3.0	9.6	70	0.4	0.9
Station 226	64.0	32.3	3.5	9.5	81	0.6	2.0
Station 215	81.1	15.4	3.4	2.8	33	0.3	0.6
Station 219	29.0	61.9	8.9	11.0	77	0.7	3.4
Station 227	79.0	19.0	2.0	23.0	160	0.5	2.0
Station 225	50.0	45.6	4.5	12.5	87	0.6	2.4
Station 221	76.0	20.7	3.4	11.0	97	0.4	2.4
Station 217	61.5	33.1	5.6	3.7	33	0.4	0.8
Station 222	50.0	45.0	4.6	14.5	101	0.6	2.5
Station 210	73.0	23.2	3.2	16.5	110	0.5	1.8
Station 211	76.5	20.5	2.8	11.5	103	0.4	0.6
Station 223	44.0	50.3	5.5	7.6	55	0.6	2.6
Station 224	63.0	33.2	3.7	19.0	125	0.5	1.7
PSQG SEL Conc (mg/g dry weight)					100	2.0	4.8

Shading indicate sediment nutrient concentrations that exceed PSQG–SELs.

Trace Metal Sediment Concentrations

Bulk sediment samples were analyzed for 11 trace metals (Tables 4; 4A). The sediment metal concentrations were compared to Severe Effect Level (SEL) and Lowest Effect Level (LEL) concentrations as outlined in the Provincial Sediment Quality Guidelines (PSQGs) (Persaud *et al.*, 1992). The SEL is defined as that chemical concentration in the sediment that is considered to be detrimental to the majority of the macrobenthos and the LEL is the sediment contaminant concentration which can be tolerated by most benthic species.

The 1992 and 1995 sediments contained relatively low metal concentrations. Only Fe surpassed the PSQG-SEL concentration most frequently. Sediment Fe concentrations were only slightly higher than the PSQG-SEL concentration of 4.0% beginning at Bellevue Marine park, and within Lake George Channel at the East End STP site and the site near Bell Point. Sediment from Tannery Bay (stn 35) had the highest concentration of Cr at 2,600 μg/g, which is 23 times higher than the PSQG-SEL guideline of 110 μg/g. The area is known to be historically impacted from wastes from the Northwestern Leather Company tannery operations. A 1991 study reported Cr sediment concentrations ranging from 2,100 to 40,000 μg/g at several locations throughout Tannery Bay adjacent to the Cannelton Industries site (USEPA, 1991).

Organic Chemical Sediment Concentrations

Concentrations of 20 organochlorine pesticides and 12 chlorinated organic compounds in the 1992 and 1995 test sediments were below the respective detection limits (Tables 5; 5A). Measurable amounts of total PCBs (60 ng/g) were found at stns 169 and 172, in the 1992 study. Trace amounts of hexachlorobenzene (2 ng/g) were noted in stn 211 1995 sediment.

Field sediment was submitted for total PAH analysis in 1992 and 1995 (Tables 6; 6A). Concentrations of 16 individual PAH compounds and the sum total were compared to PSQG-SEL concentrations, where available. None of the PAH compounds either singly or in combination were above SEL concentrations, after correction for TOC. Total PAH sediment concentrations typically exceeded LEL concentrations, particularly in the Bellevue Marine park samples. In the 1992 study, total PAH concentrations were 14,587 ng/g or lower, with the exception of stn 183. The Algoma Slip sample had the highest concentration of 291,718 ng/g and consisted primarily of low molecular weight (LMW) and smaller 4-ring high molecular weight (HMW) PAHs. Measured as a percentage of the total PAH concentration, the latter included fluoranthene (26%), phenanthrene (22%) and pyrene (18%). At the other 1992 sites, no single PAH compound comprised more than 17% of the sum total and the distribution pattern indicated a common occurrence of fluoranthene and pyrene being present in the highest amount.

The 1995 Bellevue samples had total PAH sediment concentrations varying from 10,970 ng/g in the reference sediment to a maximum of 85,230 ng/g at stn 224. The biggest difference in total PAH sediment composition among sites was due to the relative amounts of naphthalene associated with each sample. Six stations (221, 224, 226, 227, 210, 214), which exhibited the highest total PAH sediment concentrations also had a higher proportion

TABLE 4. Bulk concentrations of trace metals in control(s) and St. Marys River 1992 sediment (μg/g dry weight) used in sediment bioassays.

Station	*Al %*	*As*	*Cd*	*Cr*	*Cu*	*Fe %*	*Hg*	*Mn*	*Ni*	*Pb*	*Zn*
Control	2.0	4.8	1.2	40	20	3.0	0.08	820	30	44	120
Upstream Reference Station 52	0.6	3.3	0.9 <T	26	24	0.8	0.02 <T	100	9	13	44
Algoma Slip Station 183	0.6	8.2	0.5 <T	28	25	2.1	0.08	730	19	25	98
Tannery Bay Station 35	0.3	4.3	1.0 <T	2600	9	0.7	0.50	100	5	54	70
Bellevue Marine Park Station 165	0.9	15	1.2	75	59	5.5	0.13	570	30	59	190
STP – East End Station 172	0.9	11	1.2	91	60	4.4	0.39	390	22	88	250
W of Bell Pt Station 169	0.6	14	1.0 <T	56	55	4.9	0.18	560	26	73	220
Little Lake George Station 87	0.7	4.0	0.7 <T	27	21	1.5	0.06	210	14	27	93
Lake George Station 102	1.7	8.0	1.2	50	43	3.2	0.09	430	29	47	170 170
PSQG SEL Conc.	NA	33	10	110	110	4.0	2.0	1100	75	250	820
PSQG LEL Conc.	NA	6.0	0.6	26	16	2.0	0.20	460	16	31	120

<T – Trace Amount; Shading indicate sediment trace metal concentrations that exceed PSQG–SELs.

Underlining indicate sediment trace metal concentrations that exceed PSQG–LELs; NA – Not Available.

TABLE 4A. Bulk concentrations of trace metals in control(s) and St. Marys River 1995 field sediment (μg/g dry weight).

Station	Al %	As	Cd	Cr	Cu	Fe %	Hg	Mn	Ni	Pb	Zn
Control	2.4	4.1	1.4	50	27	4.1	0.06	960	38	60	160
Upstream Reference Station 213	0.3	6.3	0.5 <T	67	15	3.3	0.05	380	13	19	57
Bellevue Marine Park Station 214	0.6	11.5	1.2	120	46	6.0	0.16	725	23	77	140
Station 226	0.7	10.6	1.0	60	49	4.7	0.14	505	21	55	170
Station 215	0.4	6.2	0.3 <T	37	16	2.7	0.06	338	10	23	84
Station 219	1.1	15.0	2.5	85	98	6.6	0.21	725	38	86	320
Station 227	0.5	13.5	0.8 <T	66	53	4.1	0.15	430	21	53	180
Station 225	0.8	16.0	1.8	87	78	7.2	0.15	780	35	76	285
Station 221	0.5	13.0	0.9 <T	57	43	4.5	0.13	520	20	42	165
Station 217	0.4	5.3	0.3 <T	28	18	2.1	0.06	235	11	22	84
Station 222	0.8	18.0	1.6	86	84	6.6	0.18	750	37	77	320
Station 210	0.5	15.5	1.4	66	66	5.0	0.15	535	21	55	175
Station 211	0.4	10.0	0.9	49	27	3.4	0.12	390	15	40	135
Station 223	0.9	6.4	1.6	47	52	3.9	0.17	460	23	41	165
Station 224	0.7	24.5	1.9	97	87	7.4	0.13	805	39	87	365
PSQG SEL Conc.	NA	33	10	110	110	4.0	2.0	1100	75	250	820
PSQG LEL Conc.	NA	6.0	0.6	26	16	2.0	0.20	460	16	31	120

<T – Trace Amount; Shading Indicate sediment trace metal concentrations that exceed PSQG–SELs.
Underlining indicate sediment trace metal concentrations that exceed PSQG–LELs; NA–Not Available.

TABLE 5. Bulk sediment concentrations for chlorinated organics and pesticides in reference control and St. Marys River 1992 sediment (ng/g, dry weight) used in sediment bioassays.

All Stations	Total PCBs	20 <W
	Heptachlor	1 <W
	Aldrin	1 <W
	Mirex	5 <W
	a–BHC	1 <W
	b–BHC	1 <W
	g–BHC	1 <W
	pp–DDE	1 <W
	Heptachlor epoxide	1 <W
	a–Chlordane	2 <W
	g–Chlordane	2 <W
	Oxychlordane	2 <W
	op–DDT	5 <W
	pp–DDD	5 <W
	pp–DDT	5 <W
	Methoxychlor	5 <W
	Endosulphan I	2 <W
	Dieldrin	2 <W
	Endrin	4 <W
	Endosulphan II	4 <W
	Endosulphan sulphate	4 <W
	Hexachlorobutadiene	1 <W
	Hexachlorobenzene	1 <W
	Octachlorostyrene	1 <W
	123–Trichlorobenzene	2 <W
	124–Trichlorobenzene	2 <W
	135–Trichlorobenzene	2 <W
	1234–Tetrachlorobenzene	1 <W
	1235–Tetrachlorobenzene	1 <W
	1245–Tetrachlorobenzene	1 <W
	Hexachloroethane	1 <W
	Pentachlorobenzene	1 <W
	236–Trichlorotoluene	1 <W
	245–Trichlorotoluene	1 <W
Station 169 & 172	Total PCBs	60 <T

<W – Not Detected; <T – Trace Amount.

TABLE 5A. Bulk sediment concentrations for chlorinated organics and pesticides in reference control and St. Marys River 1995 field sediment (ng/g, dry weight).

All Stations	Heptachlor	1 <W
	Aldrin	1 <W
	Mirex	5 <W
	a–BHC	1 <W
	b–BHC	1 <W
	g–BHC	1 <W
	pp–DDE	1 <W
	Heptachlor epoxide	1 <W
	a–Chlordane	2 <W
	g–Chlordane	2 <W
	Oxychlordane	2 <W
	op–DDT	5 <W
	pp–DDD	5 <W
	pp–DDT	5 <W
	Methoxychlor	5 <W
	Endosulphan I	2 <W
	Dieldrin	2 <W
	Endrin	4 <W
	Endosulphan II	4 <W
	Endosulphan sulphate	4 <W
	Hexachlorobutadiene	1 <W
	Hexachlorobenzene	1 <W
	Octachlorostyrene	1 <W
	123–Trichlorobenzene	2 <W
	124–Trichlorobenzene	2 <W
	135–Trichlorobenzene	2 <W
	1234–Tetrachlorobenzene	1 <W
	1235–Tetrachlorobenzene	1 <W
	1245–Tetrachlorobenzene	1 <W
	Hexachloroethane	1 <W
	Pentachlorobenzene	1 <W
	236–Trichlorotoluene	1 <W
	245–Trichlorotoluene	1 <W
Station 211	Hexachlorobenzene	2 <T

<W – Not Detected; <T – Trace Amount.

TABLE 6. Bulk concentrations of polycyclic aromatic hydrocarbons in St. Marys River 1992 field sediment (ng/g, dry weight).

Parameter	Upstream Reference Stn 52	Algoma Slip Stn 183	Tannery Bay Stn 35	Bellevue Marine Park Stn 165	STP East End Stn 172	West of Bell Point Stn 169	Little Lake George Stn 87	Lake George Stn 102
Acenaphthene	20 <W	7337	20 <W	152 <T	58 <T	75 <T	20 <W	20 <W
Acenaphythylene	20 <W	955	20 <W	136 <T	143 <T	128 <T	25 <T	21 <W
Anthracene	20 <W	13293	20 <W	250	103 <T	197 <T	27 <T	38 <T
Benzo[a]anthracene	29 <T	14119	46 <T	972	829	1250	196 <T	388
Benzo[k]fluoranthene	44 <T	7980	46 <T	812	990	1143	213	441
Benzo[b]fluoranthene	60 <T	6418	51 <T	1071	1118	1260	267 <T	549
Benzo[ghi]perylene	48 <T	2200	44 <T	611	776	721	188	376
Benzo[a]pyrene	29 <T	5000	28 <T	726	565	850	220 <T	518
Chrysene	54 <T	12321	60 <T	1104	1089	1322	219	396
Dibenzo[ah]anthracene	40 <W	339	40 <W	171 <T	215 <T	99 <T	66 <T	102 <T
Fluoranthene	125 <T	77009	112 <T	2285	1737	2334	307	520
Fluorene	223	11336	96 <T	206	73 <T	116 <T	21 <T	21 <T
Indeno[123-cd]pyrene	46 <T	2492	45 <T	617	804	718	230 <T	540
Naphthalene	65 <T	13436	44 <T	2517	301	907	91 <T	135 <T
Phenanthrene	71 <T	64682	67 <T	1243	641	969	122 <T	220
Pyrene	72 <T	52802	93 <T	1708	1346	1842	256	456
Total PAHs	966 <T	291718	832 <T	14587	10788	13931	2468	4741

<W – Not Detected; T – Trace Amount Measured.

Underlining indicate sediment PAH concentrations that exceed PSQG–LELs.

PSQG's not available for acenapthene, acenaphthylene, benzo[b]fluorene and naphthalene.

