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Assessment of Mercury Contamination and Biological Impacts in the St. Clair River

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ASSESSMENT OF MERCURY CONTAMINATION AND BIOLOGICAL IMPACTS IN THE ST. CLAIR RIVER

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ABSTRACT

This report describes sediment and biota quality in the St. Clair River, identified by the International Joint Commission as an 'Area of Concern' due to habitat, water, and sediment quality issues. Elevated levels of mercury and other contaminants in the sediment and subsequent detrimental effects on the benthic biota have been identified in parts of the St. Clair River. As part of the GL2020 Action Plan, site assessments in the St. Clair River were made using BEAST (Benthic Assessment of Sediment) methodology. BEAST methodology involves the assessment of sediment quality based on a multivariate technique using data on benthic invertebrate communities, the functional responses of laboratory organisms in sediment toxicity tests, and the physical and chemical attributes of the sediment and overlying water. Data from test sites are compared to biological criteria developed for the St. Clair River and Laurentian Great Lakes (revised BEAST model). The bioavailability of sediment mercury and its potential for effects on fish and wildlife through biomagnification was also assessed. This involved (a) analysis of the relationships of mercury concentrations in resident benthic invertebrates to those in sediment, and (b) predictions of concentrations of methyl mercury in representative consumers of benthic invertebrates and their predators using screening-level trophic transfer models. Sample sites were located mainly in upper reach of the river, extending from an area adjacent to the industrial sector to downstream of Stag Island. Locations upstream and downstream of this area were also sampled.

In September 2001 and 2004, sediment, overlying water, the benthic invertebrate community and resident invertebrate tissue samples (chironomids, oligochaetes) were collected from a total of 26 sites. Samples were analyzed for total and methyl mercury concentrations and a series of physico-chemical variables in the sediment and overlying water. Benthic community composition and sediment toxicity were assessed and compared to reference site data. Mercury concentrations in sediment and invertebrates were compared to concentrations in upstream reference sites. Relationships between mercury in each invertebrate taxon and mercury in sediment were evaluated by regression analysis. Physico-chemical sediment and water variables were included as additional predictors. Concentrations of methyl mercury in the tissues of fish and wildlife receptors (White Sucker, Yellow Perch, Walleye, Great Blue Heron, Mink) were

predicted by multiplying measured body concentrations in the resident invertebrates by relevant biomagnification factors obtained from a review of pre-existing studies.
Total sediment mercury concentrations ranged from 0.01 to 49 µg/g dry weight with the highest concentrations observed adjacent to the industrial sector. Mercury sediment concentrations at almost all sites were greater than concentrations upstream of the industrial zone. There was no evidence of severe sediment toxicity. Benthic communities (sampled in 2001 only) were mostly different than reference, with enrichment (increased abundances of Chironomidae and Tubificidae) and a greater diversity of taxa observed at the majority sites, including upstream sites. Some St. Clair River sites were not well matched to any reference site groups based on habitat attributes; therefore, results for these sites should be interpreted with caution.

Resident benthic invertebrates from the majority of sites (79 to 89%) had total mercury levels above the maximum upstream site concentrations; for methyl mercury, this percentage was slightly greater (84 to 95%). The concentration of total mercury and methyl mercury in sediment was strongly predictive of total and methyl mercury concentration in invertebrates, respectively (analysed without allowing gut clearance). Other sediment and overlying covariables (i.e., water nutrients, sediment iron, manganese and particle size) improved the models. Assuming average mercury exposure and uptake conditions, the trophic transfer modelling outcomes for walleye indicated that most sites could be considered of concern because the predicted tissue concentrations of methyl mercury exceeded the Canadian tissue residue guideline (92 ng/g ww) and the maximum predicted concentration at upstream reference sites. Thus, screening level predictions of methyl mercury concentrations in fish receptors suggest that there are several sites on the river where mercury could bioaccumulate in receptors to levels that are not protective of adverse effects. However, the likelihood of realizing this degree of mercury biomagnification is not clear due to uncertainties associated with predicting receptor mercury concentrations.

A risk-based, decision-making framework for the management of contaminated sediment, recently developed under the Canada/Ontario Agreement respecting the Great Lakes Basin Ecosystem, was applied to the St. Clair River study. The overall assessment of each site was achieved by integrating the information obtained from both within and among the lines of evidence. The need to fully assess the risk of mercury biomagnification was indicated for 16 sites.

RÉSUMÉ

Ce rapport décrit la qualité des sédiments dans la rivière Sainte-Claire, désignée comme secteur préoccupant à cause de problèmes de qualité des habitats, de l'eau et des sédiments. Dans le cadre du plan d'action sur les Grands Lacs 2020, on a appliqué le logiciel d'évaluation benthique des sédiments (BEAST) à 26 sites au total le long de la rivière, qui ont été échantillonnés en 2001 et en 2004. La technologie BEAST consiste à évaluer la qualité des sédiments en se servant des techniques de l'analyse multivariable au moyen de données sur les communautés benthiques, les réactions fonctionnelles des organismes de laboratoire aux analyses de toxicité et les propriétés physicochimiques des sédiments et de l'eau qui les surplombe. Les données des sites expérimentaux sont ensuite comparées aux critères biologiques conçus pour les Grands Lacs de la région laurentienne. En outre, on a mesuré le mercure dans les tissus d'invertébrés benthiques qui habitent la rivière afin d'en déterminer la biodisponibilité. À l'aide de modèles de transfert trophique de dépistage, ces données ont servi à évaluer les éventuels risques pour les espèces réceptrices de niveau trophique supérieur à cause d'une bioamplification.

Les concentrations de mercure total dans les sédiments de surface (couche supérieure de 10 cm) variaient de 0,01 à 49 µg/g en poids sec tandis que les concentrations de méthylmercure oscillaient entre 0,5 et 296 ng/g; la contamination la plus forte a été observée juste à côté du secteur industriel. Les concentrations de mercure total et de méthylmercure dans les sédiments dans pratiquement tous les sites étaient supérieures aux concentrations observées dans les sites en amont de la zone industrielle. Il n'y avait pas de preuve convaincante de toxicité. Les communautés benthiques (échantillonnées seulement en 2001) étaient essentiellement différentes des communautés de référence des Grands Lacs, en vertu d'un enrichissement (abondance accrue des chironomidés et des tubificidés) et d'une plus grande diversité des taxons observés dans la majorité des sites, notamment les sites en amont. Toutefois, les sites de la rivière Sainte-Claire étaient mal jumelés avec les sites de référence des Grands Lacs en général.

Les invertébrés benthiques provenant de la majorité des sites (79 % à 89 %) avaient des concentrations de mercure total supérieures aux concentrations maximales des sites en amont; pour ce qui est du méthylmercure, ce pourcentage était légèrement supérieur (84 % à 95 %). La concentration de mercure total et de méthylmercure dans les sédiments avait une forte valeur de

prédiction respectivement de la concentration de mercure total et de méthylmercure dans les invertébrés (analysés sans tenir compte de l'évacuation du tube digestif). Si l'on présume des taux d'exposition et d'absorption moyens du mercure, les résultats du modèle de transfert trophique en ce qui concerne le doré jaune récepteur indiquent que jusqu'à 16 sites peuvent être jugés préoccupants étant donné que les concentrations prévues de méthylmercure dans les tissus du doré jaune dépassaient les recommandations canadiennes pour les résidus dans des tissus (92 ng/g p.h.) et la concentration maximale prévue dans les sites de référence en amont. Ainsi, les prédictions de dépistage des concentrations de méthylmercure dans les poissons récepteurs incitent à penser qu'il existe plusieurs sites dans la rivière où le mercure peut se bioaccumuler dans les récepteurs à des concentrations qui ne les protègent pas contre ses effets délétères.

Un cadre décisionnel fondé sur les risques pour la gestion des sédiments contaminés, récemment conçu dans le cadre de l'accord Canada-Ontario sur l'écosystème du bassin des Grands lacs, a été appliqué à l'étude de la rivière Sainte-Claire. On a procédé à l'évaluation globale de chaque site en intégrant les données recueillies dans et entre les sources de données. L'étude a révélé qu'il était nécessaire d'évaluer intégralement le risque de bioamplification du mercure au sujet de 16 sites.

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ABBREVIATIONS, ACRONYMS AND SYMBOLS

adj	adjusted
ANCOVA	analysis of covariance
AOC	Area of Concern
BEAST	Benthic Assessment of Sediment
BMF	biomagnification factor
BSAF	biota-sediment accumulation factor
CCME	Canadian Council of Ministers of the Environment
CI	confidence interval
CL	confidence limit
dw	dry weight
d/s	downstream
FCM	food chain multiplier
GLWQA	Great Lakes Water Quality Agreement
Hg	mercury; used where form (MeHg or THg) is unspecified
HMDS	hybrid multidimensional scaling
IJC	International Joint Commission
inv	invertebrate
LEL	lowest effect level
max	maximum
MeHg	methyl mercury
min	minimum
MOE	Ministry of the Environment
PCA	principal components analysis
PEL	probable effect level
QA/QC	quality assurance/quality control
RAP	Remedial Action Plan
rec	receptor
ref	reference
reg	regression
regr	regression
sed	sediment
SEL	severe effect level
THg	total mercury
TKN	total Kjeldahl nitrogen
TOC	total organic carbon
TP	total phosphorus
TRG	tissue residue guideline
UCL	upper confidence limit
wt	weight
ww	wet weight
$[x]_i$	concentration of substance *x* in matrix *i*

1 INTRODUCTION

1.1 Background and Mandate

In the 1970's, the International Joint Commission (IJC) identified 42 "problem areas" where aquatic environments were considered to be severely degraded. Of these, 17 were along Canadian lakeshores or in rivers shared by Canada and the U.S. In 1985, the IJC Great Lakes Water Quality Board recommended a Remedial Action Plan (RAP) be developed and implemented for each problem area. The goal of the RAP was to restore the "beneficial uses" of the aquatic ecosystem in each problem area, which were now called "Areas of Concern" (AOCs). The RAP approach and process is described in the 1987 Protocol to the *Great Lakes Water Quality Agreement* (GLWQA). Fourteen possible "impairments of beneficial use", which could be caused by alterations of physical, chemical or biological conditions in the area, are defined in Annex 2 of the GLWQA.

The Canadian government's commitment to the GLWQA was renewed in 2000 with the Great Lakes Basin 2020 Action Plan, under which the efforts of eight federal departments to "restore, conserve, and protect the Great Lakes basin" over the next five years were coordinated. Environment Canada's contribution included the funding of detailed chemical and biological assessments of sediments in Canadian AOCs. Under the terms of reference for Environment Canada's mandate, the Benthic Assessment of Sediment (BEAST) methodology of Reynoldson and co-workers (1995, 2000) was applied to the AOC assessments. The methodology involved the evaluation of sediment contaminant concentrations, laboratory toxicity, and benthic invertebrate communities (see description below). Recent reviews of the BEAST framework have recommended the inclusion of an additional line of evidence – information on the bioaccumulation of contaminants liable to biomagnify (Grapentine et al. 2002).

1.2 Decision Framework for Sediment Assessment

The underlying philosophy of Environment Canada's approach to sediment assessment is that observations of elevated concentrations of contaminants alone are not indications of ecological degradation. Rather, it is the biological responses to these contaminants that are the concern. A recommendation on remedial activity requires evidence to be provided of an adverse biological

effect either on the biota resident in the sediment, or on biota that are affected by contaminants originating from the sediment, either by physical, chemical or biological relocation.
It is recognized that to make decisions on sediment quality and the need to remediate, four components of information (in addition to knowledge on the stability of sediments) are required (Krantzberg et al. 2000):

Sediment chemistry and grain size – Quantifies the degree to which sediments are contaminated. Indicates exposure (or at least potential exposure) of organisms to contaminants (with consideration of exposure pathways). Provides information on physicochemical attributes of the sediment to assist in the interpretation any observed biological effects.

Benthic invertebrate community structure – Used to determine whether natural faunal assemblages in contaminated sediments differ from those in uncontaminated reference locations. The benthic community can indicate a biological response to sediment conditions. Organisms which reside in and ingest sediments experience the most ecologically relevant exposures to contaminants present, and represent important food web components.

Sediment toxicity - Differences in resident invertebrate communities between contaminated and uncontaminated sites alone cannot be conclusively attributed to toxic chemicals. Sediment toxicity data provides supporting evidence that responses observed in the community are associated with sediment contaminants rather than other potential stressors.

Invertebrate body burdens - Measurements of contaminants in tissues of resident benthic fauna provide evidence of bioavailability, and that the contaminants are responsible for observed effects on the organisms (Borgmann et al. 2001). In addition, the information can be used to assess the risk to higher trophic levels due to biomagnification. Some contaminants, although bioavailable, may not accumulate in benthic invertebrates to sufficient concentrations to induce effects. A few of these contaminants (e.g., mercury, polychlorinated biphenyls (PCBs)) have the property of biomagnifying up the food chain to produce adverse responses in higher trophic level organisms.

An overall assessment of a site is achieved by integrating the information obtained both within and among the above four lines of evidence. The decision-making framework, which is based on ecological risk assessment principals, was developed from the Sediment Triad (Long and Chapman 1985; Chapman 1996) and the BEAST (Reynoldson et al. 1995, 2000) frameworks, and is described in detail elsewhere (Grapentine et al. 2002; Chapman and Anderson 2005).

1.3 BEAST Methodology

The BEAST (Benthic Assessment of Sediment) is a predictive approach for assessing sediment quality using multivariate techniques (Reynoldson et al. 1995, 2000; Reynoldson and Day 1998). The approach utilizes data from nearshore reference sites that were sampled from the Laurentian Great Lakes over a three-year period. Information includes benthic invertebrate community composition (the type and number of macroinvertebrates present), selected habitat variables, and responses (survival, growth and reproduction) of four benthic invertebrates in sediment toxicity tests. The reference sites establish normal conditions for selected endpoints, and determine the range of 'normal' biological variability. Expected biological conditions at test sites are predicted by applying relationships developed between biological and habitat conditions at reference sites. Expected conditions are compared to observed sediment toxicity and benthic community composition to determine biological degradation.

This assessment method has been used to assess the condition of benthic invertebrate communities and toxicity in a number of AOCs, e.g., Collingwood Harbour, St. Lawrence River (at Cornwall), Peninsula Harbour and Hamilton Harbour (Reynoldson et al. 1995; Reynoldson 1998; Milani and Grapentine 2005, 2006).

1.4 St. Clair River Area of Concern

The St. Clair River RAP reports – Stage 1: Environmental Conditions and Problem Definition (St. Clair River RAP Team 1991) and Stage 2: Recommended Plan: Water Use Goals, Remedial Measures and Implementation Strategy (St. Clair River RAP/BPAC Team 1995) have identified several problems for the St. Clair River. Due to point and non-point sources in the area, causes for concern in sediments include:

- Nutrients (nitrogen and phosphorus)

- Trace metals (arsenic, mercury, cadmium, copper, chromium, iron, lead, nickel, zinc, manganese)
- Organic contaminants (oil and grease, PCBs, hexachlorobenzenes and polycyclic aromatic hydrocarbons).

Of the 14 beneficial uses evaluated for St. Clair River, 9 are listed as impaired in the Stage 1 RAP. Sediment has been associated as either the cause of impairment or as a source of the problem for five:

- restriction on fish consumption,
- animal deformities (chironomid mouth parts),
- degradation of benthos,
- restrictions on dredging activities, and
- loss of fish and wildlife habitat.

Improvements have been made in the St. Clair River over the last ten years due to remedial efforts. However, elevated levels of sediment mercury and other trace metals, organics, ammonia and hydrogen sulphide still remain. The presence of pollution tolerant benthic species in the river is the result of urban and historical industrial pollution and euthrophication (St. Clair River RAP/BPAC Team 1995). Based on a 1990 Ontario Ministry of the Environment (MOE) study, three sediment impact areas have been prioritized (St. Clair River RAP/BPAC Team 1995). These priority areas were located in the upper reaches of the river and were characterized by:

- Severe effect level exceedences (SEL; Persaud et al. 1992)), degraded benthos and sediment toxicity (Priority 1),
- SEL exceedences and impaired benthos (Priority 2), and
- SEL exceedences (Priority 3).

Within the Priority 1 area, 3 sediment impact zones were further identified (Study Zones 1, 2 and 3). Recently, Thorburn et al. (2003) simplified these 3 zones in their 2001 study by grouping sites in Study Zone 1 to south of the Dow Chemical Canada Inc. (Dow) property line, now referred to as "Zone A", and sites in Study Zones 2 + 3, now referred to as "Zone B". These Zone A and Zone B designations are applied in the current study and are shown in Figure 1.

In September of 2001 and 2004, the Environment Canada sampled Zone A and B of the St. Clair River (as well as upstream and downstream locations) to provide further information on the degree of sediment contamination, focusing primarily on sediment mercury. This report presents the results of these investigations and provides a spatial description of the state of the sediments in the St. Clair River and the degree of contamination.

2 EXPERIMENTAL DESIGN

2.1 Sampling Design

Test sites were located in the upper reaches of the river extending from just upstream of the Dow property to the Suncor property (Zone A) and from south of Suncor to the south end of Stag Island (Zone B) (Figure 1). Locations upstream of Zone A and downstream of Zone B were also sampled (Figure 1). Stations were sampled for sediment and overlying water chemistry, benthic invertebrate community composition, sediment toxicity tests, and resident invertebrate tissue. The locations of stations were selected to (a) represent a wide range of mercury (Hg) levels in sediment, (b) include areas identified as requiring further characterization, (c) represent least contaminated/reference conditions in the area, and (d) overlap locations of previous studies.

For the biomagnification component of the study, this control/potential impact sampling design allowed several types of comparisons for assessing the distribution of Hg in sediment and biota. Using all sites, relationships between sediment and invertebrate Hg levels were examined. In addition, Hg levels at sites located upstream of the industrial zone were compared to Hg levels at all other sites. The array of the sites also allowed a spatial analysis of Hg conditions, where locations of elevated Hg in sediment, invertebrates and receptors (predicted from models) were identified.

2.2 Biomagnification Potential

Purpose and objectives

The purpose of biomagnification component of this study is to determine if Hg from sediments in the St. Clair River bioaccumulate in the tissues of benthic invertebrates, and if Hg could potentially be transferred through benthic invertebrates to fish or wildlife. The results of this study should lead to one of two alternate conclusions: (a) Hg is unlikely to concentrate in the

food web at levels that can cause adverse effects, or (b) Hg **could potentially** concentrate in the food web at levels that can cause adverse effects. The determination of whether Hg biomagnification and adverse effects to higher trophic level organisms (fish, wildlife, human) are actually occurring in the St. Clair River is beyond the scope of this study, and would need to be addressed by a more comprehensive assessment such as a detailed risk assessment. The latter conclusion (b) is of **potential** biomagnification, but does not determine **actual** biomagnification.

The purpose of the biomagnification component of the study was achieved through two objectives:

A. Determining if benthic invertebrates in locations where Hg is elevated are a potential source of mercury to higher trophic levels.

B. Determining if the amount of Hg potentially available is of concern.

The first objective was addressed by comparing concentrations of Hg in benthic invertebrates from test sites in the St. Clair River to those from sites upstream of the industrial zone, and by determining whether sediment Hg concentration was related to invertebrate (whole body) Hg concentration. For the second objective, the concentrations of Hg in selected trophically linked receptor species (i.e., consumers of benthic invertebrates and their predators) were predicted based on measured [Hg] in invertebrates and literature-derived biomagnification factors. (Traas et al. (2002) is an example of an application of this approach.) The predicted receptor species concentrations were then compared to appropriate tissue mercury guidelines established for the protection of higher trophic level organisms. Whereas predictions of receptor tissue Hg concentrations focused on methyl mercury (MeHg), because it is the most toxicologically relevant and predominant form of mercury in tissues of fishes and higher trophic level receptors (USEPA 1997b; Environment Canada 2002), determinations of Hg distributions and bioaccumulation in sediment and invertebrates were made on the basis of both total mercury (THg) and MeHg to allow comparisons with results from other studies and guidelines that involve THg.

The biomagnification modelling was broken down into four steps:

- Identification of receptors of potential concern for the St. Clair River AOC,
- Measurement of contaminant concentrations in invertebrates and sediment,
- Selection of biomagnification factors, and
- Prediction of possible receptor species tissue concentrations.

Knowledge of the food web structure of a site was needed to determine relevant receptor species (fish, bird, mammal). These are identified below. Determinations of concentrations of mercury in sediment ($[Hg]_{sed}$) and invertebrates ($[Hg]_{inv}$) are described in the methods section. The identified receptors determined the biomagnification factors (BMFs) to use for predicting receptor mercury concentrations and the appropriate criteria (e.g., guidelines for protection of wildlife consumers of aquatic biota) for comparison. The review and selection of BMFs are discussed in the data analyses section (Section 3.6) and Appendix A. How [Hg] in the tissues of receptor species was estimated is also described in Section 3.6.

Measurement endpoints

Invertebrates (oligochaetes and chironomids) and sediment for mercury analyses were collected at locations of sediment deposits potentially exposed to past discharges of mercury-containing effluent, as well as from upstream and downstream locations. Sediment was obtained from the top 0 - 10 cm layer of river bed. This layer includes the vertical home range of most benthic invertebrates. Two distinct invertebrate taxa (chironomids and oligochaetes) were targeted for collection from each location. Analyses of total and methyl mercury were performed on samples composited from organisms within each of two taxa (i.e., taxa were analyzed separately). Invertebrates were not allowed time to clear sediment from their guts because predators consume whole organisms, and mercury associated with sediment, as well as that incorporated into tissues, is potentially available for transfer through the food chain.

Model assumptions

For the prediction of Hg concentrations in the tissues of upper trophic level biota, bioaccumulation is considered to occur predominantly through dietary pathways. This is suggested by several experimental and modelling studies (Bodaly et al. 1997; Downs et al.

1998). In modelling the exposure to and uptake of Hg by receptors, several conservative assumptions (i.e., maximum potential exposure to Hg) have been made. These include:

- For fish receptor
  - Fish consume invertebrates only from the site.
  - Fish feed on same invertebrate taxa as those collected in field sampling.
- For wildlife receptor
  - 100% of the diet is fish.
  - Fish are consumed only from the site in question.

In addition, the flux of mercury between sediment, water and biota compartments were considered to be in equilibrium.

Receptors of concern for the St. Clair River

Based on generic food webs for the Great Lakes (e.g., Diamond et al. 1994), information on fauna resident in the St. Clair River AOC RAP Team (1991, 1995) and guidelines from Environment Canada (2002), receptors representative of four trophic levels were selected for biomagnification modelling:

- Benthic invertebrates (trophic level 1): **chironomids and oligochaetes**. Previous studies indicated impaired benthic communities in the upper reaches of the St. Clair River with the dominance of pollution tolerant species (Farara and Burt 1997).
- Benthivorous fish (trophic level 2): **white sucker**. The white sucker spawns in the St. Clair River, and is a year round resident in the river.
- Small piscivorous fish (trophic level 3): **yellow perch**. Yellow perch are an important species in the St. Clair River. They are fished recreationally in the St. Clair River, and spawn in the river.
- Large piscivorous fish (trophic levels 3 and 4): **walleye**. The St. Clair River provides a spawning ground and a migration corridor for the walleye. Walleye are an important recreational fish.
- Piscivorous bird (trophic levels 3 and 4): **great blue heron**. Great blue herons are widespread. Fishes (mostly <25 cm in length) are the preferred prey (Environment Canada

2002). The breeding distribution of the heron extends along the St. Clair River (CWS 2002), and this bird is found throughout the delta.

- Piscivorous mammal (trophic levels 3 and 4): **mink**. Mink are associated with numerous aquatic habitats and are opportunistic feeders (Environment Canada 2002). The St. Clair delta provides habitat for the mink.

As part of the MOE Sport Fish Contaminant Monitoring Program, walleye, yellow perch and white sucker (as well as other fish species) are collected regularly from the upper (from Lake Huron to just north of Ethyl Corp.), middle (from Ethyl Corp./Stag Island to just north of Lambton generating station) and lower (from generating station to Lake St. Clair) portions of the river. Sport fish consumption restrictions for total mercury for the general population begin at levels above 610 ng/g ww and total restriction is advised for levels above 1840 ng/g ww (MOE 2005). Contaminants are at levels that warrant consumption advisories for a group of compounds that includes mercury for the sucker, perch and walleye (MOE 2005). In the upper river, there are restrictions to 4 meals per month for walleye 60-65 cm long and to 2 meals per month for walleye 65-75 cm. In the middle river, there are consumption restrictions to 4 meals per month for 50-55 cm white sucker and 4 meals per month for yellow perch 30-35 cm long. In the lower river, there are consumption restrictions to 4 meals per month for walleye 50-75 cm long (MOE 2005).

A model of the feeding relationships linking these receptors with each other and benthic invertebrates and sediment is shown in Appendix A, Figure A1.