TABLE 6A. Bulk concentrations of polycyclic aromatic hydrocarbons (ng/g), total polychlorinated biphenyls (ng/g) and total petroleum hydrocarbons (ug/g) in St. Marys River 1995 field sediment. Concentrations reported as dry weight.

Parameter	Upstream Reference Stn 213	Bellevue Stn 214	Bellevue Stn 226	Bellevue Stn 215	Bellevue Stn 219	Bellevue Stn 227	Bellevue Stn 225	Bellevue Stn 221	Bellevue Stn 217	Bellevue Stn 222	Bellevue Stn 210	Bellevue Stn 211	Bellevue Stn 223	Bellevue Stn 224
Acenaphthene	90	310	300	196	160	390	140	410	100	210	270	200	130	510
Acenaphythylene	110	400	220	166	180	190	150	410	80 <T	220	330	140	90	430
Anthracene	260	690	870	586	410	1010	370	2460	270	490	850	640	330	930
Benzo[a]anthracene	920	2400	2750	1533	1750	3050	1450	5150	840	2050	3300	1900	1200	5100
Benzo[b]fluoranthene	1170	2850	3400	1683	2400	3500	2150	6300	1040	2750	3400	2100	1600	9550
Benzo[k]fluoranthene	700	1800	1250	873	750	1250	750	2550	430	930	2800	1310	530	4900
Benzo[ghi]perylene	540	1600	1500	878	480	1450	1050	2950	500	1280	1950	1060	720	2900
Benzo[a]pyrene	820	2400	2350	1333	1430	2400	1350	5050	760	1750	3200	1750	970	4500
Chrysene	1110	2750	2850	1718	1750	2950	1550	5250	910	2100	3600	2250	1150	4550
Dibenzo[ah]anthracene	80 <T	320	420	180	240	420	220	830	80 <T	340	480	140 <T	180	660
Fluoranthene	1620	4950	5000	3483	3200	5750	2500	9250	1950	3750	5450	3900	2550	11200
Fluorene	140	440	430	273	240	470	220	680	140	290	390	240	200	500
Indeno[123-cd]pyrene	540	1850	1800	938	1360	1600	1100	3450	540	1300	2100	1090	800	3350
Naphthalene	560	37500	13500	2256	3200	16500	3100	24000	1120	4500	25500	1750	880	27100
Phenanthrene	1130	3000	2900	2116	1500	2900	1550	4600	1010	1950	2350	2000	1600	3450
Pyrene	1210	3800	3750	2550	2500	4300	2200	6900	1450	3300	4550	4900	1850	5600
Total PAHs	10970	66860	43090	20763	21550	48130	19850	80220	11220	27210	60520	23370	14780	85230
Total PCBs	20 <W	100	20 <W	20 <W	60	20 <W	30	40	20 <W		30	20 <W	20 <W	60
TPHs	350	2050	4755	761	112500	7630	7600	4900	928	10810	5550	1800	3170	9145

<T – Trace Amount; Underlining indicate sediment PAH concentrations that exceed PSQG-LELs; PSQG's not available for acenapthene, acenaphthylene, benzo[b]flouranthene and naphthalene.

of naphthalene (29% to 56%). Five stations (225, 219, 215, 217, 222) had substantially lower naphthalene concentrations, comprising on average 14% of the total PAH. Fluoranthene, pyrene and phenanthrene were among the most abundant PAH compounds in each of the test sediments, which were also common to the reference sediment. For both studies, concentrations of at least 15 of the 16 individual PAH compounds were significantly correlated with sediment TOC.

Total petroleum hydrocarbon (TPH) concentrations in 1995 sediments also co-varied with TOC but failed to correspond with total PAH ($r = +.472$; $p < 0.08$). This suggests that PAH may be a subset of TPH but that other substances may be acting as an additional source of organic contamination. TPH sediment concentrations ranged from 761 μg/g to 112,500 μg/g in the test sediments (Table 6A).

Among the Bellevue Marine park test sediments, stn 214 had the greatest concentration of total PCBs at 100 ng/g, with quantifiable amounts from 30 to 60 ng/g at five stations and at the limit of detection (< 20 ng/g) at seven stations.

Total 2,3,7,8-tetraCDD TEQ data indicate a uniform range in value among the 1992 sediment samples, 1.6 to 6.0 pg/g (Table 7). The lowest TEQ was recorded for the upstream reference site (0.3 pg/g). Relative to other large river systems in the Great Lakes, the St. Marys river sediments had a substantially reduced carcinogenic potency for PCDDs and PCDFs (Kauss, 1994).

3.3 Mayfly (*Hexagenia limbata*) 21-day Lethality and Growth Results

The biological data for the two endpoints, mortality and growth, are summarized in Tables 8; 8A, for 1992 and 1995, accordingly. Mortality in the control and reference sediment was nil in both studies. In 1992, significantly higher mortality occurred for Algoma Slip (96% mortality), Bellevue Marine park (23% mortality) and Bell Point (20% mortality), relative to the two control sediments (ANOVA; $p < 0.0001$). Mortality in the remaining sediments was less than 10%. Growth data for the 1992 samples resulted in average mayfly weights ranging from 6.8 mg to 24.7 mg, and overlapped with the control weight (8.0 mg) and reference control weight (10.2 mg) (Figure 3). Animals exposed to the Tannery Bay sediment (stn 35) actually obtained a body size significantly higher than the controls and each of the other test sediments.

Time-to-death observations made throughout the toxicity test revealed a high loss of mayflies in the Algoma Slip (stn 183) exposures which was preceded by a period of strong avoidance behaviour. All of the nymphs were observed either above or on the sediment surface within the initial 24 hours. Normal mayfly behaviour is represented by an immediate burrowing reaction. By Day-4, some of the nymphs were partially burrowed into the sediment, while most remained on the surface. Death commenced on Day-6 and average percent mortality was 70% by Day-10, evidence of an acute toxic response. All other test sediments showed no obvious signs of stress.

Significant differences in survival among the 1995 test exposures was not assessed due to the lack of replication at most locations. Assuming a percent mortality above the

TABLE 7. Bulk concentrations of polychlorinated dibenzo–p–dioxins and polychlorinated dibenzofurans in St. Marys River 1992 field sediment (pg/g, dry weight).

Parameter	Upstream Reference Stn 52	Algoma Slip Stn 183	NW Tannery Stn 35	Bellevue Marine Park Stn 165	STP East End Stn 172	West of Bell Point Stn 169	Little Lake George Stn 87	Lake George Stn 102
TetraCDD	5.3	ND	1.9	ND	19	5.3	3.9	6.5
PentaCDD	3.1	ND	4.0	17	22	4.4	2.0	3.5
HexaCDD	ND	20	12	70	49	28	ND	18
HeptaCDD	16	130	69	170	120	100	54	130
OctaCDD	41	410	250	460	360	590	170	370
TetraCDF	11	7.9	ND	8.0	33	34	17	34
PentaCDF	5.1	6.3	ND	14	60	5.7	6.0	12
HexaCDF	ND	19	ND	ND	120	19	ND	ND
HeptaCDF	ND	34	27	61	49	45	20	35
OctaCDF	ND	30	19	71	ND	36	ND	ND
	2,3,7,8 – Substituted Isomers							
2,3,7,8–TetraCDD	ND	ND	1.9	ND	3.0	2.3	1.7	4.2
1,2,3,7,8–PentaCDD	ND	ND	ND	4.1	1.9	ND	ND	ND
1,2,3,4,7,8–HexaCDD	ND	ND	ND	ND	ND	ND	ND	ND
1,2,3,6,7,8–HexaCDD	ND	ND	ND	ND	ND	ND	ND	ND
1,2,3,7,8,9–HexaCDD	ND	ND	ND	ND	ND	ND	ND	ND
1,2,3,4,6,7,8–HeptaCDD	8.1	61	36	88	64	53	27	65
2,3,7,8–TetraCDF	2.1	4.6	ND	8.0	6.2	6.9	3.8	7.0
1,2,3,7,8–PentaCDF	ND	ND	ND	ND	ND	ND	ND	ND
2,3,4,7,8–PentaCDF	ND	ND	ND	ND	ND	ND	ND	ND
1,2,3,4,7,8–HexaCDF	ND	ND	ND	ND	ND	ND	ND	ND
1,2,3,6,7,8–HexaCDF	ND	ND	ND	ND	ND	ND	ND	ND
2,3,4,6,7,8–HexaCDF	ND	ND	ND	ND	ND	ND	ND	ND
1,2,3,7,8,9–HexaCDF	ND	ND	ND	ND	ND	ND	ND	ND
1,2,3,4,6,7,8–HeptaCDF	ND	13	14	29	16	15	8.0	15
1,2,3,4,7,8,9–HeptaCDF	ND	ND	ND	ND	ND	ND	ND	ND
Total 2,3,7,8–TetraCDD TEQ:	0.3	1.6	2.7	4.5	5.7	4.3	2.6	6.1

ND=Not Detected';

TEQs calculated assuming that ND=zero.

TABLE 8. Summary of biological results on mayfly, midge and minnow sediment bioassays for control(s) and St. Marys River 1992 sediments.

Mean values (± standard deviation) where sample size n=3 replicates.

Test Organism	*Hexagenia limbata* (Mayfly)		*Chironomus tentans* (Midge)		*Pimephales promelas* (Fathead Minnow)
Station	*% Mortality*	*Ave. Individual Body Weight* (mg wet wt.)	*% Mortality*	*Ave. Individual Body Weight* (mg wet wt.)	*% Mortality*
Control	A 0 (0)	BC 8.00 (1.4)	AB 4.4 (4)	B 7.95 (0.3)	A 0 (0)
Upstream Reference Station 52	A 0 (0)	BC 10.24 (0.6)	A 2.2 (4)	B 8.27 (0.6)	A 0 (0)
Algoma Slip Station 183	C ** 96.6 (6)	–	C ** 95.5 (8)	–	A 3.3 (6)
Tannery Bay Station 35	A 0 (0)	A 24.76 (2.5)	AB 6.6 (7)	A 10.75 (0.8)	A 3.3 (6)
Bellevue Marine Park Station 165	B ** 23.3 (11)	C 6.85 (2.0)	B ** 22.2 (10)	F 2.11 (0.4)	A 0 (0)
STP – East End Station 172	AB 10.0 (0)	C 6.82 (0.5)	AB 4.4 (4)	DE 4.78 (0.4)	A 3.3 (6)
W of Bell Pt Station 169	B ** 20.0 (0)	C 7.55 (0.4)	AB 4.4 (4)	E 3.70 (0.4)	A 3.3 (6)
Little Lake George Station 87	A 3.3 (6)	B 11.63 (1.7)	AB 6.6 (7)	C 6.23 (1.4)	A 0 (0)
Lake George Station 102	A 0 (0)	BC 8.92 (0.5)	AB 4.4 (8)	CD 6.05 (0.2)	A 0 (0)
% MSD % C.V. D.P.	9.9 14.7 38.6	– 11.3 14.9	13.5 37.1 15.0	– 8.9 15.4	8.1 185 1.2

** %Mortality value is significantly different than the control and reference sediment (Dunnett's t–test;$p<0.05$).

A Means sharing a common letter within a column are not significantly different; Tukey's HSD test for % Mortality ($p<0.05$) and planned comparisons using LSMEANS for comparing Body Weight ($p<0.01$).

MSD – Minimum Significant Difference; C.V. – Coefficient of Variation; D.P. – Discriminatory Power.

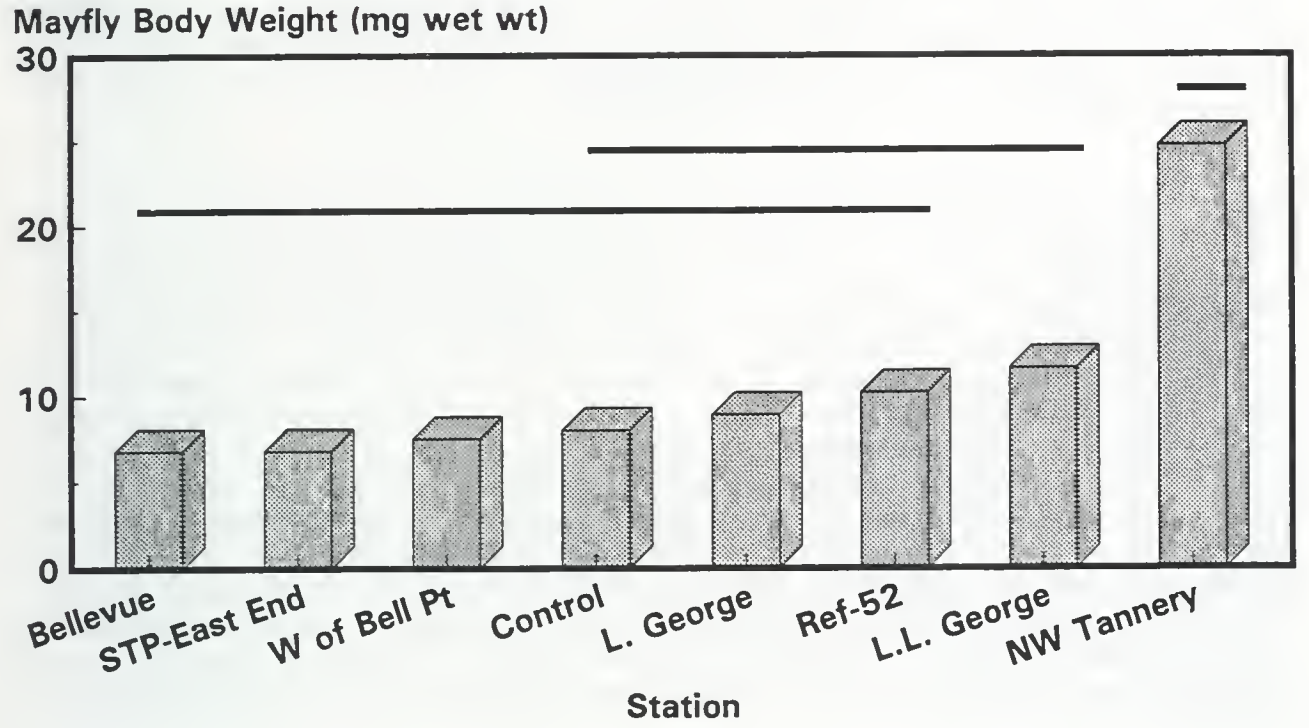
TABLE 8A. Summary of biological results on mayfly, midge and minnow sediment bioassays for control(s) and St. Marys River 1995 sediments.