3 METHODS

3.1 Sample Collection and Handling

Sediment, overlying water, the benthic community and resident biota samples were collected at 16 sites September 17 – 20, 2001 and at 12 sites September 27 – October 1, 2004 (Figure 1). Two sites collected in 2001 were repeated in 2004. (Total number of sites = 26.) Ammonia was measured in 2004 only. Benthic invertebrate community samples were collected in 2001 only. Due primarily to substrate conditions, some samples were not collected. Sediment for toxicity

tests was not collected at site 6663 in 2001 because of gravel and small stones interfering with the Ponar grab operation. Resident benthic invertebrate tissue and sediment for the analyses of methyl mercury and organic contaminants were not collected at sites 6660, 6663 and 6664 (2001) because of high sand or gravel content of the substrate. Sampling techniques and methods for the collection of samples are fully described in Reynoldson et al. (1995, 1998a) and outlined below. Station positions are given in Table 1 and environmental variables measured at each site are provided in Table 2.

Prior to sediment collection, temperature, conductivity, pH and dissolved oxygen were measured in the water column approximately 0.5 m above the bottom with HYDROLAB water quality instruments. Water samples were collected for analysis of alkalinity, total Kjeldahl nitrogen, total phosphorus, nitrates/nitrites and ammonia from 0.5 m above the bottom using a van Dorn sampler. Total phosphorus samples (125 mL) were preserved with 1 mL of 30% sulphuric acid. Water samples were stored at 4°C for later analysis.

A 40 cm × 40-cm mini-box corer or Ponar sampler was used to obtain the benthic invertebrate community and sediment chemistry samples. Benthic community samples were subsampled from the mini-box core using 10 cm length × 6.5 cm diameter acrylic tubes. Samples were sieved through a 250-µm mesh screen and the residue preserved with 5% formalin for later identification. The remaining top 10 cm of sediment from each box core was removed, homogenized in a Pyrex dish and allocated to containers for chemical and physical analyses of the sediment. At sites where the mini-box core could not be used because of the high proportion of sand or sand/clay, which prevented the box core to seal, a Ponar sampler was used to obtain the sediment and benthic community samples. Three ponar grabs were collected for the benthic invertebrate community and one ponar grab was collected for chemical and physical properties of the sediment. Each benthic community ponar sample was sieved in its entirety and the residue preserved as described above. Sediment samples were stored at 4°C.

Five mini-Ponar grabs were collected per site for the laboratory toxicity tests (approximately 2 L sediment per replicate). Each of the five sediment grabs was placed in separate plastic bag, sealed, and stored in a 10 L bucket at 4°C.

A mini-Ponar sampler was used to collect the invertebrate tissue from the sediment. From each grab, a sample of the top 10 cm of sediment was removed and set aside in a glass tray, and the remaining sediment from the grab was placed in a 68-L tub. This process continued until the tub was approximately ¾ full (~10 to 15 grabs). The sediment set aside was then homogenized in the glass tray and distributed to pre-cleaned polyethylene bottles for analysis of total and methyl mercury by Flett Research laboratory. Samples were frozen.

Invertebrates were removed from the sediment in the 68-L tubs by wet sieving with river water using 12-inch stainless steel, 500-µm mesh sieves. Biota were sorted into separate taxa (chironomids, oligochaetes) in glass trays using stainless steel instruments. Biota were then rinsed with deionized water and placed in pre-weighed and pre-cleaned (20 % HCL) 5-mL scintillation vials, weighed, and frozen. A layer of parafilm was placed between vial and cap. Invertebrate samples were later freeze-dried and reweighed. The wet:dry weight ratios were used in converting invertebrate mercury concentrations from a dry weight to wet weight basis (see Section 3.6).

Stainless steel sieves and instruments were detergent washed between stations. If persistent organic matter remained on the sieve after the detergent wash (on visual inspection), a more aggressive cleaning solution was implemented with caustic ethanol. Homogenizing and sorting trays and scoops were detergent washed and rinsed with 20% HCl.

3.2 Taxonomic Identification

Benthic community samples were transferred to 70% ethanol after a minimum of 72 hours in formalin. Invertebrates in the benthic community samples were sorted, identified to the lowest practical level, and enumerated at the Environment Canada Invertebrate Laboratory (Burlington, ON). Slide mounts were made for Oligochaetae and Chironomidae for identification using high power microscopy.

3.3 Sediment Toxicity Tests

Four sediment toxicity tests were performed: *Chironomus riparius* 10-day survival and growth test, *Hyalella azteca* 28-day survival and growth test, *Hexagenia* spp. 21-day survival and growth test, and *Tubifex tubifex* 28-day adult survival and reproduction test. Sediment handling

procedures and toxicity test methods are described fully elsewhere (Borgmann and Munawar 1989; Borgmann et al. 1989; Krantzberg 1990; Reynoldson et al. 1991, 1998b). All tests passed acceptability criteria for their data to be used in the site assessments. The criteria are based on percent control survival in a reference sediment (Long Point Marsh, Lake Erie): i.e., ≥ 80% for *H. azteca* and ≥70% for *C. riparius* (USEPA 1994; ASTM 1995); ≥80% for *Hexagenia* spp., and ≥75% for *T. tubifex* (Reynoldson et al. 1998b). Toxicity tests were performed by the Environment Canada Ecotoxicology Laboratory (Burlington, ON).

Water chemistry variables (pH, dissolved oxygen (mg/L), conductivity (µS/cm), temperature (°C), and total ammonia (mg/L)) were measured in each replicate test beaker on day 0 (start of test – prior to introduction of organisms) and at completion of the test. Tests were run under static conditions in environmental chambers at 23 ± 1°C, under a photoperiod of 16L: 8D and an illumination of 500 - 1000 lux. The *T. tubifex* test was run in the dark.

***Hyalella azteca* 28-day survival and growth test**

The *H. azteca* test was conducted for 28 days using 2 – 10 day old organisms. On day 28, the contents of each beaker were rinsed through a 250-µm screen and the surviving amphipods were counted. Amphipods were dried at 60°C for 24 hours and dry weights recorded. Initial weights were considered zero.

***Chironomus riparius* 10-day survival and growth test**

The *C. riparius* test was conducted for 10 days using first instar organisms. On day 10, the contents of each beaker were wet sieved through a 250-µm screen and the surviving chironomids were counted. Chironomids were dried at 60°C for 24 hours and dry weights recorded. Initial weights were considered zero.

***Hexagenia* spp. 21-day survival and growth test**

The *Hexagenia* spp. test was conducted for 21 days using preweighed nymphs (5 – 8 mg wet weight/nymph). On day 21, the contents of each jar were wet sieved through a 500-µm screen and surviving mayfly nymphs were counted. Nymphs were dried at 60°C for 24 hours and dry weights recorded. Initial mayfly wet weights were converted to dry weights using the following

equation from a relationship for nymphs from the Ecotoxicology Lab that was previously determined by regression analysis: Initial dry weight = (wet weight + 1.15)/ 7.35. Growth was determined by final dry weight minus initial dry weight.

***Tubifex tubifex* 28-day reproduction and survival test**

The *T. tubifex* test was conducted for 28 days using sexually mature worms (gonads visible). On day 28, the contents of each beaker were rinsed through a 500-μm and 250-μm sieve sequentially. The number of surviving adults, full cocoons, empty cocoons, and large immature worms were counted from the 500-μm sieve and the numbers of small immature worms were counted from the 250-μm sieve. Survival and reproduction was assessed with four endpoints: number of surviving adults, total number of cocoons produced per adult, percent of cocoons hatched, and total number of young produced per adult.

3.4 Sediment and Water Physico-Chemical Analyses

Overlying water

Analyses of alkalinity, total phosphorus, nitrates/nitrites (NO_3/NO_2), total ammonia (NH_3), and total Kjeldahl nitrogen (TKN) were performed by the Environment Canada's National Laboratory for Environmental Testing (NLET) (Burlington, ON) by procedures outlined in Cancilla (1994) and NLET (2001).

Sediment particle size

Percents gravel, sand, silt, clay and 25th, 75th and mean percentiles were determined by the Sedimentology Laboratory (Burlington, ON) following the procedure of Duncan and LaHaie (1979).

Sediment trace metals and nutrients (Caduceon Laboratory)

Freeze dried sediment was analyzed for trace elements (hot aqua regia extracted), major oxides (whole rock), loss on ignition, total organic carbon, total phosphorus, and total Kjeldahl nitrogen by Caduceon Laboratory (Ottawa, ON), using USEPA/CE (1981) standard methodologies or in house procedures. For the analysis of total mercury in sediment, 0.5 g of freeze dried sediment was digested with HNO_3:HCl for two hours. $SnCl_2$ was added to reduce Hg to volatile metallic

form. If there was high organic material, $KMnO_4$ was added to the digestion solution to destroy organo-mercury bonds. Hydroxyl amine hydrochloride was then added to neutralize $KMnO_4$ excess so $SnCl_2$ could react with Hg in solution. Digestion was followed by measurement using a cold vapour atomic absorption spectrometer. The detection limit was 5 ng Hg/g sediment.

Total and methyl mercury in sediment and biota (Flett Laboratory)

Total and methyl mercury in sediment and biota was analyzed by Flett Research Ltd. (Winnipeg, MB), based on procedures of Bloom and Crecelius (1983), Horvat et al. (1993) and Liang et al. (1994), and are summarized below.

Total mercury in sediment biota

Between 100 and 1000 mg of thawed sediment sample (or spiked sediment, blanks or reference material) was digested overnight (16-18 hours) in 3 mL of 7:3 nitric/sulfuric acid at 150°C. After cooling, the sample was diluted to 25 mL with low-mercury deionized water, spiked with BrCl and allowed to react. The residual BrCl was then destroyed by addition of hydroxylamine hydrochloride. An aliquot of the sample (100 µL – 2 mL) was placed into a sparging vessel, to which was added stannous chloride. The elemental mercury produced was purged onto a gold trap with Hg-free nitrogen. The gold trap was heated with UHP argon carrier gas passing through it, and the mercury released was measured by a Brooks-Rand CVAFS model-2 detector. The detection limit was 1-5 ng/g dw.

The same procedure as described for analysis of total mercury in sediment was used for biota, with the following differences in the sample digestion: up to 100 mg of thawed invertebrate sample (or spikes, blanks or reference material) was digested for 6 hours in 10 mL of 1:2.5 nitric/sulfuric acid at 250°C; after cooling, the sample was diluted to 25 mL with low mercury deionized water, spiked with BrCl and allowed to react.

Methyl mercury in sediment

Sediment was prepared for analysis by distilling 200-300 mg of homogenized sample (or spikes or blanks) in ~45 mL of low-mercury deionized water. Approximately 40 mL of distillate was collected and acidified with KCl/H_2SO_4. (Note: Since methyl mercury results were ≤ 0.1% of the

total mercury results, a methylene chloride extraction was carried out on some of the highest total mercury samples. No significant difference in methyl mercury concentrations was observed between results obtained by either method. Therefore, it is assumed that insignificant methyl mercury production was occurring in the distillation process and thus all samples were processed by distillation.) An aliquot of the prepared sample (1-2 mL, depending on observed interferences from the matrix) was ethylated in solution (final volume ~ 40 mL) using sodium tetraethyl borate. The solution was buffered to pH 5.5. The resulting ethylmethyl mercury was purged onto a Tenax trap with mercury-free nitrogen. The trap was heated, purged with UHP argon onto a GC column (for separation of the ethylmethyl mercury from Hg° and diethyl mercury), run through a pyrolizer (to reduce all mercury to Hg°), and then sent to a cold vapour atomic fluorescence analyser for detection. (GC oven: Perkin Elmer 8410 GC; column: chromasorb WAW-DMSC 60/80 mesh with 15% OV-3; detector: Brooks-Rand CVAFS model-2.) The detection limit was 0.25 ng/g dw.

Methyl mercury in biota

Freeze dried biota (5-10 mg of homogenized sample, spike, blank or reference material) were digested overnight with ~500 µL of KOH/methanol at 75 °C. Sample aliquots (50-60 µL) were then treated and analysed as described above for the ethylation and subsequent steps in the determination of methyl mercury in sediment. The detection limit was 1.2 ng/g dw.

Organic contaminants

Analysis of polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and organochlorine (OC) pesticides was performed on sediment and biota samples by the MOE Laboratory Service Branch of the MOE (Etobicoke, ON), following Ontario Ministry of Environment standard methods (MOE 1993, 1994a, 2003a).

3.5 Biota-Sediment Accumulation Factors

A biota-sediment accumulation factor (BSAF) was calculated for each invertebrate taxon and site combination, for total and methyl mercury. The BSAF equation used was that defined by Thomann et al. (1995), and is the ratio of the metal concentration in the organism to that in the sediment:

$BSAF = [Hg]_{inv}/[Hg]_{sed}$

A BSAF assumes that the concentration of contaminant in the organism is a linear function of the contaminant concentration in the sediment.