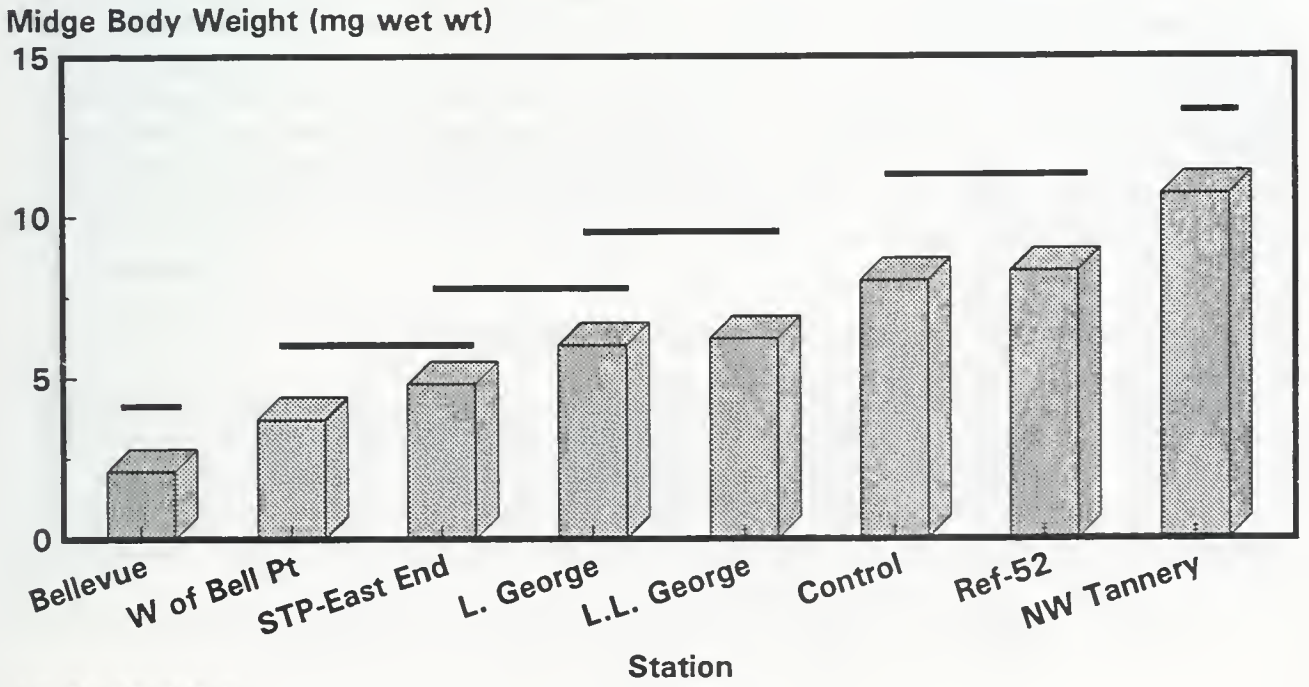
Mean values (± stand. deviation) where sample size n=3, otherwise n=1 replicate.

Test Organism	*Hexagenia limbata* (Mayfly)		*Chironomus tentans* (Midge)		*P. promelas* (Fathead Minnow)
Station	*% Mortality*	*Ave. Individual Body Weight* (mg wet wt.)	*% Mortality*	*Ave. Individual Body Weight* (mg wet wt.)	*% Mortality*
Control	0.0 (0)	7.97 (1.0) BC	0.0 (0)	11.05 (0.7) A	6.6 (6)
Upstream Reference Stn 213	0.0 (0)	10.21 (1.9) B	2.2 (4)	11.51 (0.7) A	0.0
Bellevue Marine Park					
Station 214	10.0	7.22 C	0.0	5.23 BC	0.0
Station 226	0.0	6.29 C	6.6	3.58 CD	0.0
Station 215	0.0	19.06 A	0.0	13.08 A	0.0
Station 219	10.0 (17)	6.09 (0.8) C	33.3	1.00 D	10.0
Station 227	3.3 (6)	7.59 (0.8) C	24.4 (27)	5.84 (0.4) B	0.0 (0)
Station 225	20.0	7.03 C	42.1 (7)	1.43 (0.3) D	0.0
Station 221	20.0	6.58 C	13.3	4.30 BC	0.0
Station 217	0.0	22.17 A	6.6	5.52 BC	Not Tested
Station 222	0.0	8.08 BC	6.6	3.95 BC	20.0
Station 210	3.3 (6)	7.57 (0.3) C	11.0 (4)	4.65 (1.8) BC	13.3 (15)
Station 211	0.0	20.70 A	0.0	12.03 A	0.0
Station 223	0.0	11.50 B	0.0	4.24 BC	0.0 (0)
Station 224	10.0	7.05 C	6.6	5.26 BC	10.0

A Means sharing a common letter within a column are not significantly different; planned comparisons using LSMEANS for comparing Body Weight ($p<0.01$).

Figure 3. Mayfly and Midge Growth for St. Marys River 1992 Sediments





Lines indicate significant groups.

control mortality criterion (15% mortality), as an indication of a potential significant effect, only two stations (225 and 221) showed borderline toxicity. Eleven of the Bellevue sediments exhibited percent mortality of $\leq$10%. None of the 1995 test sediments caused a reduction in growth of greater than 50% relative to the control or reference control weights (Figure 4). Some sites received a lower ranking relative to the reference control (stns 214, 226, 219, 227, 225, 221, 210, 224) but were comparable to the control weight of 7.9 mg. The level of significance would be a conservative estimate of a significant difference since the variability in body weight is based on within-jar rather than among-jar variability due to the lack of treatment replication. Enhanced growth (approximate doubling of reference weight) was observed at three locations (stns 211, 215 and 217).

3.4 Chironomid (*Chironomus tentans*) 10-day Lethality and Growth Results

Results for chironomid growth and lethality are reported in Tables 8, 8A. Chironomid mortality rate in both controls and for both studies, averaged 0% to 4%. This is well below the acceptable maximum control mortality of 25%. In 1992, significantly higher mortality relative to the control sediments was apparent for Algoma Slip (stn 183) at 95%, and Bellevue Marine park (stn 165; 22% mortality) (ANOVA; $p<0.0001$). Mortality in the other sediments ranged from 4% to 6% and was not significantly different than the control and reference control sediment. Sublethal larval growth data indicated varying degrees of impairment. The majority of the samples tested in 1992 had significantly lower weights than either control exposures (ANOVA; $p<0.0001$) (Figure 3). The smallest midge size was obtained for Bellevue Marine park (stn 165), with an average weight of 2.1 mg. This translates into a 74% reduction in growth relative to either of the control exposures which had an average weight of 8.1 mg. Severe growth reductions were was also noted at stns 172 and 169 (41% to 54% reduction) and moderate growth impairment was found at stns 87 and 102 (23%-25% reduction).

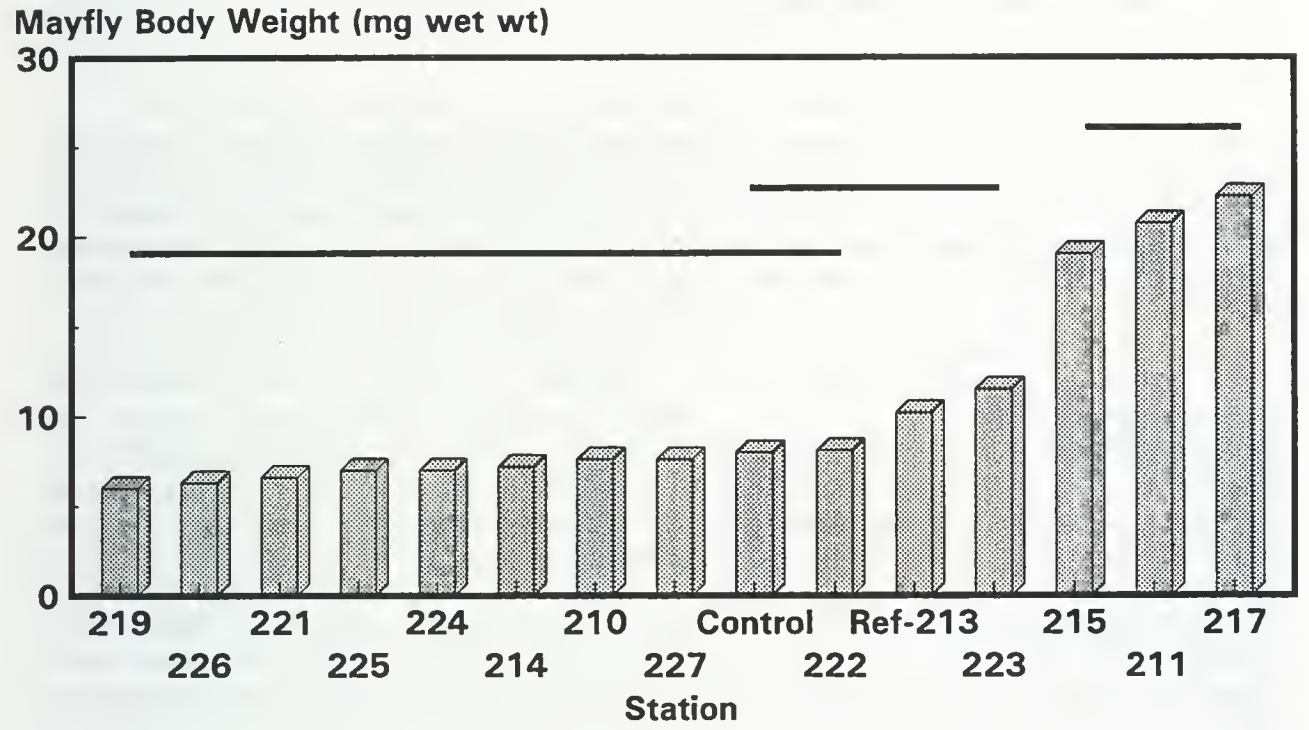
Among the 1995 Bellevue Marine park sediments, *C. tentans* mortality equalled or exceeded the acceptable control criterion of 25% at three locations, stns 219 (33%), 227 (24%) and 225 (42%). Direct statistical comparison with the control exposures was not possible due to the lack of treatment replication. The remaining ten stations had minimal lethality, with values less than 13%. Significantly lower body weights were noted most frequently in the 1995 Bellevue Marine park sediments (Figure 4). Eleven of the 13 test sediments had final body weights (1.0 mg to 5.8 mg) that were 48% to 91% lower than the control and reference control animals (Ave: 11.2 mg).

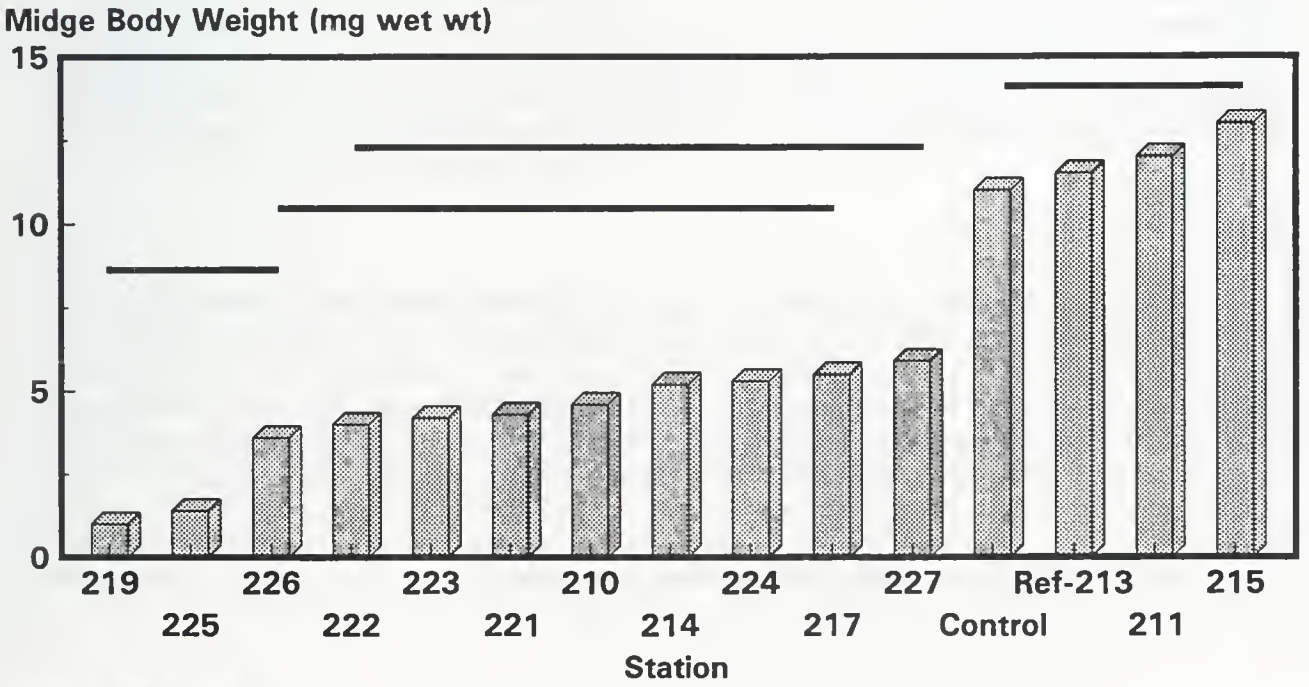
3.5 Fathead Minnow (*Pimephales promelas*) 21-day Lethality Results

Juvenile fathead minnow percent mortality data is reported in Tables 8; 8A, for the 1992 and 1995 studies, respectively. In 1992, control survival was 100% for both the control and reference control exposures. Minnow mortality at all test locations was not statistically different either among sites (0%-3% mortality) or relative to the controls (ANOVA; $p<0.74$).

In the 1995 toxicity test, minnow survival was at least 80%. Station 222 incurred a

Figure 4. Mayfly and Midge Growth for St. Marys River 1995 Sediments





Lines indicate significant groups.

20% mortality, which is slightly above the acceptable control criterion of 15% mortality. It is not anticipated that the degree of toxicity at the remaining sites (Range: 0% to 13%) would be statistically higher than the control (6% mortality) or reference control (0% mortality). Laboratory inspection of all test chambers did not reveal any abnormal activity.

3.6 Quality Assurance Toxicity Tests

Replicated Sediment Toxicity Test

The results of the 1992 sediment toxicity test were used to evaluate the repeatability of the test data. A similar assessment was not carried out for the 1995 toxicity test since only a few randomly selected sites were subjected to between-sample replication. However, given the striking similarity in the lethal and sublethal data for each test species between the 1992 and 1995 toxicity tests in both control sediments, the quality assurance data calculated in 1992 is considered a good estimate of relative rankings among the 1995 sites.

Coefficient of variation was calculated for each endpoint and showed excellent test precision (Range: 8% to 37% C.V.) across benthic species and test response (Table 8). The unusually high %C.V. obtained in the minnow assay is a result of the general insensitivity in organism response among all sites. The lower the C.V., the greater the confidence in the precision or accuracy of the test results. Another useful quantitative measure of test precision is the minimum significant difference or MSD, which describes the ability to detect a significant effect in the paired response between the control versus the test sample. The MSD was determined for percent mortality and was similar among each toxicity test (MSD = 8% - 13%). In other words, the test design was adequate to detect even small differences in mortality between the test and control sediments as being significant. Other reported MSDs for *C. tentans* 10-day sediment lethality tests include MSD = 38% (Becker *et al.*, 1995) and MSD = 14% (Burton *et al.*, 1996). The latter value is based on interlaboratory performance which tends to be higher than that calculated for intralaboratory studies, as was the case in this report. The mortality endpoint in the *Hexagenia* toxicity test yielded the best discriminatory power value (D.P. 38). Mayfly growth, midge growth and midge survival also provided equally reasonable capability of measuring differences in sediment quality (D.P. 15). The minnow lethality endpoint was the least sensitive with a very poor D.P. of 1.

Reference Toxicity Tests

The 48-hour copper LC50 (95% C.I.) for the water-only reference toxicant exposures for *H. limbata* for the 1995 study was 1.81 (1.01 - 5.26) mg/L. This value was within the acceptable 48-h LC50 (± 2 s.d.) range of 1.41 (1.33) mg/L, according to a previous series of reference toxicant tests. Similarly, for *C. tentans*, the LC50 was 0.82 (0.69 - 1.01) mg/L, as compared to an expected 48-h LC50 (± 2 s.d.) of 1.53 (0.93) mg/L. This indicates that the relative sensitivity of the test organisms fell within a normal response range.

3.7 Chemical Bioaccumulation in *Pimephales promelas*

The examination of chemical availability to aquatic organisms is valuable for assessing the potential for chemical transfer through the food web. The primary objective of this test procedure is to make general observations on whole organism tissue concentrations as they relate to overall bulk chemical concentrations in the sediment and differences in chemical uptake among sites. Surviving fathead minnows were submitted for the analysis of trace metals in 1992 and for individual PAHs in 1995. All values are based on whole-body tissue concentrations. Values are provided as dry weight for the inorganic data using a dry to wet conversion ratio of 0.15 and cited on a wet weight basis for the PAH minnow tissue results.

The sources of inorganic and organic compound accumulation to forage fish include direct contact with the sediment and uptake from the overlying water. Factors that control chemical accumulation by forage fish include those that affect chemical speciation, adsorption and desorption such as sediment organic content, redox potential, pH, Fe and Mn oxides, particle size distribution and chemical partition coefficient, also known as the octanol-water partition coefficient, Kow (Lake *et al.*, 1990). More recently, acid-volatile sulfides appear to be an important factor in the chemical bioavailability of certain divalent trace metals (Ankley, 1996). Biotic factors affecting uptake include chemical-specific toxicokinetics, metabolism and lipid content (Campbell *et al.*, 1988; Boese *et al.*, 1995).

Table 9 summarizes the Cd, Cu, Mn, Ni, Pb and Zn tissue concentrations and associated standard deviations measured in surviving juvenile fathead minnows from the 1992 sediment toxicity test. Whole-organism chemical concentrations are based on triplicate samples. For most trace metals, the tissue residue concentrations found in minnows exposed to the test sediments correspond with those levels achieved in either the control or reference control sediment exposure ($p<0.05$). Although the Cu tissue residue reported for Bellevue Marine park (stn 165) of 17.1 μg/g was significantly higher than either of the control Cu residue concentrations, the value was within a two-fold difference. Metals including Cd, Ni and Pb could be sufficiently explained to have arisen from contact via food provided during testing and considered as background levels.

Concentration factors were calculated to assess the relative availability of each trace metal for the test and control sediments. The biota-sediment accumulation factor or BSAF is defined as the ratio of metal chemical concentration in the fathead minnow to that in the bulk sediment (Lake *et al.*, 1990, Ankley *et al.*, 1992). Each individual replicate that was analyzed consisted of approximately ten individual animals.

$$BSAF = C_t / C_s$$

where,

C_t = tissue metal contaminant concentration (μg/g tissue, dry weight)
C_s = sediment metal contaminant concentration (μg/g sediment, dry weight)

BSAFs >1.0, indicating that the metal found in the organism surpassed those levels found in the bulk sediment, were reported for Zn at each test location. Equally high BSAFs were also reported for the control and reference control sediment exposures (BSAF: 3.1 and 8.2). Zinc uptake is homeostatically regulated via an active transport mechanism and is considered an essential micronutrient which can attain relatively high levels in the organism even when exposure concentrations are relatively low (Hodson, 1988). Zinc tissue concentrations were held at a fairly constant tissue concentration of 344 $\pm$ 43 μg/g, among

TABLE 9. Mean metal concentrations in fathead minnows exposed to control(s) and St. Marys River 1992 sediments in the laboratory and associated biota–sediment accumulation factors (BSAFs).

Tissue concentrations reported as μg/g dry weight; Mean values ± standard deviation; Sample size n=3.

Station	Cd	Cu	Mn	Ni	Pb	Zn
Water/Food Control	A 0.55 (.10)	BC 15.63 (3.7)	A 21.2 (2.7)	A 5.58 (1.0)	A 8.26 (1.5)	C 632 (100)
Georgian Bay Control	A 0.33 (.07)	A 9.38 (2.0)	CDE 87.1 (23.2)	A 3.25 (.30)	A 4.91 (.38)	AB 377 (42)
BSAF	0.27	0.46	0.10	0.10	0.11	3.14
Upstream Reference Station 52	A 0.37 (.14)	AB 10.27 (1.4)	A 23.2 (6.7)	A 3.79 (1.4)	A 5.80 (2.0)	AB 361 (26)
BSAF	0.41	0.42	0.23	0.42	0.44	8.20
Algoma Slip Station 183	A 0.33 (.07)	AB 10.05 (2.3)	E 167.5 (63.9)	A 3.35 (0.6)	A 6.03 (1.7)	AB 354 (75)
BSAF	0.66	0.40	0.22	0.17	0.24	3.61
Tannery Bay Station 35	A 0.33 (.00)	ABC 11.61 (0.3)	ABC 41.2 (7.7)	A 3.35 (0.0)	A 8.71 (6.9)	B 428 (34)
BSAF	0.33	1.29	0.41	0.67	0.16	6.11
Bellevue Marine Park Station 165	A 0.37 (.11)	C 17.19 (1.0)	DE 93.8 (13.4)	A 5.94 (3.1)	A 6.94 (0.9)	AB 370 (36)
BSAF	0.37	0.29	0.16	0.19	0.11	1.94
STP – East End Station 172	A 0.77 (.88)	ABC 12.28 (1.0)	AB 37.2 (15.8)	A 2.99 (0.3)	A 5.11 (1.1)	A 303 (28)
BSAF	0.77	0.20	0.09	0.13	0.05	1.21
W of Bell Pt Station 169	A 0.28 (.04)	A 9.60 (1.0)	AB 33.5 (6.7)	A 2.90 (0.4)	A 4.24 (0.4)	A 296 (15)
BSAF	0.28	0.17	0.05	0.11	0.05	1.34
Little Lake George Station 87	A 0.28 (.04)	AB 10.72 (0.7)	ABC 40.3 (4.5)	A 2.90 (0.4)	A 4.46 (0.7)	AB 321 (7)
BSAF	0.28	0.51	0.19	0.20	0.16	3.45
Lake George Station 102	A 0.30 (.04)	ABC 12.50 (2.5)	BCD 52.9 (18.8)	A 3.68 (0.7)	A 4.46 (0.1)	AB 323 (19)
BSAF	0.25	0.29	0.12	0.12	0.16	1.90

A Means sharing a common letter within a column are not significantly different using Tukey's HSD test ($p<0.05$).

all locations. BSAFs for Cd, Cu, Mn, Ni and Pb were consistently below 1.0, suggesting minimal availability. The only exception occurred for Tannery Bay (stn 35), with a reported BSAF of 1.2 for Cu. This represents Cu being twice as available relative to other locations, yet the final tissue concentration matched those attained in the upstream reference site.

Table 10 summarizes the individual and total PAH juvenile fathead minnow tissue concentrations (ng/g, wet weight) for the 1995 fish samples. Duplicate samples were available for three test and one control sediment; otherwise, values are based on single samples consisting of about ten animals each. Trace amounts or non-detectable concentrations were reported in the control exposures and were similar to those observed at 10 of the 12 test sites. Slightly higher concentrations of total PAHs (310 - 860 ng/g) were found for stns 214 and 226. Among individual PAHs, only naphthalene achieved quantifiable levels. The increased uptake of naphthalene is a likely result of its high water solubility. Station 214 sediment contained the largest fraction of naphthalene (56%) among the 16 individual PAH compounds, while stn 226 sediment had 31% naphthalene.

4.0 DISCUSSION

A ranking system was used to identify differences in sediment quality among sites for the two independent data sets. This was determined by the magnitude of an effect using statistical test methods. Each endpoint was considered as being either a significant, toxic (T) or non-significant, non-toxic (N) response. In addition, the lethality endpoint received a greater weighting over the respective sublethal endpoint, where applicable. The final rating is based on the total number of positive hits recorded for each of the five biological endpoints. Each sediment fell into one of the following classifications (listed from least impacted (high quality) to most impacted (very low quality)): non-impacted (high); slightly impacted (slight); intermediately impacted (moderate); strongly impacted (low); and very strongly impacted sites (very low) (Tables 11; 11A). Since the 1995 toxicity tests were completed primarily on unreplicated samples, either the MSD value observed in the 1992 toxicity test or a default value representing the required acceptable control mortality criteria was used in the assessment of the 1995 toxicity data.

Examination of the 1992 toxicity test results revealed an acute lethal response in the Algoma Slip (stn 183) sample, for both the mayfly and midge. Concurrent laboratory observations on mayfly avoidance behaviour confirmed the adverse nature of the sediment. Minor differences in mortality between test and reference exposures were noted at some sites situated in the Lake St. George Channel. The Bellevue Marine park (stn 165) sediment elicited a slight level of toxicity (>20% mortality) to benthic organisms with a strong growth impairment of 74% observed in the *Chironomus* test and mayfly body weight was also the lowest recorded. A marginal sublethal effect was apparent further downstream, just west of Bell Point at stn 169. Tannery Bay (stn 35), Little Lake George (stn 87) and Lake George (stn 102) sediments were deemed non-impacted according to the lack of significant biological responses.