3.6 Data Analysis

BEAST analysis of benthic invertebrate communities and sediment toxicity

For the analysis of benthic invertebrate communities, a limitation to the use of the BEAST model is that it can only be applied with confidence to test sites within the range of habitats and geographic areas contained in the reference data set. This reference dataset is restricted to harbours, embayments, and nearshore waters of the Laurentian Great Lakes. Therefore, the standard BEAST model was modified to include reference sites from connecting channels, specifically in the St. Clair River, for use in site assessments for the St. Clair River AOC (Reynoldson et al. 2003). In general, the modified model is more conservative in assessing sites than the standard model, and its performance indicates the importance of having some reference sites in connecting channels. The model predicts the invertebrate community group that should occur at a test site based on natural environmental conditions and is based on 52 macroinvertebrate families. Multiple discriminant analysis was used to predict the test sites to 1 of 6 reference community groups using a previously computed relationship between 11 environmental variables and the community groups (Reynoldson et al. 2003). Benthic community assessments were conducted at the family level, as this taxonomic detail is shown to be sensitive for the determination of stress (Reynoldson et al. 2000). All community data were standardized to be equivalent to the box-core. To adjust for the efficiency of the Ponar relative to the box core, benthic abundances for sites collected with the Ponar were divided by 0.69, with the exception of the chironomids, oligochaetes, sphaeriids, nematodes and hirudinea where, 0.52, 0.55, 0.75, 0.64, and 0.71 were used, respectively. All counts were then adjusted for area. Community data for the test sites were merged with the reference site invertebrate data of the matched reference group only (i.e., group to which the test site has the highest probability of belonging) and ordinated using hybrid multidimensional scaling (HMDS; Belbin 1993), with Bray-Curtis distance site × site association matrices calculated from raw data. Toxicity data were analysed using HMDS, with Euclidean distance site × site association matrices calculated from range-standardized data. Toxicity endpoints for the test sites were compared to those for all

reference sites. (There are no distinct habitat-associated groups as with the benthic community assessment.) Principal axis correlation (Belbin 1993) was used to identify relationships between habitat attributes and benthic community or toxicity responses. This did not include organic contaminant data, which were not measured in the reference sediments. Significant endpoints and environmental attributes were identified using Monte-Carlo permutation tests (Manly 1991). Test sites were assessed by comparison to confidence bands of appropriate reference sites. Probability ellipses were constructed around reference sites, establishing four categories of difference from reference: equivalent /non-toxic (within the 90% probability ellipse), possibly different/ potentially toxic (between the 90 and 99% ellipses), different/toxic (between the 99 and 99.9% ellipses), and very different/severely toxic (outside the 99.9% ellipse). Test site toxicological responses were also compared to numerical criteria previously established for each category (non-toxic, potentially toxic and toxic) and species from reference site data (Reynoldson and Day 1998).

Test data were analyzed in subsets to maintain the ratio of test: reference sites ≤0.10. Multiple discriminant analysis was performed and probability ellipses were produced using the software SYSTAT (Systat Software Inc. 2002). HMDS, principal axis correlation, and Monte-Carlo tests were performed using the software PATN (Blatant Fabrications Pty Ltd. 2001).

Comparison of upstream to downstream benthic communities

Additional analyses were performed to compare sites adjacent to or downstream of the industrial area to sites upstream of the industrial area. The St. Clair River sites were ordinated again by HMDS, as a single group and without the Great Lakes reference site data. Correlations between site scores from the ordination and habitat variables, including organic contaminant data, were determined. Using the ordination axes scores from HMDS, major family abundances and taxon diversity, analyses of variance with adjustments for covariates (ANCOVAs) were performed using Minitab (2000). The covariates selected for the ANCOVAs were those found to be most highly correlated to the ordination axes scores. Bonferroni simultaneous tests were performed to compare upstream sites (control) to all other sites.

Biomagnification potential

Mercury distribution in sediment and biota

Sites in which concentrations of Hg in invertebrates ($[Hg]_{inv}$) were significantly elevated above background levels for the study area were identified by comparing $[Hg]_{inv}$ for the test sites to the upper 99th % percentile (= maximum) for the upstream reference sites. This was done separately for MeHg and THg and for each invertebrate taxon.

Relationships between concentrations of Hg in sediment and invertebrates were determined using regression analysis, again separately for MeHg and THg and for each invertebrate taxon. The approach was used to estimate the degree to which Hg in invertebrates is predictable from Hg in sediment, with and without environmental covariables. Simple linear regression (ordinary least squares) was used for the single predictor ($[Hg]_{sed}$) model. "Best subset" multiple linear regression (Draper and Smith 1998; Minitab 2000) was used for the fitting of multiple predictor models. Included in the models were the environmental variables expected to potentially influence uptake of Hg from sediment by biota (based on reviews such as Braga et al. 2000; Lawrence and Mason 2001), such as sediment concentrations of total organic carbon, total phosphorus, total Kjeldahl nitrogen, iron and manganese; sediment particle size fractions of sand, silt and clay; overlying water dissolved O_2, pH, alkalinity, conductivity; NO_3/NO_2, total Kjeldahl nitrogen, temperature and site depth. To increase normality of data distributions and linearity of relations between variables, some data were transformed: log(x) for THg and MeHg in sediment and invertebrates; log(x) for overlying water variables, sediment nutrients, iron and manganese and site depth; and arcsine-square root(x) for the particle size fractions. Normality and linearity of alkalinity and pH data were not generally improved by transformations, so these were analyzed untransformed.

All models fitted to the data included $[Hg]_{sed}$ as a free predictor (i.e., it was not forced to be in the model). The specific null hypothesis of interest was that "the effect of $[Hg]_{sed}$ on $[Hg]_{inv} = 0$, after accounting for effects of other predictors". For the best subset regressions, models were fitted for all combinations of predictors. Determination of the "best" model was based on several criteria (in roughly decreasing order of importance):

- maximum $R^2_{adjusted}$

- significance of partial F-tests (= t-tests) for predictors (especially $[Hg]_{sed}$)
- significance of F-test for regression
- variance inflation factors (VIFs) for predictors < 10
- homoscadastic and normally distributed residuals
- Mallow's C_p statistic not >> number of predictors

Lack-of-fit tests for curvature in response-predictor relationships and interactions between predictors were performed and examined for nonsignificance. Observations having large standardized residuals or large influence on the regression were also considered in model evaluations. The best model was identified based on the overall meeting of these criteria. Both single and multiple predictor models were then examined for the degree to which $[Hg]_{sed}$ predicts $[Hg]_{inv}$, as indicated by the significance of the t-test of the coefficient for $[Hg]_{sed}$.

Prediction of mercury concentrations in receptors

A review of information on BMFs was conducted using typical methods of electronic database and chain-of-citation searches as well as consultation with leading researchers in the field of mercury ecotoxicology and risk assessment. Details on the methods and the results of the review are described in Appendix A.

It is widely recognized that mercury is transferred through trophic levels primarily in the methyl form (USEPA 1997b). It is also accepted that mercury in the tissues of fishes and higher trophic level organisms is almost entirely in the organic (methyl) form. Environment Canada (2002) states that "total mercury" concentrations in piscivorous fishes are probably ~99% methyl mercury, and Bloom (1992) suggests that previous studies reporting methyl mercury fractions in fishes less than 95% were likely in error. Therefore, mercury concentration in receptors was predicted on a MeHg basis, using (a) MeHg measurements in invertebrates and (b) combined THg and MeHg BMF values (assuming that reported THg concentrations largely represent MeHg concentrations).

Concentrations of MeHg in the tissues of receptors were predicted by multiplying measured body concentrations in the resident invertebrates by the food chain multiplier relevant for the

receptor. The predicted MeHg concentrations in receptors are generic in that they are not specific to particular tissues.

$$C_{rec} = FCM \times C_{inv}$$

where:

C_{rec} = mean contaminant concentration in the consumer (receptor) species

C_{inv} = mean contaminant concentration in invertebrates

FCM = food chain multiplier

The FCM represents the biomagnification of a substance from one trophic level to a higher trophic level (USEPA 1997c). Whereas a BMF applies to only one trophic level-transfer, a FCM refers to one or more, and may be a multiple of more than one BMF. Thus, $FCM = BMF_1 \times BMF_2 \times BMF_3 \times \ldots \times BMF_n$, where 1,2,3,..., n are transfers of one trophic level. The BMFs used to obtain FCMs and calculate C_{rec} values are in Table A1, which shows the low, medium and high BMFs from the literature review for each transfer between trophic levels as shown in Figure A1. In Table 3, the FCM for transfer from benthic invertebrates to each receptor is estimated by multiplying the BMFs for the intermediate steps from Table A1. Low, medium and high FCM values are obtained from use of all minimum, all medium or all maximum estimates for each BMF. For the walleye, heron and mink, it is recognized that they could be level 3 as well as trophic level 4 predators. Therefore, FCMs were estimated for both food chain pathways.

Invertebrate methyl Hg concentrations used in the predictions of Hg in receptors include observed $[Hg]_{inv}$ values for the two taxa collected from the site. These were used to obtain minimum and maximum observed $[Hg]_{inv}$ for the taxa collected from the site. "Medium" $[Hg]_{inv}$ for the site was calculated as the mean of the values. Since fish contaminant data are reported for the most part on a wet weight basis, and the guidelines used in this study are also based on wet weights, methyl Hg concentrations in invertebrates were converted to wet weight. Biota comprised on average 86% water. The ratio of wet to dry weight was determined for each individual sample submitted for analysis (rather than using an overall average ratio for each taxon). Wet weights were determined using the following conversion:

$[Hg]_{inv}$ (ng/g dry weight) / (ratio of wet: dry weight) = $[Hg]_{inv}$ (ng/g wet weight)

Total and methyl mercury concentrations in each invertebrate taxon, converted to wet weight values, are provided in Appendix B, Tables B1 and B2.

For each site, minimum, intermediate and maximum concentrations of MeHg for each receptor were predicted by:

$$[Hg]_{rec} = FCM \times [Hg]_{inv}$$

using corresponding low, medium and high $[MeHg]_{inv}$ and FCMs. For the walleye, heron and mink, FCMs for both food chain pathways were combined. From the available values, the lowest and the highest FCMs were used for the minimum and maximum prediction, the mean of the two medium values was used for the intermediate prediction.
If a predicted contaminant concentration in the receptor exceeded the guideline and the maximum predicted concentration at reference sites, a potential risk of adverse effects due to biomagnification was concluded. Alternatively, if the predicted contaminant concentration in the receptor was less than the guideline, no potential risk was concluded.

3.7 Quality Assurance/Quality Control

Field replication

Triplicate overlying water and sediment samples were collected at 2 randomly selected sites (6668 and 6669) for determination of within-site and among-sample variability. Variability in the measured analyte was expressed as the coefficient of variation (CV = standard deviation / mean × 100).

Laboratory

Flett Research Ltd. conducted determinations of total and methyl mercury in sediment and benthic invertebrates. Quality control evaluation for these procedures included analyses of sample duplicates, matrix spikes and certified reference materials, as well as evaluations of sample recoveries. For sediment, sample duplicates were analyzed at least once every 15 samples, and matrix spikes were performed on every tenth sediment sample to determine mercury recoveries. The NRC certified sediment reference material "MESS-2" , "Hg standards

1 – 5", and "OPR (solids)" were concurrently digested and analysed for total Hg, and "IAEA", "DORM 2" and "alpha" were concurrently digested and analysed for methyl Hg. For biota, "DORM-2", "Hg Standards 1 – 5", "OPR (solids)", and "MQAP fish check samples" were concurrently digested and analysed for analyzed for total Hg, and "DORM-2" and "alpha" were concurrently digested and analysed for methyl Hg with each lot of 10 - 20 samples. Each invertebrate taxon was represented in the analyses of sample duplicates and matrix spikes.

Caduceon Environmental Laboratory analyzed sediment for trace metals (including total mercury), major oxides, total phosphorus, total Kjeldahl nitrogen, and total organic carbon. Quality control procedures involved control charting of influences, standards, and blanks. Reference material was used in each analytical run. Calibration standards were run before and after each run. Run blanks and reference standards were run 1 in 20 samples, while duplicates were run 1 in 10 samples. Sample duplicate measurements of sediment metals, major oxides and nutrients were expressed as the relative percent difference: $(x_1 - x_2) / ((x_1 + x_2)/2) \times 100$.

An inter-laboratory comparison of analyses for total Hg was conducted based on results from Flett Research and Caduceon Laboratory. Data were compared by regression analysis. The slope of the regression line is a measure of the overall agreement in [THg] determinations, whereas the scatter of points about the line should indicate joint laboratory measurement error.