The indication of negative growth on mayfly nymphs and midge larvae found at Bellevue Marine park in 1992 was further confirmed in the follow-up study completed in 1995.

TABLE 10. Polycyclic aromatic hydrocarbon concentrations in fathead minnows exposed to control(s) and St. Marys River 1995 sediments in the laboratory.

Tissue concentrations reported es ng/g wet weight. Sample size as indicated.

Parameter	Pre-exposure	Control		Upstream Reference Stn 213	Stn 214	Stn 226	Stn 215	Stn 219	Stn 227	
	Rep 1	Rep 1	Rep 2	Rep 1	Rep 1	Rep 1	Rep 1	Rep 1	Rep 1	Rep 2
Acenephthene	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W
Acenaphythylene	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W
Anthracene	20 <W	20 <W	20 <W	40 <T	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W
Benzo[a]anthracene	20 <W	20 <W	20 <W	20 <W	40 <T	20 <W	20 <W	20 <W	20 <W	20 <W
Benzo[b]fluoranthene	20 <W	20 <W	20 <W	20 <W	80 <T	20 <W	20 <W	20 <W	20 <W	20 <W
Benzo[k]fluoranthene	20 <W	20 <W	20 <W	20 <W	40 <T	20 <W	20 <W	20 <W	20 <W	20 <W
Benzo[ghi]perylene	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W
Benzo[e]pyrene	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W
Chrysene	20 <W	20 <W	20 <W	20 <W	60 <T	20 <W	20 <W	20 <W	20 <W	20 <W
Dibenzo[ah]anthracene	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W
Fluoranthene	20 <W	20 <W	20 <W	20 <W	60 <T	20 <W	20 <W	40 <T	20 <W	20 <W
Fluorene	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W
Indeno[123-cd]pyrene	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W
Naphthalene	20 <W	20 <W	20 <W	20 <W	340	160	20 <W	20 <W	40 <T	60 <T
Phenanthrene	20 <W	20 <W	20 <W	40 <T	60 <T	20 <W	20 <W	20 <W	20 <W	20 <W
Pyrene	20 <W	20 <W	20 <W	20 <W	60 <T	20 <W	20 <W	40 <T	20 <W	20 <W
Total PAHs	200 <W	200 <W	200 <W	260 <T	860	350	200 <W	260 <T	230 <T	250 <T

<W – Not Detected; <T – Trace Amount Measured; One-half the detection limit value was used to calculate the total PAH tissue concentration.

TABLE 10. Continued.

Parameter	Stn 225	Stn 221	Stn 222	Stn 210		Stn 211	Stn 223		Stn 224
	Rep 1	Rep 1	Rep 1	Rep 1	Rep 2	Rep 1	Rep 1	Rep 2	Rep 1
Acenaphthene	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W
Acenaphthylene	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W
Anthracene	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W
Benzo[a]anthracene	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W
Benzo[b]fluoranthene	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W
Benzo[k]fluoranthene	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W
Benzo[ghi]perylene	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W
Benzo[a]pyrene	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W
Chrysene	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W
Dibenzo[ah]anthracene	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W
Fluoranthene	20 <W	40 <T	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W
Fluorene	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W
Indeno[123-cd]pyrene	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W
Naphthalene	20 <W	40 <T	80 <T	60 <T	120	40 <T	20 <W	20 <W	20 <W
Phenanthrene	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W
Pyrene	20 <W	40 <T	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W
Total PAHs	200 <W	290 <T	270 <T	250 <T	310	230 <T	200 <W	200 <W	200 <W

<W – Not Detected; <T – Trace Amount Measured; One-half the detection limit value was used to calculate the total PAH tissue concentration.

TABLE 11. Spatial variability in sediment toxicity and sediment quality for St. Marys River 1992 samples.

Station	Sediment Quality	Sediment Total PAHs (ng/g dry wt)	Mayfly Mortality	Mayfly Ave wt	Midge Mortality	Midge Ave wt	Minnow Mortality
Reference Stn 52	High	966 <T	N	N	N	N	N
Tannery Bay Stn 35	High	832 <T	N	N	N	N	N
Little Lake George Stn 87	High	2468	N	N	N	T	N
Lake George Stn 102	High	4741	N	N	N	T	N
STP – East End Stn 172	High	10788	N	N	N	T	N
W of Bell Pt Stn 169	Slight	13931	T	N	N	T	N
Bellevue Marine Park Stn 165	Moderate	14587	T	N	T	T	N
Algoma Slip Stn 183	Very Low	291718	T	–	T	–	N

N – Not Toxic, % mortality $p>0.05$ and $p>0.10$ for growth data;
T – Toxic, % mortality $p<0.05$ and $p<0.10$ for growth data.

TABLE 11A. Spatial variability in sediment toxicity and sediment quality for St. Marys River 1995 samples.

Station	Sediment Quality	Sediment Total PAHs (ng/g dry wt)	Sediment TPH (µg/g dry wt)	Mayfly Mortality	Mayfly Ave wt	Midge Mortality	Midge Ave wt	Minnow Mortality
Reference Stn 213	High	10970	350	N	N	N	N	N
Bellevue Marine Pk Stn 215	High	20763	761	N	N	N	N	N
Stn 211	High	23370	1800	N	N	N	N	N
Stn 217	High	11220	928	N	N	N	T	Not Tested
Stn 222	High	27210	10810	N	N	N	T	N
Stn 223	High	14780	3170	N	N	N	T	N
Stn 224	Slight	85230	9145	N	T	N	T	N
Stn 214	Slight	66860	2050	N	T	N	T	N
Stn 227	Slight	48130	7630	N	T	N	T	N
Stn 221	Slight	80220	4900	N	T	N	T	N
Stn 210	Slight	60520	5550	N	T	N	T	N
Stn 226	Moderate	43090	4755	N	T	N	T	N
Stn 219	Low	21550	112500	N	T	T	T	N
Stn 225	Low	19850	7600	N	T	T	T	N

N – Not Toxic, % mortality less than control criteria and $p>0.10$ for growth data;
T – Toxic, % mortality greater than control criteria and $p<0.10$ for growth data.

Toxicity results showed widespread degradation based on the sublethal data, particularly in the *Chironomus* toxicity test. Sediments associated with a higher toxicological effect were situated in the nearshore region in a small embayment bordering from Simpson Street to the marina. Midge growth was reduced to a point that appeared to compromise organism survival. For instance, at stn 219, midge growth was 91% lower than the controls, with a corresponding mortality rate of 33%. Similarly, an 87% growth reduction was reported at stn 225 where mortality was 42%. Mayfly biomass was also statistically lower than the reference control exposure at these two sites, although no differences were detected relative to the negative control weight. This was likely due to a difference in storage time between the control sediment (~12 months) versus the freshly collected test samples (2 weeks). Mayfly growth is sensitive to the quality of detrital material associated with the sediment, since supplemental feeding was not provided throughout the test. Several other sites caused a high degree of growth reduction (50%) in the midge assay.

Spearman rank correlation coefficients were calculated among each test species and endpoint for the 1992 and 1995 studies (Table 12). Among all the endpoints, benthic invertebrate growth effects were highly intercorrelated in both studies ($r = +0.71$ to 0.90, $p < 0.01$). The growth endpoint of both benthic species represented an equally sensitive indicator of sediment quality. This relationship enhances the use of the sediment toxicity test results in distinguishing differences in quality for future site-specific studies on the St. Marys River. The number of strong positive correlations recorded in the 1992 study was biased due to the clear difference in toxic and non-toxic sites. The minnow lethality test endpoint failed to identify any differences in sediment quality and was inconsistent relative to the benthic invertebrate toxicity results. It appears that gross mortality is an inadequate determination of sediment quality and a more subtle test response is required. Mayfly 10-day sediment toxicity tests were performed in 1987 at six sites that corresponded with five of the 1992 test locations (Jaagumagi *et al.*, 1991). At total PAH exposure concentrations of 2.8 to 49.4 μg/g, percent mortality did not surpass 20%, further illustrating a general lack of response in lethality. The above study did not include mayfly growth measurements.

The toxicity endpoints were also compared to sediment physical, nutrient and chemical variables to aid in determining potential causes for the observed laboratory effects. The correlation summary for the 1992 sediments showed a higher tendency for 15 of 16 individual PAH compounds, as well as total PAH bulk sediment concentrations, to be negatively (inversely) correlated with organism survival and growth (Table 13). Each of the individual PAH compounds also covaried significantly with sediment TOC (data not shown). At least 9 of the 15 PAHs that originally correlated with the toxicity data continued to be significantly correlated after adjustment for variation in sediment TOC.

Among the 1992 test sediments, only Algoma Slip (stn 183) sediment had total PAH bulk sediment concentrations that most closely approached the PSQG-SEL concentration of 1,000 μg/g (corrected for a maximum organic content of 10%). The actual total PAH concentration in field sediment was 291 μg/g or about 1/3 of the SEL concentration and best explained the acute toxicity observed in the mayfly and midge bioassays. The PSQG is established using field-derived numbers that describe benthic community structure and abundance. The SEL guideline for total PAHs also agrees favourably with laboratory-derived LC50s at other PAH-contaminated sites. A recent study at the Northern Wood Preservers site located near Thunder Bay, Ontario permitted a series of toxicity tests to be performed on a

TABLE 12. Spearman rank correlation coefficients indicating significant positive (direct) correlations among toxicity data for St. Marys River 1992 and 1995 sediments.

	Year	Mayfly Survival	Mayfly Growth	Midge Survival	Midge Growth
Mayfly Growth	1992 1995	+ .805 * + .707 **			
Midge Survival	1992 1995	n.s. + .628 *	n.s. + .627 *		
Midge Growth	1992 1995	+ .927 ** n.s.	+ .904 ** + .718 **	n.s. n.s.	
Minnow Survival	1992 1995	n.s. n.s.	n.s. n.s.	n.s. n.s.	n.s. n.s.

** $p < 0.01$; * $p < 0.05$; n.s. – Not Significant at $p > 0.05$.

TABLE 13. Spearman rank correlation analysis summary indicating significant negative (inverse) or positive (direct) correlation between biological endpoints and sediment physical and chemical parameters for St. Marys River 1992 samples.

Toxicity Endpoint	Mayfly Survival	Mayfly Growth	Midge Survival	Midge Growth	Minnow Survival
Bulk Concentration	– Ac ** – Acy ** – An ** – B(a)An ** – B(a)P ** – Chy ** – Ft ** – N ** – Ph ** – P ** – Total PAH ** – B(b/k)Ft * – BPer * – DB(ah)An * – IP * – As * – Mn *	– An ** – B(b)Ft ** – BPer ** – DB(ah)An ** – IP ** – N ** – Ph ** – Total PAH ** – Ac * – Acy * – B(a)An * – B(k)Ft * – B(a)P * – Chy * – Ft * – P * – TOC * – Cu * – Mn *		– Ac ** – An ** – B(a)An ** – B(b/k)Ft ** – B(a)P ** – Chy ** – Ft ** – N ** – Ph ** – P ** – Total PAH ** – Acy * – BPer * – DB(ah)An * – IP * – As * – Mn *	
TOC corrected[a] Concentration	– An ** – Ft ** – N ** – Ph ** – P ** – Total PAH ** – Ac * – Acy * – B(a)An * – Chy *	– An * – Acy * – B(a)An * – B(b/k)Ft * – Chy * – Ft * – N * – Ph * – P * – Total PAH *	– Ac **	– B(a)An ** – Chy ** – Ft ** – N ** – Ph ** – P ** – Total PAH ** – Acy * – An * – B(b)Ft *	

a Included All PAHs except for fluorene.

** $p < 0.01$; * $p < 0.05$.

gradient of PAH-contaminated sediments (Jaagumagi *et al.*, 1996a). Appendix 2A summarizes the chemical and biological parameters pertaining to sediments used in the laboratory toxicity tests. Linear regression analysis between organism survival and sediment total PAH bulk concentrations was completed in order to obtain effects-level PAH concentrations. The resulting 21-day mayfly LC50 was 538 μg/g (462 μg/g; lower 95% C.I.) and the 10-day midge LC50 was 718 μg/g (584 μg/g; lower 95% C.I.). The regression data was based on a sample size of 14. Therefore, the average lower 95% confidence interval for the two benthic species lethality endpoint is 511 μg/g and is analogous to the projected PSQG-SEL of 460 μg/g, based on the average sediment TOC content of 4.6%. In other words, the existing PSQG-SEL of 10,000 μg/g for total PAH adjusted for sediment TOC, is a reliable measure of potential toxic effects expected to occur under laboratory conditions. Laboratory toxicity tests that were performed in 1990 on a number of highly contaminated Algoma Slip sediments reported a high degree of toxicity (>80% mortality) that also coincided with elevated PAH sediment concentrations (>685 μg/g) (Bedard and Petro, 1992).