Benthic Invertebrate Community Sorting

To evaluate control measures for benthic invertebrate enumeration, each month, a randomly selected sample that was already sorted was re-sorted, and the number of new organisms found counted. The percent of organisms missed (%OM) was calculated using the equation:

%OM = # Organisms missed / Total organisms found × 100

The desired sorting efficiency is a %OM ≤ 5% (or >95% recovery). If the %OM was > 5%, two more replicate samples were randomly selected and the %OM calculated. The average %OM was calculated based on the three samples re-sorted, and represents the standard sorting efficiency for that month. The average %OM is based on only one replicate sample if %OM is < 5%.

4 RESULTS

4.1 Sediment and Water Physico-Chemical Properties

Overlying water

Conditions of overlying water 0.5 m above the sediment are generally similar across at all sites (Table 4), with overlapping ranges and similar medians for each variable. Upstream sites have only slightly lower levels of nutrients (total phosphorus, total Kjeldahl nitrogen, and NO_3/NO_2) compared to the rest of the sites overall. Fairly narrow ranges of dissolved oxygen, pH, conductivity, alkalinity, temperature, phosphorus, total Kjeldahl nitrogen, NO_3/NO_2 and ammonia are observed at sites along the river (ranging over 2.3 mg/L, 0.3 pH units, 29 µS/cm, 12.5 mg/L, 3.6 °C, 0.03 mg/L, 0.16 mg/L, 0.16 mg/L and 0.03 mg/L, respectively), suggesting a relatively homogeneous water mass. Dissolved oxygen is ≥7.3 mg/L at all sites.

Sediment particle size

Sediment particle size data for St. Clair River are shown in Table 5. St. Clair sediments are coarse generally, consisting mainly of sand, ranging from 51 to 99% (median 89%), followed by silt, ranging from 1 to 30% (median 6%). Percent gravel ranges from 0 to 38% (median 0.4%). (15 of 26 sites contain gravel.) Sites 6663, 6664 and 66M144 are very coarse, with 32, 38 and 28% gravel, respectively. There is very little or no clay at most sites, ranging from 0 to 19% (median 0%). (Only six sites contain clay.)

Sediment Mercury

The sediment samples analyzed by Flett Research Ltd., as opposed to those analyzed by Caduceon Laboratory (see Sec. 4.1), better represent resident invertebrates Hg exposure because each sample analyzed consisted of a subsample from each of the mini-Ponar grabs collected for resident biota Hg determinations. Also the same sample was used to determine both total and methyl Hg concentrations. Accordingly, the Flett Laboratory sediment Hg results are presented below and were also used in the determination of the biota-sediment accumulation factors and in determination of the relationships between mercury in the sediment and mercury in the benthic invertebrates. Exceptions include the Hg data for sites 6663 and 6664 (adjacent to Dow) and 6660 (upstream) where Flett data were not available; for these sites, Caduceon Laboratory data

were used. Complete total Hg results from Caduceon Laboratory are provided in Appendix C, Table C1.

Total mercury

On a dry weight (dw) basis, the lowest total Hg levels were found at sites upstream of the industrial area, which range from 0.008 to 0.07 μg/g (mean of 0.024 μg/g) (Table 6, Figure 2). Total Hg concentrations in Zone A (adjacent to the industry) range from 0.2 to 49.3 μg/g and in Zone B (to the end of Stag Island) range from 0.8 to 3.8 μg/g. Total Hg concentrations at the three sites downstream of Zone B range from 0.04 to 0.5 μg/g; the site farthest downstream in the delta (6651) has a similar concentration as the upstream reference sites. The highest Hg concentrations are at sites 6663 and 6664 in Zone A (from Caduceon data; Appendix C, Table C1), and there is an overall decrease in Hg with distance downstream of 6663. The SEL (2.0 μg/g) is exceeded at 11 of the 26 sites; some sites in Zone B are just slightly above the SEL.

Methyl mercury

There are no MeHg data for site 6660 (upstream) and sites 6663 and 6664 (Zone A) (see Section 3.1 for explanation). However, using the mean fraction of methyl Hg to total Hg for upstream sites (10.3%), methyl Hg at 6660 was estimated to be 7 ng/g. Using the mean fraction of methyl Hg to total Hg for sites in Zones A and B (0.6%), methyl Hg concentrations for sites 6663 and 6664 were estimated to be 296 and 97 ng/g, respectively. For upstream sites, MeHg concentrations range from 0.5 to 7 ng/g (mean of 2.5 ng/g) (Table 6, Figure 3). Methyl [Hg]s range from 2.4 to 296 ng/g in Zone A, range from 4.9 to 16.0 ng/g in Zone B, and range from 1.2 to 3.8 ng/g at sites downstream of Zone B. The highest (estimated) MeHg concentration is for site 6663 and overall there is a decrease in methyl Hg with distance downstream although values tend to fluctuate along the river. The mean fraction of measured methyl mercury relative to total mercury for all sites is 2.5% (95% confidence interval (CI) of 0.78 to 4.26%), but is much higher at the upstream sites (mean of 10.3%) compared to sites in Zones A and B (mean of 0.6%). Four of the five upstream sites and the site in the delta have a percent MeHg greater than the upper CI. A significant positive correlation ($r^2 = 0.78$, $P<0.001$) was found between the methyl and total mercury concentrations in the sediment (Figure 4).

Comparison of sediment mercury at upstream (reference) sites to downstream sites

For total mercury, all test sites exceed the maximum upstream site concentration, with the exception of site 6651 (located in the delta) (Figure 2). Almost all St. Clair test sites are between 1 to 3 orders of magnitude higher in [THg] than the 99th percentile of the upstream reference sites. The median [THg] of all test sites is 170× higher than the median of the upstream reference sites.

For methyl Hg, 4 of the 5 sites in Zone A and 10 of the 13 sites in Zone B exceed the 99th percentile for the upstream reference sites (Figure 3). (Note: the maximum upstream concentration was estimated – see above). Methyl Hg concentrations at the sites downstream of Zone B do not exceed the 99th percentile for the upstream sites. The median [MeHg] of all test downstream sites is ~5× higher the median of the upstream reference sites.

Sediment trace metals and nutrients

Total phosphorus (TP), total Kjeldahl nitrogen (TKN), and total organic carbon (TOC) are provided in Table 7. The SEL is not exceeded for any nutrient variable at any site. TOC ranges from 0.3 to 3.2% (median 1.3%), TKN ranges from 190 to 2610 µg/g (median 583 µg/g), and TP ranges from 123 to 772 µg/g (median 239 µg/g). Sediment nutrient concentrations throughout the river are similar, with some slightly higher values observed for test sites in Zone B. The highest TKN and TP and high TOC is noted for site 66M253, located just below the Talfourd Creek (see Figure 1). The highest TOC is noted for site 6663 (Zone A). Trace metals and the corresponding provincial lowest effect levels (LEL) and SELs are also provided in Table 7. There are similar concentrations of trace metals throughout the river. Metals exceeding the LELs include arsenic, cadmium, copper, nickel and lead.

Nutrient and metal contaminant concentrations reported to exceed dredged material disposal (DMD) guidelines in the river in previous studies (St. Clair River Rap Team 1991 - total Kjeldahl nitrogen, total phosphorus, arsenic, cadmium, copper, chromium, iron, lead, nickel, zinc, manganese) do not exceed DMD guidelines in the current study with the exception of TKN at site 66M253 (Zone B) and nickel at site 6663 (Zone A).

Organic contaminants

Sediment organic contaminant concentrations are provided in Appendix D, Tables D1 (2001 sites) and D2 (2004 sites). Concentrations of PCBs, PAHs, Hexachlorobenzene (HCB), Hexachlorobutadiene (HCBD), and Octachlorostyrene (OCS) are elevated compared to sediments upstream of the industrial area, similar to that found in previous studies (St. Clair River RAP Team 1991). Total PCBs range from < detection limit (DL) to 0.2 µg/g and total PAHs range from 0.08 to 9.94 µg/g. The Lowest Effect Level for total PCBs (0.07 µg/g) is exceeded at 7 sites, for total PAHs (4 µg/g) at 1 site. Upstream reference concentrations range from < DL to 0.08 µg/g for total PCBs and from < DL to 0.2 to 0.3 µg/g for total PAHs. Hexachlorobenzene concentrations range from < DL to 0.89 µg/g, HCBD ranges from < DL to 0.26 µg/g, and OCS ranges from < DL to 0.11 µg/g. Upstream reference site concentrations range from < DL to 0.004 µg/g for HCB, and concentrations are below the DL for HCBD and OCS. The sites located farthest downstream (6654 and 6651) have similar levels of organic contaminants as the upstream sites. The highest concentrations of PAHs, HCBD and OCS are found at sites in Zone A, and the highest concentrations of HCB and PCBs are found in Zone B. Organic contaminants were not analyzed at sites 6663 and 6664 and upstream site 6660 (see Section 3.1 for further explanation). (Sites 6663 and 6664, located adjacent to the Dow property, have the highest [Hg] – see Appendix C, Table C1.)

4.2 Benthic Invertebrate Community

Using a revised BEAST model which includes 10 reference sites in the St. Clair River itself (Reynoldson et al. 2003), St. Clair River sites (collected in 2001 only, n=16) have the highest probability of belonging to reference Group 3 (15 sites) or to reference Group 1 (1 site, located in the delta) (Table 8). Many sites, however, do not have a high probability of membership in a single reference group. Ten of the 16 sites have < 60% probability of group membership, and 4 sites have < 50% probability of group membership (probability range: 42 to 77%; median: 54%).

Benthic communities in the St. Clair River sites consist predominantly of Chironomidae (Diptera) and Tubificidae (Oligochaeta), which are present at all sites (Tables 9a-d). At upstream sites (n=5), tubificid densities range from 2451 to 45,819 per m^2 (mean of 19,198/m^2) and chironomid densities range from 3016 to 20,812 per m^2 (mean of 12,660/m^2) (Table 9a).

Naididae (Oligochaeta) are present at all upstream sites ranging from 101 to 2238 per m^2 (mean of 744/m^2). Other macroinvertebrate taxon groups present at most or all upstream sites include ephemerid (9 to 60/m^2) and caenid (9 to 60/m^2) mayflies (Ephemeroptera), and gammarid amphipods (Amphipoda) (9 to 188/m^2) (Table 9a; Appendix E, Table E1). With the exception of site 6662 (just upstream of the Dow property; tubificid density of 56,152/m^2), tubificid densities in Zone A (945 to 5386/m^2) are lower than upstream whereas densities in Zone B (range of 9711 to 59650/m^2) are overall higher than upstream (Tables 9b-c). Chironomid densities in Zones A (including 6662) (range of 1990 to 8158/m^2) and B (range of 1327 to 11037/m^2) are generally lower than upstream sites. Naidid worms are present at most sites in Zones A and B (8 of 9), with densities ranging, where present, from 34 to 4610/m^2 (median: 236/m^2); most sites have lower densities than the upstream mean. Ephemerids are absent at all test sites with the exception of 6664 (Zone A; 9/m^2) and 6651 (delta; 181/m^2; Appendix E, Table E1)) and caenids are present at 1 Zone A site (6663; 9/m^2), at 4 Zone B sites (range of 60 to 1146/m^2), and at site 6654 (Stokes Pt; 1093/m^2) (Table E1). Gammarids are present in Zone A (2 sites) Zone B (3 sites) (range of 3 to 1206/m^2) but are absent in the delta (site 6651). Macroinvertebrate family diversity (based on revised 52-family model – see Section 3.6) ranges from 8 to 23 at the upstream reference sites (mean of 14 families) (Table 9a), from 2 to 16 taxa in Zone A (Table 9b) and from 6 to 18 taxa in Zone B (Table 9c). With the exception of sites 6662 (Zone A), 6667 (Zone B) and 6651 (delta), the number of taxa present is greater than the lowest number found at reference sites (8 taxa) (Tables 9b-d). Six of the 11 test sites have ≥ 14 taxa present (≥ than the upstream mean). Site 6662, located just upstream of the Dow property in Zone A, has the lowest number of taxa with only tubificids and chironomids present, followed by Site 6667 in Zone B with 6 taxa.

The mean relative density of the predominant macroinvertebrate taxa are provided in Appendix E, Table E2. On average, upstream sites are comprised mainly of tubificids (52%), followed by chironomids (41%). Naidid worms comprise 2.1%, while amphipods, mayflies, caddisflies (Trichoptera) and snails (Gastropoda) comprise a minor component (≤2.2% in total). Other groups (i.e., mites (Acari), dreissenids (Mollusca), other oligochaetes) comprise 2.3%. Zone A sites are variable, with tubificids dominating at 1 site (96.6%), chironomids dominating at 2 (62.5% and 85.9%) and 1 site has a similar density of both taxa. With the exception of Site 6662

and 6665, other groups comprise between 2 and 7% of the total. Site 6662 is distinctive as it is comprised of ~97% tubificids, with a minor component chironomids and no other major taxa present, indicative of a degraded community. Site 6665 has a very minor combined component of naidids (0.4%), as well as trichopterans and other taxa (≤0.4% each). In Zone B, tubificids dominate, comprising 72 to 85% of the community, followed by chironomids (2.4 to 20.9%). Gastropods (0 to 10%) and naidids (0.1 to 5.5%) are also mostly present. Other groups (i.e., mites, enchytraeid worms (Oligochaeta), empidid flies (Diptera)) comprise between 0.7 and 7.2% of the total.

Reference Group 3

Reference Group 3 is based on 51 sites, primarily from Georgian Bay (20), as well as the North Channel of Lake Huron (10), the St. Clair River (9), Lake Ontario (7), Lake Erie (3), and Lake Huron (2). This group is characterized by Chironomidae, Tubificidae and Sphaeriidae (Bivalvia), occurring at 100%, 94 and 82% of reference sites, respectively. Chironomids comprise 37.7% of the total abundance of families in Group 3, tubificids 19.3%, and Sphaeriids 12.5%. To a lesser degree, Naididae, Valvatidae (Gastropoda), Sabellidae (Polychaeta), Asellidae (Isopoda) and Ephemeridae are also present in Group 3 (occurring at 31 to 67% of reference sites and comprising 1.4 to 6.5% of the total abundance). Tables 9a-c show the mean abundance of these families at the 15 St. Clair River sites that have the highest probability of belonging to reference Group 3. Chironomids and tubificids are present at all sites in increased abundance compared to reference sites (from ~1.1 to 17× and from ~1.5 to 96× higher, respectively). Sphaeriids are either absent or present in decreased abundance with the exception of one site (6669-Zone B), and naidids are present at all sites except one (6662-upstream of Dow property). Remaining families are absent from the majority of sites, and with some exceptions, families are present in decreased abundance compared to reference. Four of the five upstream sites have mayflies present, while mayflies are present at only 2 downstream sites (6664 and 6651 – see reference Group 1 below). With the exception of 3 sites (6662, 6665, and 6667), family diversity is the same or higher than the reference mean. Upstream US site 6698 has the greatest diversity (22 taxa), while 6662, located just upstream of the Dow property, has the lowest (2 taxa).

Reference Group 1

Reference Group 1 is based on 35 sites, primarily from Lake Erie (22), as well as L. Michigan (5), Georgian Bay (4), Lake Ontario (3), and the St. Clair River (1). This group is characterized by Tubificidae (occurring at 100% of reference sites), Chironomidae (occurring at 97% of reference sites) and Sphaeriidae (occurring at 83% of reference sites). Tubificids comprise 53.8% of the total abundance of families in Group 1, chironomids 16.4%, and sphaeriids 12.3%. To a lesser degree, Naididae, Dreissenidae and Valvatidae are also present in Group 1(occurring at between 43 to 74% of reference sites and comprising 0.6 to 4.1% of the total abundance). Table 9d shows the mean abundance of these families at site 6651 (located in the North Channel of the delta), which has the highest probability of belonging to reference Group 1. Tubificidae and Chironomidae are present in increased abundance compared to reference sites (~2.5× and 8.2× higher, respectively), while Sphaeriidae are in decreased abundance (~6.7× lower). The remaining 3 predominant reference families are absent from 6651. However, Ephemeridae (mayfly), which have a low percent occurrence (5.7%) and low mean abundance (3.5/m^2) at the reference sites, are present at 6651 in increased abundance compared to reference (181/m^2; Appendix E, Table E1). Enchytraeidae (Oligochaeta) are also present at 6651 (60/m^2; Appendix E, Table E1). These worms are only present occasionally in Group 1 reference sites (8.6%) and in low abundance (reference mean of 8.7/m^2). Taxon diversity at site 6651 (5 taxa) is below the Group 1 reference mean (~7 taxa) (Table 9d).

Results of the BEAST benthic invertebrate community evaluation are summarized in Tables 9a-d. Ordinations are shown in Appendix F, Figures F1 to F4 (stress ≤ 0.16). Four separate ordinations were performed each with a subset of 1 to 5 St. Clair River sites.

St. Clair sites fall into the following bands of similarity to reference conditions:

Band 1 (equivalent to reference):	1 site	(6663)
Band 2 (possibly different):	4 sites	(6660, 6664, 6665 and 6651)
Band 3 (different):	4 sites	(6697, 6667, 6668 and 6654)
Band 4 (very different):	7 sites	(6648, 6661, 6698, 6662, 6699, 6666 and 6669)

Macroinvertebrate families that are most highly correlated to the ordination axes scores are Tubificidae and Chironomidae (r^2: 0.50 to 0.93 and 0.31 to 0.71, respectively), followed by Sphaeriidae (r^2: 0.40 to 0.57). Generally, movement of sites outside of the reference condition is associated with increased abundances of several taxa, predominantly Chironomidae and Tubificidae, which are maximally correlated to the movement of sites outside of reference and are shown as vectors in the ordinations (Appendix F, Figures F1 to F4 - some families are difficult to see in the ordinations as they are superimposed on each other). The relationship between the community response and habitat variables was examined by correlation of the ordination of the community data and the habitat information. Sixteen habitat variables are significantly ($p \leq 0.01$; $r^2 \geq 0.20$) correlated with the three ordination axes scores: Hg, Cu, depth, loss on ignition (LOI), particle size fractions of the sediment (mean, 75th, and 25th percentiles), CaO, total organic carbon (TOC), MgO, P_2O_5, temperature (Temp), NO_3/NO_2, total phosphorus in the overlying water (TP(W)), clay and dissolved oxygen (DO). Those oriented with the position of the St. Clair River sites are illustrated in Figures F1 to F4. Most notable is that Hg appears associated with the movement of some sites outside of reference (Zone B sites - Figure F3). The contribution of organic contaminants are not known (organic contaminants were not measured in the Great Lakes reference sites and therefore a comparison to test sites is not possible using BEAST multivariate methods).

Comparison of Upstream to Downstream Sites

The HMDS (using St. Clair River invertebrate family data only) reveals that three axes define the structure in the data (stress = 0.12). The data, summarized on Axes 2 and 3, are shown in Appendix F, Figure F5. The degree of similarity among sites is indicated by the spatial proximity of sites in ordination space; sites in close proximity are similar in community composition. Of the upstream sites, 6661 and 6698 are most similar to each other but generally upstream sites show variability along all three axes. Downstream sites also show variation along all three axes. Families highly correlated with the ordination axes scores include Tubificidae ($r^2 = 0.87$) and Chironomidae ($r^2 = 0.65$) (shown as vectors in Figure F5). Also significantly correlated ($p \leq 0.05$) are the moth Pyralidae (Lepidoptera) ($r^2 = 0.48$), the caddisfly Brachycentridae ($r^2 = 0.47$), and the snail Hydrobiidae ($r^2 = 0.42$). Higher abundances of Tubificidae are associated with sites in Zone B (6699, 6666, and 6669) and higher abundances of

Chironomidae are associated with upstream sites (6698 and 6661) as well as the site in the delta (6651). Two environmental variables are significantly correlated to the ordination site scores: particle size (25th percentile, r^2=0.87), and %silt (r^2=0.64). Mercury is not significant. Sites 6648 (upstream), 6651 (delta) and some sites in Zone B are located along an increasing gradient of silt and a lower particle size (as 25th percentile). Sites in Zone A, alternatively, are located along an increasing particle size (25th percentile) gradient; these sites are coarse, containing a fairly high percentage of gravel.

The ordination site scores were used to compare benthic communities of St. Clair River downstream sites to those of upstream (reference) sites. The ANCOVAs were performed, separately for each of the three axis ordination scores. Covariates selected for the ANCOVAs were the significantly correlated variables (25th percentile particle size, %silt). The F-tests indicate no significant differences between upstream and downstream sites. Site comparisons made using log(x)-transformed family diversity and log(x)-transformed abundances of tubificids and chironomids also indicate no significant differences between upstream and downstream sites.

4.3 Sediment Toxicity Tests

Mean species survival, growth, and reproduction in sediment from St. Clair River sites are provided in Table 10. The established numeric criteria for each category (non-toxic, potentially toxic and toxic) and for each species are also included. (Note: Toxicity tests were not performed at 6663 – see Section 3.1 for further explanation).

There is reduced mayfly survival at two sites: 6664 (Zone A - 78%) and 6666 (Zone B - 76%). However, the majority of sites (16 of 26) show enriched mayfly growth (greater than two standard deviations (SD) above the Great Lakes reference mean). The amphipod and midge also show enriched growth at 1 site each. Reproduction (*Tubifex* cocoon and young production) is low at site 66M144 (Zone B). Sites 6667 and 6669, which were sampled in 2001 and 2004, generally show similar results.

Results of the BEAST toxicity evaluation are summarized in Table 10. Ordinations are shown in Appendix G; Figures G1 to G3 (stress ≤ 0.09). Each figure represents a separate ordination with

a subset of St. Clair River sites. Toxicity endpoints that are most highly correlated ($r^2 \geq 0.884$) to axes scores are *Chironomus* survival (Crsu), *Tubifex* young production (Ttyg), and *Hyalella* survival (Hasu). Monte-carlo random permutations reveal that these endpoints are significant in the ordination space (rather than a random artifact of the data). Measured environmental variables are weakly correlated ($r^2 \leq 0.11$) to the axes scores in all ordination; the most highly correlated significant environmental variables are depth (r^2: 0.097 to 0.11, Figures G1 to G3), temperature (r^2: 0.081 to 0.10, Figures G1 and G2) and Na_2O (r^2: 0.083 to 0.089, Figures G1 and G3) and TOC ($r^2 = 0.094$, Figure G2). Mercury is not significantly correlated (Figures G2 and G3), or is very weakly correlated (r^2=0.075; Figure G1).

St. Clair sites fall into the following bands of similarity to reference conditions:

Band 1 (non-toxic):	22 sites
Band 2 (potentially toxic):	3 sites (6664, 6666, and 66M144)
Band 3 (toxic):	0 sites
Band 4 (severely toxic):	0 sites

Most sites are non-toxic. One site in Zone A (6664) and two sites in Zone B (6666 and 66M144) are potentially toxic.

4.4 Biomagnification Potential

4.4.1 Invertebrate mercury levels

Total mercury

On a whole-body, dw, uncleared-gut basis, chironomids and oligochaetes show a similar range of [THg] across sites: chironomid [THg] ranges from 58 to 1710 ng/g (median 277 ng/g); oligochaete [THg] ranges from 42 to 1626 ng/g (median 251 ng/g) (Table 11). Overall lower THg in biota are found at the upstream sites for both taxa (range of 58 to 198 ng/g; mean of 94 ng/g) compared to sites in Zone A (range of 49 to 1710 ng/g; median of 712 ng/g), Zone B (range of 155 to 1190 ng/g; median of 319 ng/g) and downstream (range of 42 to 279 ng/g; median of 189 ng/g). Logged concentrations of THg in chironomids and oligochaetes are significantly correlated (r^2=0.42, $P<0.001$).

Methyl mercury

Chironomids show a greater range of [MeHg] than oligochaetes across all sites. Chironomid [MeHg] ranges from 8.1 to 148 ng/g (median of 51 ng/g) and oligochaete [MeHg] ranges from 0.3 to 49 ng/g (median of 13 ng/g) (Table 11). Chironomids accumulate more MeHg than oligochaetes at all sites. Overall, biota from upstream sites have lower [MeHg]s (range of 0.3 to 23.8 ng/g; mean of 10.2 ng/g) than Zone A (range of 4.4 to 148 ng/g; median of 36.8 ng/g), Zone B (range of 7.9 to 104.5 ng/g; median of 37.0 ng/g) and downstream sites (range of 1.6 to 72.5 ng/g; median of 14.2 ng/g). The correlation between chironomids and oligochaetes for $\log[MeHg]_{inv}$ is significant (r^2=0.66, P<0.0001).

Comparison of mercury in biota at upstream sites to downstream sites

Total and methyl mercury in chironomids and oligochaetes at the upstream reference sites compared to downstream sites are shown in Figures 5 and 6, respectively.

Chironomids – Total Hg All sites except 4 (6662, 66M253, 6654 and 6651) have [THg] greater than the maximum (99th percentile) of the reference site concentrations (Figure 5). The highest accumulation occurs at sites 66M76 and 6665 (Zone A). (Note: Biota were not collected from the sites that have the highest THg (6663 and 6664) – see Section 3.1 for further explanation.) Overall, there is a decrease in THg levels with distance downstream of Zone A.