The 1992 St. Marys River toxicity test findings afforded an excellent opportunity to develop a sublethal dose-response relationship with sediment PAH concentrations. This was measured directly, given the emphasis on growth reduction and the wide range in final organism sizes that were obtained among sites. Mayfly growth, expressed as percent growth reduction relative to reference control values, significantly regressed with total PAH bulk sediment concentration ($p<0.02$). The amount of variation explained was 77% and the 21-day mayfly IC50 (IC50 is the chemical sediment concentration associated with a 50% growth reduction) was 25 μg/g, after the removal of two outliers from the equation (Figure 5). An even stronger relationship was found using the 10-day *Chironomus tentans* growth data, with 82% of the variation explained at a significance level of $p=0.004$. Figure 5A illustrates the bulk sediment total PAH plotted against midge growth reduction, where one outlier was omitted. The midge IC50 was 11 μg/g total PAH sediment concentration and was similar to the mayfly effects-level concentration. Sediments from stns 172, 169 and 165, with total PAH concentrations above 10 μg/g, did yield a higher percentage of smaller-sized surviving organisms.

The above IC50 values can also be compared to the PSQG-SEL. The average TOC among the St. Marys River 1992 samples was 3.9%, thereby providing an SEL of 390 μg/g. The SEL would represent a concentration where lethal rather than sublethal responses are prevalent. In order to assess the likelihood of sublethal effects occurring, an appropriate safety factor would need to be applied. A commonly recognized acute to chronic ratio is an order of magnitude lower than the acute value i.e. 0.10 (McCarty, 1986; McCarty *et al.*, 1992a). Therefore, sediments with a total PAH sediment concentration near 39 μg/g would have a greater chance of eliciting a degree of growth impairment. This value was slightly higher than the laboratory-derived IC50 of 11 to 25 μg/g, but is within a reasonable range, given the high variability of TOC in the 1992 test sediments (see Table 3).

The robust relationship between sediment PAH and percent growth reduction suggests the possibility that PAHs are acting in an additive fashion. PAH compounds belong to a class of chemicals that express toxicity as a non-specific mode of action to aquatic invertebrates (Landrum *et al.*, 1991). These narcotic compounds can act either singly or in combination, as long as the final concentration at the target attains a certain concentration that eventually causes death (McCarty *et al.*, 1992b). This internal lethal dosage or critical body residue

FIGURE 5. Regression Analysis of Mayfly 21-d Percent Growth Reduction on Bulk Sediment total PAH Concentration for 1992

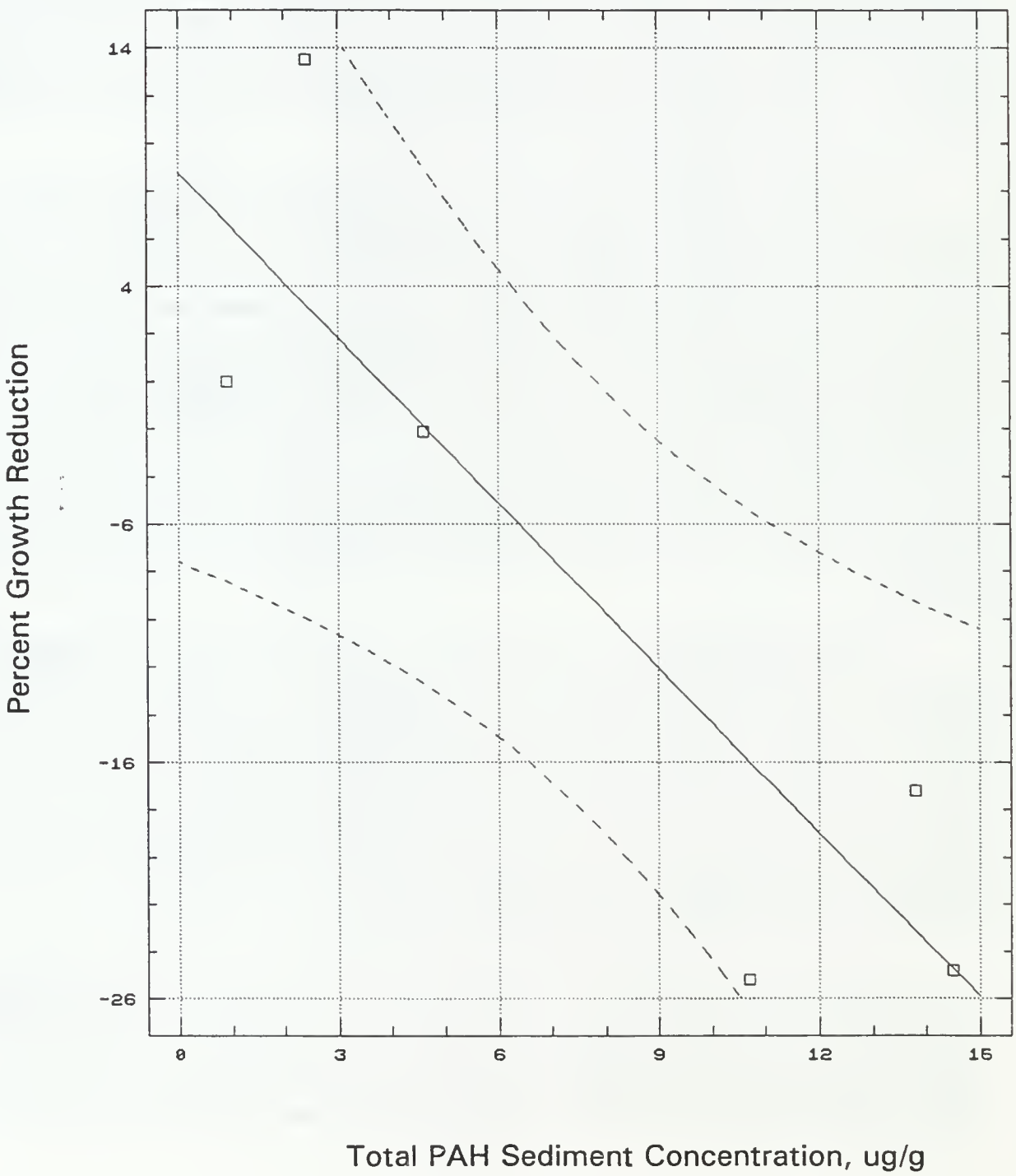
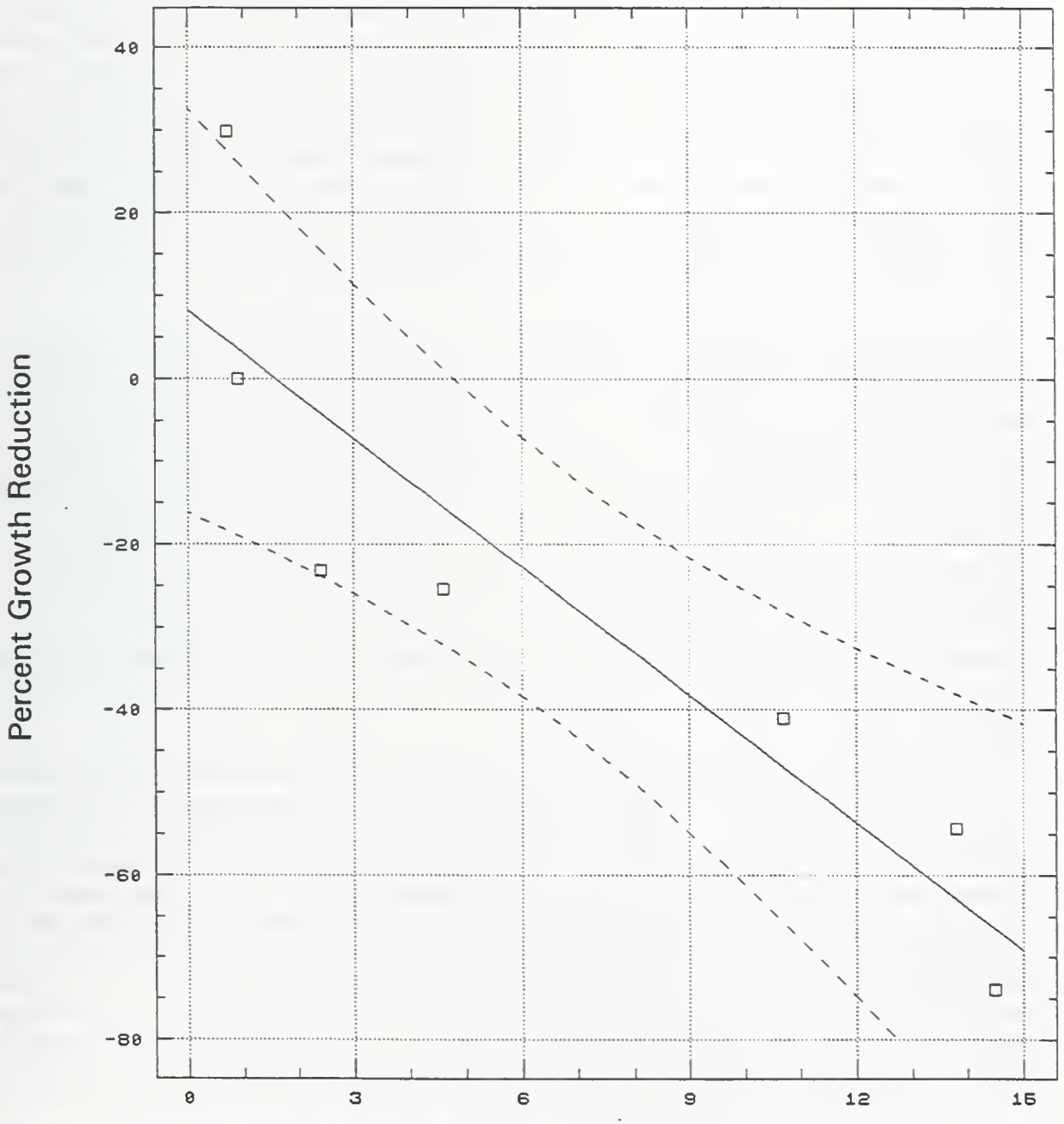


FIGURE 5A. Regression Analysis of Midge 10-d Percent Growth Reduction on Bulk Sediment total PAH Concentration for 1992



(CBR) is a constant, while the external bulk sediment concentration does not necessarily reflect the truly bioavailable portion of sediment-sorbed contaminants (Landrum *et al.*, 1994). Most of the studies examining the toxicological properties of different organic classes of chemicals have involved vertebrates, particularly fish, in water-borne exposures. The wet-weight CBRs varied from 4.0 mM/kg (McCarty *et al.*, 1992a), 2.8 mM/kg (Van Leeuwen *et al.,* 1992) and 2.5 mM/kg (Van Hoogen and Opperhuizen, 1988). Equilibrium partitioning theory, in conjunction with the CBR data, can be used to predict the external sediment PAH concentration likely to cause lethal effects to benthic organisms. Organic chemicals tend to partition from the contaminated media into the organism. For instance, in fish-water exposures, a chemical will partition based on its Kow or lipophilic properties, moving from the water and into the lipid fraction of the organism. In a sediment-benthos model, chemical partitioning has been described as movement from the TOC fraction of sediment into the lipid fraction of an organism. Reuber *et al.*, (1987), has shown TOC and lipid to have a similar affinity for organic chemicals over a wide Kow range. Therefore, the internal lethal dosage or CBR and the external sediment concentration or lethal sediment concentration (LSC) should be approximately equivalent. The ratio of chemical concentration between organism and sediment would be near unity or could be as much as 1.7 times greater, if one takes into account multiple routes of uptake e.g. pore water, overlying water, sediment ingestion (Lake *et al.*, 1990; Van Leeuwen *et al.*, 1992; Boese *et al.*, 1995).

Therefore the CBR should closely approximate the LSC, assuming the percent lipid and percent TOC are quite similar to each other. Therefore, the important variables in determining the CBR and LSC are % lipid and % TOC, respectively. Literature values will serve as estimates for biota % lipid: Harkey *et al.*, (1994a) cite a value of 3.7% for cultured *Chironomus* larvae and Drouillard *et al.*, (1996) 2.1% for laboratory-reared mayflies. The average TOC for 1992 St. Marys test sediments was 3.9% ± 2.6. The previously cited CBR values pertained to fish with a lipid content of approximately 5%. Correcting for both a somewhat lower partitioning component of 3% lipid and a conversion factor of 1.27 for the moisture content of sediment, the revised CBR and LSC becomes 1.6 - 2.2 mM/kg (dry weight). Incorporating an average MW of 212 for the 16 individual PAHs, generates a LSC of 339 to 466 μg/g. The PSQG-SEL for total PAHs with an average TOC of 3.9% also provides a lethal concentration of about 390 μg/g. Once again, the PSQG-SEL is a suitable surrogate for determining a lethal effect concentration to those obtained by equilibrium partitioning theory.

Obviously, the direct measurement of PAH tissue concentrations would be the best indicator of whether the CBR calculated for fish can be used in describing sediment-benthos dose-response interactions. Work by Landrum *et al.*,(1991; 1994) helps to illustrate the applicability of CBR and lethal sediment concentrations to benthic species. In the latter study, *Diporea* was exposed to sediment spiked with radiolabelled pyrene and phenanthrene at five test concentrations, in combined and single chemical exposures. The LSC derived in this study (1.6 to 2.2 mM/kg) is not unlike those obtained for PAH-spiked sediments by Landrum *et al.*, (1991) which found a sediment LC50 concentration of 0.6 - 1.1 mM/kg. The author subjected the amphipod, *Diporea*, to a series of spiked sediments over a 26 or 30 day period and directly measured chemical tissue concentrations relative to amphipod survival rates. The slightly smaller sediment LC50 may have been due to the large differences in lipid content between the amphipod (25% lipid) as compared to our test species (~2% lipid). Nevertheless, this approach appears to substantiate the relationship between toxicity and

exposure through the use of tissue concentrations whether it is used under controlled, aqueous flow-through conditions or for more complex static, sediment tests.