Oligochaetes – Total Hg All sites except two (6662 and 6651) exceed the maximum reference site concentration (Figure 5). The highest accumulation occurs at 6665 (Zone A) and the lowest accumulation at the site farthest downstream in the delta (6651).

Chironomids – Methyl Hg All test sites, except three (6662, 6654 and 6651) exceed the maximum reference site concentration (Figure 6), similar to that seen with total Hg. The highest accumulation is at 6665 (Zone A).

Oligochaetes – Methyl Hg All test sites except the one farthest downstream (6651) exceed the maximum reference concentration (Figure 6). The greatest accumulation in oligochaetes occurs

at site 6665 (Zone A), similar to what is seen for THg, as well as that seen for MeHg in chironomids.

4.4.2 Biota-sediment accumulation factors

The biota-sediment accumulation factors (BSAFs) for total and methyl mercury are shown for upstream and downstream sites for each taxon in Figure 7. For THg, BSAFs are similar for both taxa and are greater for the upstream reference sites (range: ~3 to 25), than the downstream sites (range:~ 0.1 to 2). In general, sites that show a BSAF >1 are those with the lowest sediment total mercury concentrations. The BSAFs for MeHg are greater than those for THg for the downstream sites. Chironomids accumulated more MeHg than oligochaetes at both upstream and downstream sites overall. For upstream sites, the range in BSAFs for chironomids and oligochaetes is ~9 to 48 and ~0.3 to 5, respectively, and for downstream sites is ~2 to 21 and ~0.7 to 9, respectively.

4.4.3 Relationships between mercury in biota and sediment

Total mercury

Concentrations of total Hg in each invertebrate taxon vs. total Hg in sediment are plotted in Figure 8, with fitted regression lines using sediment [THg] alone as the predictor. For both taxa, the slopes are significant ($P \leq 0.001$) with R^2 values of 0.55 (chironomids) and 0.48 (oligochaetes). Prediction of $[THg]_{inv}$ is improved with the following additional predictors: dissolved oxygen, total Kjeldahl N (overlying water), %sand, manganese and site depth for the chironomid model, and; %silt, %sand and NO_3/NO_2 for the oligochaete model (Table 12). These brought the R^2 values to 0.91 and 0.71 for chironomids and oligochaetes, respectively. For both taxa, $[THg]_{sed}$ is the strongest or an equally strong predictor ($P \leq 0.001$). Coefficients for all predictors are negative except for dissolved oxygen, %sand and manganese for the chironomid model.

Methyl mercury

The relationships between MeHg in invertebrates and MeHg in sediment (Figure 8, Table 12) are similar to those for total Hg. With $[MeHg]_{sed}$ alone as the predictor, regressions are significant for both taxa ($P \leq 0.001$), with R^2 values of 0.51 (chironomids) and 0.53 (oligochaetes). For chironomids, the regression accounts for more variability in $[MeHg]_{inv}$ with the addition of iron

(negative coefficient), and the R^2 value is increased to 0.66. As with $[THg]_{sed}$, $[MeHg]_{sed}$ is the most important predictor of $[MeHg]_{inv}$ in the multiple linear regressions for chironomids ($P \leq 0.001$). For oligochaetes, the regression accounts for more variability in $[MeHg]_{inv}$ with the addition of manganese (negative coefficient), with an increase in the R^2 value to 0.75. Both predictors are equally strong ($P \leq 0.001$). The fact that (a) the models that best predict $[MeHg]_{inv}$ include $[MeHg]_{sed}$ as the most significant term or equally significant and that (b) the magnitudes and directions of the regression coefficients are more or less stable across various models, suggest real relationships between $[MeHg]_{inv}$ and $[MeHg]_{sed}$.

4.5 Predictions of Methyl Mercury Concentrations in Receptors

4.5.1 Presentation of model outcomes

Predicted concentrations of MeHg in each receptor species for each sampling site, calculated by multiplying observed mercury concentrations in invertebrates (wet weight values from Appendix B, Table B2) by the appropriate FCMs (from Table 3), are shown in Table 13 and Figure 9. Receptor MeHg concentrations are presented separately for "minimum", "intermediate" and "maximum" levels of mercury exposure and uptake scenarios. In each subfigure, predicted $[MeHg]_{rec}$ for one of the receptors is presented in bar charts comparing upstream (reference) and downstream sites. In the bar charts, which have the same logarithmic scales in all subfigures, two criteria concentrations are marked: (1) the maximum (= 99th percentile) of the predicted $[MeHg]_{rec}$ for the reference sites, and (2) tissue residue guidelines (TRGs) for the fishes. The tissue residue guidelines (TRGs) apply only to the fish receptors. They refer to the concentrations of MeHg in the diets of wildlife that consume aquatic biota. The TRG used for MeHg is the lowest of the reference concentrations derived by Environment Canada (2002) for the protection of wildlife receptors in the AOC that consume aquatic biota: 92 ng/g ww. This pertains to the American mink (Table 12 of Environment Canada 2002). The recommended TRG for the protection of *all* wildlife species – 33 ng/g ww – was not considered appropriate because it is based on the reference concentration for Wilson's Storm Petrel, which is not native to the St. Clair River area (EC 2002).

4.5.2 Exceedences of criteria

Exceedences of both criteria are summarized in Table 14, and do not include results for sites 6663 and 6664 (Zone A), where biota could not be collected.

Methyl Hg – minimum The low predictions of $[MeHg]_{rec}$ result in 18 of 19 test sites exceeding those for the upstream sites (Figure 9). Of these 18 sites, the number of sites at which the predicted $[Hg]_{rec}$ exceeds the TRG is 0 for the sucker, 3 for the perch, and 0 for the walleye. No exceedences of the TRG are predicted for the receptors at the reference sites.

Methyl Hg – intermediate The intermediate predictions of $[MeHg]_{rec}$ result in 15 test sites exceeding those for the upstream reference sites (Figure 9). Of these 15 sites, the number of sites at which the predicted $[Hg]_{rec}$ exceeds the TRG is 0 for the sucker, 7 for the perch, and 14 for the walleye. No exceedences of the TRG are predicted for the receptors at reference sites.

Methyl Hg – maximum The maximum predictions of $[MeHg]_{rec}$ result in 15 sites exceeding those for the upstream reference sites (Figure 9). Of these 15 sites, the number of sites at which the predicted $[Hg]_{rec}$ exceeds the TRG is 1 for the sucker, 14 for the perch and 15 for the walleye. In comparison, reference site exceedences of the TRG are predicted at 0 sites for the sucker and perch, and at all sites for the walleye.

4.5.3 Overall patterns

Beyond the comparisons of predicted $[MeHg]_{rec}$ for St. Clair River sites to the upstream reference sites and to the TRG, patterns are evident in the differences in predicted $[MeHg]_{rec}$ among the five receptors, and among the three exposure and uptake scenarios.

<u>Among receptors</u>

Predicted $[MeHg]_{rec}$ generally increases with the trophic level of the receptor, with the mean mink predictions being ~2× to 50× those of the sucker. Consequently, the number of sites at which $[MeHg]_{rec}$ exceeds the TRG, and the amount by which the TRG is exceeded, increases with the trophic level of the receptor. However, the number of sites at which predicted $[MeHg]_{rec}$ exceeds the maximum of the upstream reference site concentrations is the same

among receptors. This is because within a series (i.e., any of the minimum/ intermediate/ maximum groups), $[MeHg]_{rec}$ all derive from the same $[MeHg]_{inv}$ values. Differences among predicted $[MeHg]_{rec}$ values reflect differences among uptake pathways in the FCMs from Table 3. The pattern of variability among sites is the same for all receptors within a scenario (i.e., the $[MeHg]_{rec}$ values are fully correlated among receptors).

Among exposure and uptake scenarios

Looking at the differences in results from the exposure and effect scenarios involving the same receptor, mean predicted $[MeHg]_{rec}$ ranges ~6× (sucker) to ~170× (mink). The mean $[MeHg]_{rec}$ differences between exposure and effect scenarios are very similar for the sucker and the perch and for the walleye and the mink. Differences among scenarios increase overall with trophic level of the receptor due to the increase in variability in the FCMs as the trophic pathway lengthens.

4.6 Quality Assurance/Quality Control

Field replication

Variability among site replicates in a measured analyte has three sources: natural within-site heterogeneity in the distribution of the analyte in sediment or water, differences in handling among samples, and laboratory measurement error. Among-triplicate variability indicates the overall "error" associated with quantifying conditions at a site based on a single sample.

Coefficients of variation (CV) for measured analytes in the sediment and overlying water for the field-replicated station are shown in Appendix H, Table H1. Overall, variability is low, with CVs ranging from 0 to 74.6% (median 6.0%), and differences in variability are seen among the variables. The highest variability is noted for %gravel, followed by MeHg (54.1%) and %TOC (47.4%).

Laboratory

Results for Flett Laboratory duplicates, triplicates and repeat analyses for mercury in sediment and biota are provided in Tables 10 and 11. There is good agreement between sample replicates and repeats. Mean CVs for duplicate/triplicate/repeat analyses are 16.1, 9.9, 14.0 and 9.6% for $[THg]_{sed}$, $[MeHg]_{sed}$, $[THg]_{inv}$ and $[MeHg]_{inv}$, respectively. These are lower than those reported

for other studies using gas chromatography and cold-vapour atomic fluorescence spectroscopy (Paterson et. al. 1998). Matrix spike recoveries and certified reference material recoveries are provided in Appendix H, Tables H2 to H4. For total Hg (sediment and biota), spiked recoveries range from 80 to 110% (overall mean of 99%) and reference material recoveries range from 91 to 110% (overall mean of 100%). For methyl Hg (sediment and biota), mean spiked recoveries range from 80 to 108% (overall mean of 95%) and reference material recoveries range from 77 to 99% (overall mean of 87%). The overall range of spike recoveries (80 to 110%) is comparable to that obtained by Lawrence and Mason (2001), who used similar analytical methods.

Results of Caduceon Laboratory duplicate measurements of sediment metals, major oxides and nutrients, expressed as the relative percent difference, and corresponding analyses of lab blanks and reference materials are provided in Appendix H, Tables H5 and H6. The relative percent difference ranges from 0 to 55% (mean of 8%) (Table H5). Laboratory blanks (water) range from <0.00006 to < 0.2, and percent recoveries for sample measurements range from 65 to 120% (mean of 96%). Recoveries for reference materials range from 75 to 129%, but are mostly between 90 and 100% (Table H6).

The inter-laboratory comparison for analyses of total mercury in sediment is described in Appendix H. Results show a fair agreement between measurements: the slope of Flett $[Hg]_{sed}$ vs. Caduceon $[Hg]_{sed}$ is 0.76 and the percent explained variability (r^2) is 78%. The greatest difference between the two labs is for site 6648 (THg: Caduceon 1.04µg/g; Flett 0.012µg/g). Removing 6648 from the regression results in a slope of 0.83 and an r^2 value of 0.95. It is unclear why there is a large disagreement between the two laboratories for site 6648. However, Pope (1993) reports a sediment total Hg concentration of 0.01 µg/g for site 6A (=6648) in a 1990 survey of the river, which is the same concentration that Flett Laboratory provided for site 6648 in the current study.

Benthic Invertebrate Community Sorting

The mean percent community sorting efficiency for St. Clair River samples is 3.3%, or ≥96.7% recovery. This indicates that a good representation of the benthic community present at test sites

was likely achieved. This sorting efficiency represents the average for 2 sorters over a 5 month period.

5 DISCUSSION

5.1 Mercury Levels

5.1.1 Sediment

Concentrations of THg in the upper 10 cm layer of sediment from all sites except the site farthest downstream in the delta are elevated above upstream reference site [THg] (Figure 2, Table 6). Mercury contamination is greatest in Zone A; ~60% of sites in Zones A (and Zone B) are ≥ 2 μg/g (=SEL). The CCME (1999) freshwater sediment quality guideline (Probable Effect Level (PEL) for THg (0.486 μg/g) is exceeded at all sites in Zones A and B except the 1 site just upstream of the Dow property (6662), and the 2 sites farthest downstream. Upstream reference site $[THg]_{sed}$ are in the range of 0.008 to 0.07 μg/g, which is similar to background concentrations of 0.003 to 0.16 μg/g for Lake Huron/Georgian Bay reference sites (n=76) (Unpublished data, Environment Canada 2004). The maximum [THg] in the St. Clair River (49.3 μg/g) is greater than the maximum concentrations of 5.6 μg/g and 32.2 μg/g, observed for contaminated sites in the St. Lawrence River (at Cornwall) and Peninsula Harbour, respectively (Grapentine et al. 2003a,b). For MeHg, a similar pattern is observed with the highest (estimated) concentrations in Zone A (Figure 3, Table 6). Sediment [MeHg] is strongly related to sediment $[THg]_{sed}$ (Figure 4), with MeHg making up an overall average of 2.5% of the THg (10.0% for upstream reference sites; 0.6% for sites in Zones A and B; 2.3% for sites downstream of Zone B). The percentage of MeHg to THg for the St. Clair River test sites is similar to that observed for St. Lawrence River and Peninsula Harbour test sites (0.4% and 0.2%, respectively) (Grapentine et al 2003a,b). The spatial pattern of these results is strong evidence for a local (as opposed to regional) source of Hg to Zone A. In 2001, the MOE sampled the top 5 cm of sediment at 25 transects in Zones A and B, with each transect consisting of 3 stations at increasing distances from shore. Four transects were sampled in Zone A, and 18 in Zone B (Thorburn et al. 2003). Zone A had the highest sediment [THg], ranging from 0.71 to 14 μg/g (median 2.2 μg/g), while total [Hg] in Zone B ranged from 0.01 to 9.3 μg/g (median 1.2 μg/g). The highest concentrations of other priority contaminants (HCBD, HCB, OCS and PCBs) were

also found in Zone A, similar to that found in the current study (the highest PAHs, HCBD and OCs are in Zone A and the highest HCB and PCBs in Zone B).