Extrapolation of the LSC (339 to 446 μg/g) for total PAHs to a sublethal sediment concentration will yield an estimate of 33 μg/g to 44 μg/g. As discussed previously, the IC50 is typically one order of magnitude lower than the LC50 (McCarty, 1986; McCarty *et al.*, 1992a). In comparison, the IC50 that was determined through regression analysis between percent growth reduction versus bulk sediment PAH in the 1992 laboratory toxicity tests was 11 to 25 μg/g. As before, there is good agreement in the sediment total PAH concentration that is associated with sublethal effects either measured in the 1992 laboratory toxicity tests or by using hypothetical values.

Swartz *et al.*, (1995) studied the contribution of six individual PAHs in spiked-sediment laboratory tests as it related to lethality of marine and estuarine amphipods. Toxic units for each compound were calculated based on chemical solubility, as well as the corresponding LC50 concentration in interstitial water. The model assumed that the primary route of exposure to the organism is via the interstitial water. This scenario probably applies to the midge *Chironomus* but may become less important to the mayfly *Hexagenia*, which has been shown to obtain as much as 90% of hydrophobic organic contaminants through sediment ingestion (Landrum and Poore, 1988). Swartz *et al.*, (1995) concluded that PAH toxicity was acting as an additive effect, where no individual PAH contributed more than 31% of the overall toxic unit. The toxic unit was lowest for the lower Kow (3.3 - 4.1) and LMW PAHs (128 - 166) and greatest for higher Kow (5.0 - 6.7) and HMW PAHs (202 - 252). Among the HMW PAHs, the larger 4- to 5-ring PAHs tend to possess a greater carcinogenic potential according to several studies using mammals (EC, 1992). Although present in St. Marys River sediments, the moderately lipophilic (Kow 4.5 to 5.1) and intermediate-sized MW (128 -202) PAHs, were somewhat more prevalent, perhaps explaining why the biological effects were at the sublethal rather than the lethal level. Also, in sediment exposures there is a trade-off between chemical exposure and availability. The higher Kow PAHs will result in lower concentrations in interstitial water, whereas, lower Kow PAHs with greater water solubility will be found at higher concentrations in this matrix. Depending on the rate of uptake, the lower Kow PAHs may become depleted more readily and the actual exposure concentration can diminish over time. On the other hand, the higher Kow, more persistent PAHs will be available over a sustained period of time, eventually contributing to the toxicity to a greater extent (Landrum, 1989; Landrum *et al.*, 1991; Harkey et al., 1995). Other factors that contribute to the relative availability of PAHs include the differential binding of the chemical to sediment organic matter and particle size, coupled with the selective feeding behaviour of the test organism (Harkey *et al.*, 1994b; Lake *et al.*, 1996).

Three of the 16 PAHs that were most common to the 1992 and 1995 sediment samples included phenanthrene, pyrene and fluoranthene. Naphthalene was also present in several of the 1995 Bellevue Marine park samples. Of these four PAHs, only phenanthrene appears on the OMOEE primary list of banned substances (OMOE, 1992). The PAH composition, in terms of percentages, in Algoma Slip sediment was unlike any other test sediment. The highest PAH fractions occurred for fluoranthene, 26%, phenanthrene, 22% and pyrene, 18%. A similar PAH distribution pattern was observed in 1990 for Algoma Slip sediments (Pope and Kauss, 1995). A common source for each of these PAHs is the combustion of coke and coal tar (Marvin *et al.*, 1995; Jaagumagi and Bedard, 1996b). The

Algoma Steel operation involves the production of coke with coal tar as a by-product (Kauss and Hamdy, 1991). According to point-source loadings data gathered for 1986-1988, Algoma Steel represented 76% of the total oil and grease loadings and 45% of the PAHs to the river (MOEE/MDNR, 1992; UGLCCS, 1988). Atmospheric deposition (non-point) represents the next most important source of PAHs to the area. Many of the other downstream test sites appear to be subjected to atmospheric outfall. Fluoranthene and pyrene were most frequently detected at higher concentrations in several of the downstream locations. It was only in Lake George that compounds such as benzofluoranthene and indenopyrene, occurred to the greatest extent.

Significant negative correlations were also found between the 1992 inorganic sediment chemistry and laboratory toxicity data. Relationships were noted between, arsenic, copper and manganese bulk sediment concentrations and three of five biological endpoints (Table 13). Each of these metals was considered of minor importance, given the relatively low concentrations in the sediments. On the other hand, the chromium concentration above the PSQG-SEL at the Tannery Bay test site, was considered a greater toxicological concern. The sediment concentration was as much as 23 times higher than the SEL criterion but no significant relationship was found with any of the lethal and sublethal toxicity test responses. In fact, just the opposite occurred; the sediment yielded the best growth among the 1992 test sites and percent mortality was under 7%. Other toxicity studies using the midge larvae (*Chironomus tentans*) on ten sediments collected from Tannery Bay in 1991 failed to find any differences in survival or growth at Cr sediment concentrations ranging from 2,100 μg/g to 29,000 μg/g (USEPA, 1991). The mortality results from the 10-day *Hyalella* sediment toxicity test were inconclusive due to the high loss incurred in the reference sediment (USEPA, 1991). It appears that Cr is either not in a readily available form or exists primarily in the less toxic, trivalent state. Witt and Rodgers (1991) reported that hexavalent Cr is more prevalent in less organically-enriched sediments (<0.5% TOC); therefore, Cr probably was more tightly bound in the 1992 sediment. Unfortunately, the question of Cr availability to fish was not assessed in the 1992 sediment toxicity test due to laboratory analytical limitations.

Correlation analysis for the 1995 study revealed a different set of variables in characterizing the toxicity test results (Table 13A). The study focused primarily on a specific area of the St. Marys River at Bellevue Marine park and had a finer scale of resolution compared to the 1992 study. Bulk sediment total petroleum hydrocarbon (TPH) concentrations (not measured in 1992 test sediments) were the most successful in explaining four of the five toxicity endpoints. This was also the case for TPH concentrations after correction for sediment TOC, since TOC covaried with the distribution of TPH. Unlike the 1992 results, PAH compounds, either singly or additive, generally were inadequate in describing the toxicity data. Regression analysis between percent growth reduction and sediment total PAH concentrations indicated a fairly independent relationship. This failure in the PAH-derived IC50 as a predictor of growth impact in the Bellevue Marine park sediments is likely a result of a co-occurrence of PAH with other petroleum-based compounds. Generally, those sites with lower concentrations of TPH (Range: 350 - 3,170 μg/g) resulted in either no significant effect or affected only one of the test endpoints. Sediment TPH concentrations encompassing a higher range between 4,755 and 112,500 μg/g, had two or three positive hits. The exceptions included stn 214 which had a TPH concentration of 2,050 μg/g but resulted in impaired midge and mayfly growth and stn 222, which had the second highest TPH

TABLE 13A. Spearman rank correlation analysis summary indicating significant negative (inverse) or positive (direct) correlation between biological endpoints and sediment physical and chemical parameters for St. Marys River 1995 samples.

Toxicity Endpoint	Mayfly Survival	Mayfly Growth	Midge Survival	Midge Growth	Minnow Survival
Bulk Concentration	– Acy * – B(k)Ft * – B(a)P * – DB(ah)An * – IP * – N * – As * – Cr * – Fe * – Mn * – Pb *	– B(k)Ft ** – DB(ah)An ** – IP ** – TPH * – Acy * – B(a)P * – N * – Fe ** – Pb ** – Al * – As * – Cd * – Cu * – Mn * – Ni * – Zn *	– TPH ** – As * – Cu * – Zn *	– TPH * – % Fines ** – Al ** – Cd ** – Hg ** – Ni ** – Cu * – Fe * – Mn * – Pb * – Zn *	– TPH ** – B(b)Ft ** – As ** – Cu ** – Cd * – Fe * – Mn * – Ni * – Pb * – Zn *
TOC corrected[a] Concentration	– N *	– TPH ** – N *	– TPH * – Ph * – P *	– TPH ** – Cu ** – Zn *	– TPH *

a Included As, Cu, Zn, TPH and all PAHs except for idenopyrene.

** $p < 0.01$; * $p < 0.05$.

concentration of 10,810 μg/g, yet only caused lower midge growth. The areas coinciding with a higher frequency of biological response are situated in the nearshore region. Figures 6; 6A, plot organism percent growth reduction against sediment total TPH concentrations. After the removal of three outliers in the mayfly data (stns 219, 222, 214), a highly significant relationship was found ($p = 0.001$). Similarly, the midge data also found a slightly significant response ($p = 0.06$) with two data points (stns 219, 222) eliminated prior to the regression analysis.

Stored sediment samples were also subjected to microscopic examination to differentiate the exact physical composition of 11 of the test sediments. Those sediments containing either $\geq$40% detrital matter or $\geq$25% wood fibres and vegetation chips, consistently resulted in a significant sublethal response to *Chironomus*. This suggests that midge growth may have been compromised due to physical habitat type. The presence of high amounts of loose, large fibrous particles may serve as inadequate building material, since midges prefer tightly packed and smaller-sized particles in tube construction (Ankley *et al.*, 1994). In addition, the establishment of cases could have been hindered when the jars were handled which disturbed and resuspended this lighter, flocculent material. Suedel and Rodgers (1994) found midge survival to be inversely related to the percent solid content of sediment (complementary with percent moisture) in 10-day laboratory tests. Bellevue Marine park sediments that contained high amounts of detrital or woody material did have a correspondingly lower % solids content of less than 53% and averaged 36% solids $\pm$ 10%. Mayfly growth also appeared to be compromised, probably due to the poor nutritional quality of the sediment. The unusual nature of the test material differed from typical bedded sediment and growth data should be interpreted with caution.

Physical factors in addition to sediment TPH concentrations, need to be taken into account in assessing sediment quality at Bellevue Marine park. An alteration in habitat type could eventually cause a shift in the composition of naturally-occurring benthic communities. Effects on benthic biomass and diversity has been shown to be related to increasing sediment TOC and perhaps growth rates for sediments obtained near the Bellevue Marine park site in 1985 and 1987 (Jaagumagi *et al.*, 1991). Burt *et al.*, (1988) alluded to a discrepancy between benthic communities as it related to the presence and absence of visible oil. The combination of different sediment types and the type of oil will result in a complex array of exposure regimes.

High loadings of suspended solids were reported for St. Mary's Paper, which is a groundwood pulp and paper mill from 1986 to 1988 (MOEE/MDNR, 1992; UGLCCS, 1988), with an additional source arising from Algoma Steel. These two industries are the major industries on the St. Marys River. The common occurrence of naphthalene in the majority of the 1995 sediments suggests the wood chip and fibrous material may serve as a reservoir of certain PAHs. Naphthalene is somewhat water soluble (~3 mg/L) and normally has a short residence time in sediment, but can be continuously released if the chemical is closely associated with extraneous material.

With respect to chemical bioavailability and bioaccumulation of organic chemicals, only naphthalene showed a higher tendency to be accumulated above trace levels at 23% of the 1995 sites. Naphthalene has the highest water solubility and thereby likely found in the

FIGURE 6. Regression Analysis of Midge 10-d Percent Growth Reduction on Bulk Sediment TPH Concentration for 1995

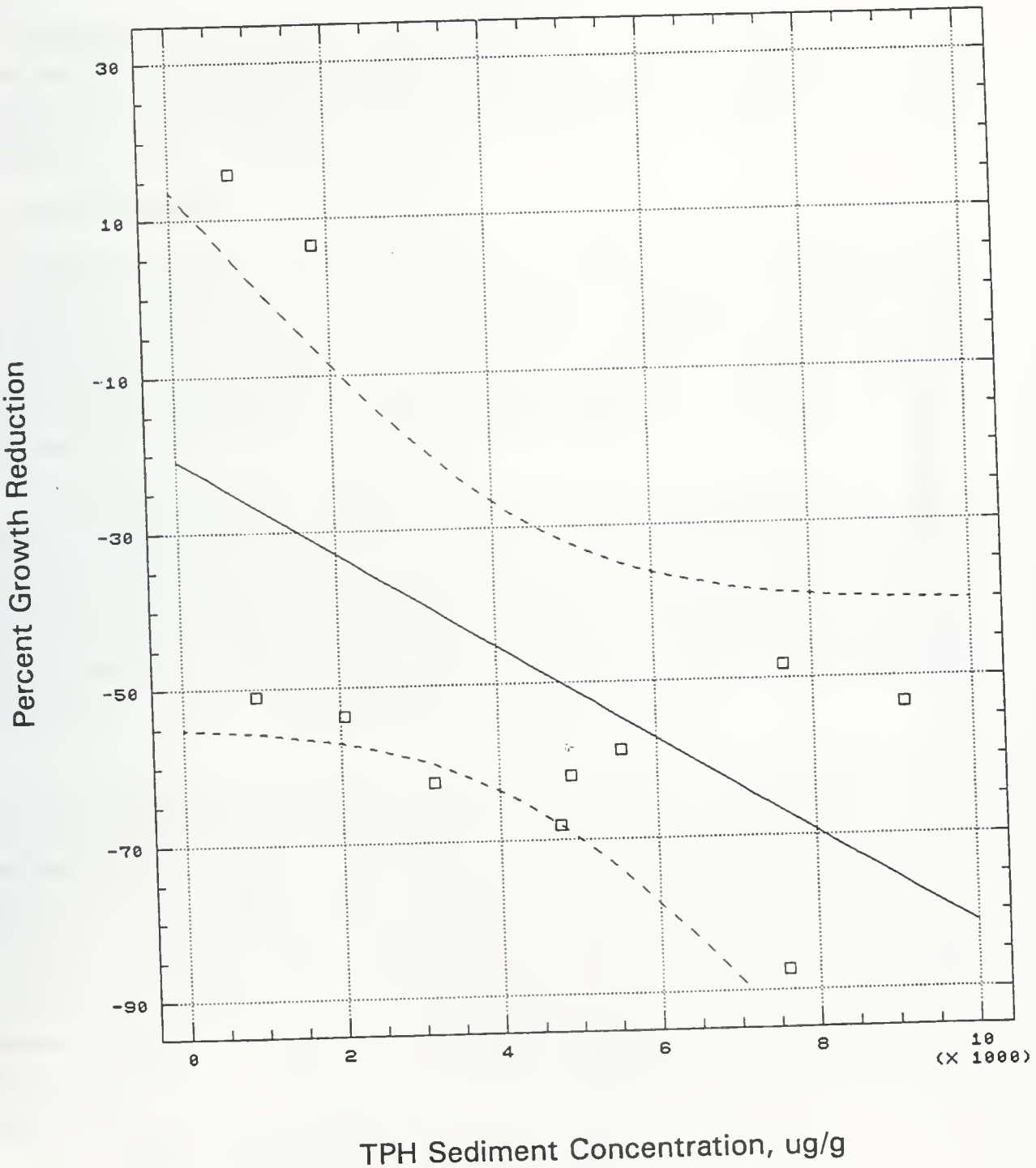
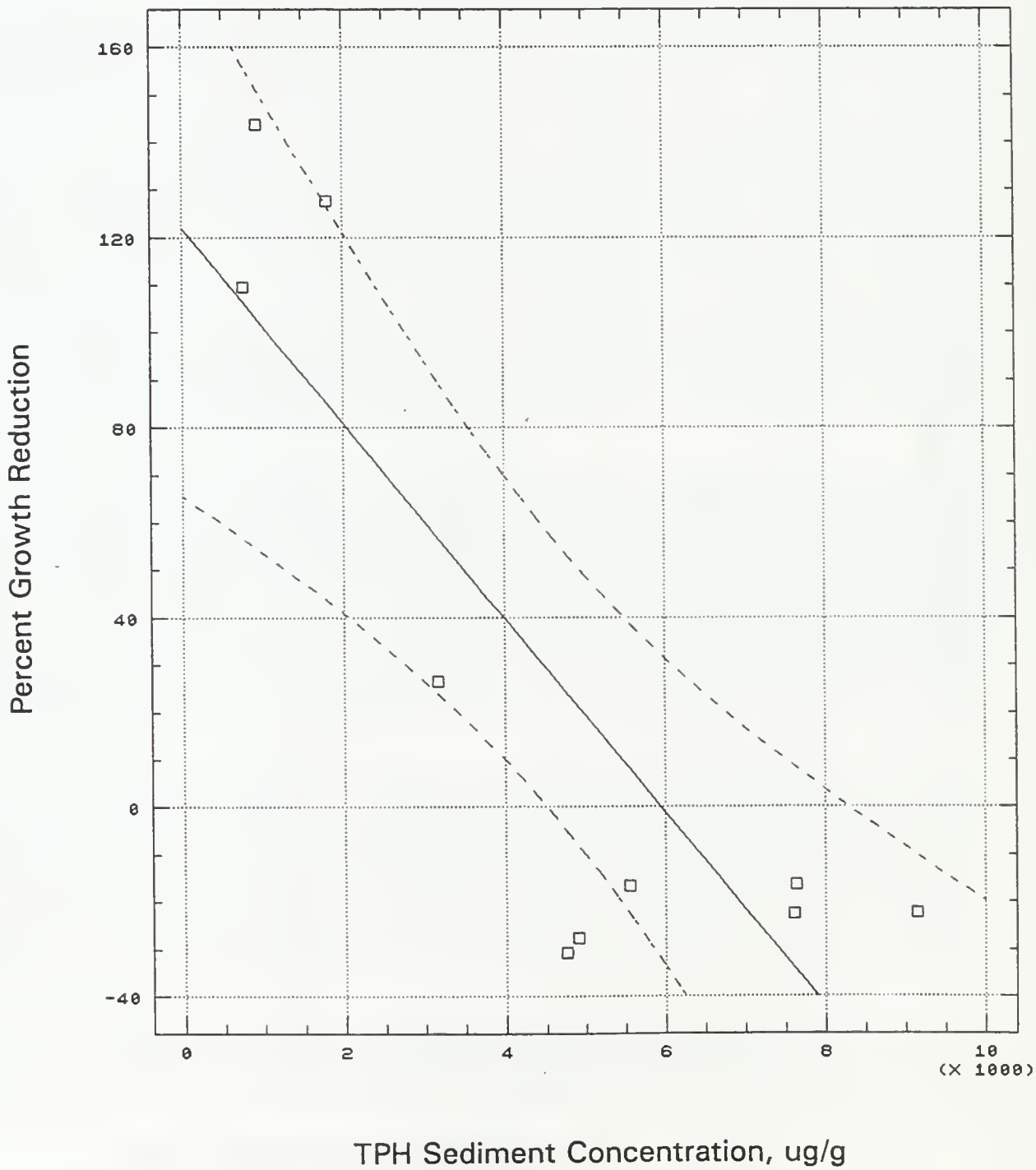


FIGURE 6A. Regression Analysis of Mayfly 21-d Percent Growth Reduction on Bulk Sediment TPH Concentration for 1995



highest concentration in the overlying water, relative to the less soluble PAHs. Uptake can then occur more rapidly through the gills of fish (Kennedy and Law, 1990; Neff and Burns, 1996). Naphthalene is more routinely detected in fish tissue in field collections (Jaagumagi *et al.*, 1991) and in caged freshwater mussels (Kauss and Hamdy, 1991). Generally, PAH accumulation in vertebrates is not likely because it can be controlled through metabolic factors that depurate the PAHs into less toxic forms (Kennedy and Law, 1990). The mixed-function oxidase (MFO) enzyme system which is principally responsible for the biotransformation of PAHs in fish and can be induced within 24 hours (Djomo *et al.*, 1996).

Fish tissue metal concentrations were either statistically similar to each other or comparable to those levels achieved in the control animals. The range in BSAFs among metals was rather large and ranged from 0.01 to 5.0, for the 1992 study. Thomann *et al.*, (1995) described several factors that can account for these differences, including metal assimilation efficiencies, metal depuration rates and routes of exposure.

5.0 CONCLUSIONS

Laboratory sediment toxicity tests performed in 1992 and 1995 on St. Marys river sediments demonstrated a range in test response, as well as differences in species sensitivity. The severest effect occurred for the sample collected in Algoma Slip (stn 183) in 1992. Mayfly and midge percent mortality averaged 95%. Among the remaining 1992 sediments collected throughout the Area of Concern, the Bellevue Marine park (stn 165) sample elicited significant growth impairment to *Chironomus tentans* and *Hexagenia limbata.* None of the 1992 sediments were found to be toxic to the fathead minnow.

Chemical analysis on the 1992 samples showed most metal sediment concentrations were representative of upstream reference conditions. The largest exceedence of the PSQG-SEL occurred at a site in Tannery Bay (stn 35) with a chromium sediment concentration of 2,600 μg/g. Total PAH sediment concentrations ranged from 0.8 to 291 μg/g. Higher total PAH sediment concentrations significantly correlated with lower benthic growth. At concentrations above 10 μg/g, midge and mayfly growth tended to be reduced. This sublethal effect concentration coincided with those derived from field-based Provincial Sediment Quality Guidelines and theoretical values using the critical tissue-residue approach. Fluoranthene and pyrene was reported in the highest amount for each test sediment.

The 1995 Bellevue Marine park toxicity test rankings were best described using sublethal growth results from the midge test, followed by those obtained using the mayfly. The majority of the test sediments that received a poor ranking were collected in the nearshore zone and included stns 225, 214, 227, 221, 210, 226, 219 and 224. Contrary to the 1992 results, contaminant levels of total PAH was insufficient in explaining the biological data. A combination of chemical contamination and physical characteristics of the test sediments was required to interpret the test results. Total petroleum hydrocarbon sediment concentration was a better indicator of potential effect. Total organic carbon above the SEL was reported at 38% of the sites and was probably related to higher loading of woody debris and coal chips, along with any associated oil. Sediments containing either > 40% detrital matter or > 25% wood fibres and vegetation, in the presence of oil, was often associated with significantly reduced midge growth. Minnow bioaccumulation results indicated naphthalene to be available to the highest degree in the 21-day exposures.

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APPENDIX

TABLE A1. Analytical detection limits for nutrients, inorganic and organic contaminants in sediment and biota samples.

Parameter	Sediment (units: dry weight)	Parameter	Sediment (units: dry weight)	Biota (unit: wet weight)
Nutrient :		Organic :		
Loss on Ignition	1.0 mg/g	Total PCBs	20 ng/g	20 ng/g
Total Organic Carbon	0.2 mg/g	Heptachlor	1 ng/g	1 ng/g
Total Kjeldahl Nitrogen	0.025 mg/g	Aldrin	1 ng/g	1 ng/g
Total Phosphorus	–	Mirex	5 ng/g	5 ng/g
		a–BHC	1 ng/g	1 ng/g
Trace Metal :		b–BHC	1 ng/g	1 ng/g
		g–BHC	1 ng/g	1 ng/g
Arsenic	–	a–Chlordane	2 ng/g	2 ng/g
Cadmium	0.05 µg/g	g–Chlordane	2 ng/g	2 ng/g
Chromium	1.0 µg/g	Oxychlordane	2 ng/g	–
Copper	0.5 µg/g	op–DDT	5 ng/g	5 ng/g
Iron	200 µg/g	pp–DDD	5 ng/g	5 ng/g
Lead	1.25 µg/g	pp–DDT	5 ng/g	5 ng/g
Mercury	0.01 µg/g	pp–DDE	5 ng/g	5 ng/g
Nickel	0.2 µg/g	Methoxychlor	5 ng/g	–
Zinc	2.0 µg/g	Heptachlor epoxide	1 ng/g	–
		Endosulphan I	2 ng/g	–
Organic:		Dieldrin	2 ng/g	–
		Endrin	4 ng/g	–
Naphthalene	20 ng/g	Endosulphan II	4 ng/g	–
Acenapthylene	20 ng/g	Endosulphan Sulphate	4 ng/g	–
Acenaphthene	20 ng/g	Hexachloroethane	1 ng/g	1 ng/g
Fluorene	20 ng/g	Hexachlorobutadiene	1 ng/g	1 ng/g
Phenanthrene	20 ng/g	2,3,6–trichlorotoluene	1 ng/g	1 ng/g
Anthracene	20 ng/g	2,4,5–trichlorotoluene	1 ng/g	1 ng/g
Fluoranthene	20 ng/g	2,6,5–trichlorotoluene	1 ng/g	–
Pyrene	20 ng/g	1,2,3–trichlorobenzene	2 ng/g	2 ng/g
Benzo[a]anthracene	20 ng/g	1,2,4–trichlorobenzene	2 ng/g	2 ng/g
Chrysene	20 ng/g	1,3,5–trichlorobenzene	2 ng/g	2 ng/g
Benzo[b]fluoranthene	20 ng/g	1,2,3,4–tetrachlorobenzene	1 ng/g	1 ng/g
Benzo[k]fluoranthene	20 ng/g	1,2,3,5–tetrachlorobenzene	1 ng/g	1 ng/g
Benzo[a]pyrene	40 ng/g	1,2,4,5–tetrachlorobenzene	1 ng/g	1 ng/g
Benzo[g,h,i]perylene	40 ng/g	Pentachlorobenzene	1 ng/g	1 ng/g
Dibenzo[a,h]anthracene	40 ng/g	Hexachlorobenzene	1 ng/g	1 ng/g
Indeno[123–cd]pyrene	40 ng/g	Octachlorostyrene	1 ng/g	1 ng/g
		Toxaphene	–	200 ng/g

TABLE A2. Sediment total PAH concentration and corresponding laboratory toxicity data for Northern Wood Preservers Inc site in Thunder Bay, Ontario 1995.

Distance from dock (metres)	Transect	Sediment Total PAHs (µg/g dry wt)	Mayfly Percent Mortality	Midge Percent Mortality
25 m	T – 5.5	539	50	58
50 m	T – EF	218	10	8
50 m	T – 5.5	129	6	5
75 m	T – 5.5	916	100	54
75 m	T – EF	90	0	16
100 m	T – 5.5	213	0	17
125 m	T – 5.5	258	10	17
150 m	T – 5.5	176	0	11
175 m	T – 5.5	29	0	0
200 m	T – 5.5	17	0	0
250 m	T – 5.5	16	0	2
300 m	T – 5.5	10	0	6
350 m	T – 5.5	8	0	4
400 m	T – 5.5	13	3	0