5.1.2 Benthic invertebrates

Both THg and MeHg are taken up by the two invertebrate taxa assessed. For THg, BSAFs (based on whole-body, uncleared-gut concentrations) are >1 for the upstream reference sites and < 1 for all sites downstream except 6651 (both taxa) and 66M76 (chironomids). For MeHg, BSAFs are >1 for all sites analyzed except 6651, 66M253, and 2 of the 4 upstream reference sites (oligochaetes). For THg, BSAFs range up to ~ 25 and ~ 2 for upstream and downstream sites, respectively; for MeHg, the corresponding maximums (including outliers) are ~ 50 (upstream) and ~ 21 (downstream sites) (Figure 7). Chironomids have higher BSAFs than oligochaetes. Tremblay et al. (1996a,b), in a study of two reservoirs and a natural lake in Quebec, reported BSAFs for detritivorous insects to be 1.9 to 2.8 for THg and 5.2 to 22.6 for MeHg, similar to the BSAFs for sites in Zones A and B in the current study. Gut contents were included in the mercury analyses of the biota in the current study, which could obscure true BSAFs. As the amount of sediment in the gut increases, the measured BSAF will converge to 1. A true BSAF < 1 will be overestimated because the concentration in the sediment is greater than the tissue concentration, whereas a true BSAF >1 will be underestimated because sediment concentrations are lower than that found in the tissue (Bechtel Jacobs 1998).

Generally, $[Hg]_{inv}$ at sites in Zones A and B are several fold higher than the $[Hg]_{inv}$ for the upstream reference sites, and total and methyl Hg invertebrate concentrations are elevated above the maximum of the reference sites at the majority of sites (79 to 95%). Site 6665 (Zone A) is highest in $[THg]_{inv}$ and $[MeHg]_{inv}$ for both taxa (except for 66M76, also in Zone A, which is highest in [THg] for chironomids.) It might be expected that the greatest Hg accumulation would have occurred at sites 6663 and 6664 where the highest sediment total Hg is observed, and where biota could not be collected for Hg tissue analysis.

5.2 Sediment Toxicity

The use of multivariate assessment for toxicity test endpoints is advantageous as it reduces the redundancy between endpoints, and also down weights the *Tubifex* endpoints (i.e., the *Tubifex*

test has four measurable endpoints while the other tests have two each) (Reynoldson 1998). There is no strong evidence of toxicity in the St. Clair River (because no sites scored beyond the 99% probability ellipse for the reference sites in Figures G1 and G2). The mayfly, *Hexagenia* spp. is most sensitive of the four laboratory organisms, showing decreased survival at 2 sites, 1 located adjacent to Dow (6664), and 1 just upstream of the Talfourd Creek outlet (6666). Also affected is the worm *Tubifex* at the site just downstream of the Talfourd Creek outlet (66M144) with a low number of cocoons produced per adult, as well as a low number of young produced. The low number of cocoons suggests that the stressor(s) effect is primarily on gametogenesis (cocoon production). The majority of sites (65%), however, show enrichment, with mayfly (or amphipod) growth exceeding two standard deviations of the Great Lakes reference mean. Total Hg is either very weakly correlated (r^2= 0.075) or not significantly correlated to toxicological response. It should be noted, however, that toxicity tests were not performed at site 6663 where the greatest sediment Hg contamination occurs (see section 3.1 for further explanation), thus it is not known whether this sediment would be toxic.

5.3 Benthic Invertebrate Community

Some of the St. Clair River test sites were not well matched to a distinct group of Great Lakes reference sites; therefore, comparison of these test site communities to the reference group communities is suboptimal. Although the BEAST model was revised to include connecting channel sites, the majority of sites in reference groups 1 and 3 consist mainly of lake sites. Group 1 (n = 35 sites) has 1 site located on the St. Clair River and Group 3 (n = 51 sites) has 9. The scoring of test sites in Band 3 or Band 4 outside of the reference area is primarily due to the high abundances of Tubificidae and Chironomidae compared to the Great Lakes reference sites. Multidimensional scaling, which uses raw counts, is more sensitive to changes in abundance as opposed to richness. On average, Group 3 reference sites are comprised of ~38% chironomids, ~19% tubificids and 12.5% sphaeriids (Table E2), whereas most of the test and upstream St. Clair River sites have ≥40% tubificids, and ≥20% chironomids and sphaeriids are absent or comprise very little of the total abundance. Other taxa present in the Group 3 reference sites, such as Sabellidae (polychaete worms) and Asellidae (isopods), are absent at all St. Clair River sites with the exception of upstream site 6698 (low abundance of asellids present) and Ephemeridae, a minor taxon in reference Group 3, is present at 4 of the 5 upstream sites but only

1 test site (6664, Zone A) (Tables 9a-c). The majority of St. Clair sites (12 of the 16) have taxon diversity that is the same or greater than the Great Lakes reference mean. Differences in biological structure between the upstream sites (local reference) and downstream sites, determined by ANOVAs with adjustments for covariates, were not significant ($p \leq 0.05$).

In a benthic community assessment of the Upper St. Clair River in 1994, most communities were found to be dominated by pollution-tolerant tubificid worms and chironomids (Farara and Burt 1997). The study consisted of 13 transects with 3 stations per transect extending from the shoreline at various distances. Stations were located in an upper, middle and lower area of Study Zone 1 (from downstream of the Sarnia STP to downstream of the Dow chemical 2nd street outfall), which would fall in Zone A in the current study. Tubificid densities in the Farara and Burt (1997) study were lower overall than that found in the current study, ranging from 82 to 33,116 per m^2 (median of $4506/m^2$, mean of $8568/m^2$), and were represented by 14 species as well as unidentifiable worms (with and without chaetal hairs). The most common tubificids were *Limnodrilus hoffmeisteri*, *L. udekemianus* and the immature tubificids without chaetal hair. In the current study, there are 16 species identified as well as the smaller unidentifiable worms. The most common tubificids included immatures (greater amount with chaetal hairs in downstream sites and greater amount without chaetal hairs at upstream reference sites), *Aulodrilus pigueti* (absent in 1994 study), *L. hoffmeisteri*, *L. udekemianus* and *Quistradrilus multisetosus* (Table E3). Differences in species composition and abundance between studies could be due to the time of sampling (June 1994 vs. September in the current study), as well as mesh size used in sieving process (600-µm in the 1994 study vs. 250-µm in the current study). A larger mesh size used in the 1994 study likely would have resulted in the loss of the smaller mature worms as well as immature worms. Therefore, reported densities could be underestimated in the Farara and Burt study. Discrepancies could also be due difference in actual sampling location. Chironomid densities in the Farara and Burt (1997) study are also lower than that found in the current study, ranging from 18 to 8898 per m^2 (median of $1601/m^2$, mean of $2273/m^2$), and were represented by 33 genera. The most common chironomids found were *Polypedilum* and *Phaenopsectra*, generally considered pollution tolerant taxa. In the current study, 38 genera were identified, with the most common being *Polypedilum* and *Tribelos* (present at all sites), followed by *Procladius* and *Chironomus*, present at 15 of the 16 sites. *Chironomus*, which are generally moderately

tolerant, were present only occasionally in the 1994 study and there were no *Phaenospectra* found in current study. Again, differences could be attributable to time of sampling, and different methodologies in sample processing (see above). In the 1994 study, chironomid pupae were found at 92% of the stations (6 to 179/m^2) indicating that they were emerging at the time of sampling in June (Farara and Burt 1997). In the current study, no pupae were found at any site.

5.4 Effects of Mercury in Sediment on Mercury in Invertebrates

Mercury concentrations in chironomids and oligochaetes from the St. Clair River are significantly influenced by sediment mercury (Table 12, Figure 8). The log-log relationship for $[Hg]_{sed}$ and $[Hg]_{inv}$ across sites is similar for both taxa when Hg alone is used as a predictor. With the addition of multiple predictors, the amount of variance explained increases, and in all cases $[Hg]_{sed}$ is the most significant or is an equally significant predictor of $[Hg]_{inv}$. In the multiple regression models for predicting $[MeHg]_{inv}$, sediment iron and manganese are significant ($P \leq 0.009$) predictors in the models and increase the amount of variability explained by ~13 – 22%. Both iron and manganese predictors are negatively correlated with $[MeHg]_{inv}$. Concentrations of Hg in the benthic invertebrates were measured without clearing their guts. Thus, a fraction of the observed $[Hg]_{inv}$ could include sediment-bound Hg in the gut. This is relevant for assessing uptake of Hg by predators of invertebrates, which consume whole organisms, and can also factor in the strength of the $[THg]_{sed}$ - $[THg]_{inv}$ relationship. Concentrations of THg in sediment are generally between 1 – 3 orders of magnitude greater than those for MeHg, and [THg] varies more among sites. The chironomids accumulated more MeHg than the oligochaetes at all sites, however the $[MeHg]_{sed}$ - $[MeHg]_{inv}$ relationship is slightly stronger for the oligochaetes.

Several other studies report similarly significant relationships between [Hg] in sediment and [Hg] in benthic invertebrates. Bechtel Jacobs (1998) reviewed data from 15 studies of [Hg] in freshwater benthic invertebrates and sediment. In 13 of these, invertebrate guts were not cleared. Slopes of $\log[THg]_{inv}$ vs. $\log[THg]_{sed}$ regressions were 0.327 ± 0.246 (mean ± S.E), and the mean r^2 was 0.12. The slope is similar to the slopes observed for the current study; 0.337 and 0.329 for chironomids and oligochaetes, respectively. Tremblay et al. (1996a,b) found a correlation between [MeHg] in chironomids and $[MeHg]_{sed}$ of $r=0.78$ ($P<0.005$, $n=18$) for a

series of Quebec lakes, very similar to the present study where there is a correlation of $r=0.74$ ($P<0.001$, $n=23$) for chironomids. In assessments of bioaccumulation by chironomids from Hg-contaminated and reference sediments in the St. Lawrence River (at Cornwall) and Peninsula Harbour using the same methods as the current study (Grapentine et al. 2003a,b), agreement between studies for $\log[Hg]_{inv}$ vs. $\log[Hg]_{sed}$ regressions is better for total Hg than for methyl Hg. The corresponding slope coefficients (Cornwall/Peninsula Harbour/St. Clair River) are:

- THg in chironomids = 0.570 / 0.431 / 0.337
- MeHg in chironomids = 0.160 / 0.163 / 0.579

Results from this assessment indicate that $[MeHg]_{inv}$ is largely determined by $[MeHg]_{sed}$. Observing positive relationships between sediment and invertebrate mercury concentrations is evidence that mercury transfers from sediment into the food web, and the relationship observed for $[MeHg]_{inv}$ (chironomids) in the current study is stronger than that observed for the Cornwall and Peninsula Harbour studies.

5.5 Predicted Methyl Mercury Concentrations in Receptor Species

5.5.1 Integration of prediction outcomes

Models involving a range of biomagnification conditions were used to predict potential [Hg] in receptors. Five receptor species were considered to encompass the trophic levels linking sediments to the top predators, where biomagnification is expected to be greatest. Three levels of dietary exposure and trophic transfer of Hg were assumed: minimum and maximum scenarios to bracket the range of potential outcomes and an intermediate scenario to characterize "average" conditions. Conclusions determined from overall evaluations of the model outcomes should consider:

- $[MeHg]_{rec}$ for exposed sites compared to $[MeHg]_{rec}$ for upstream (references) sites;
- $[MeHg]_{rec}$ relative to the TRG;
- How many receptors are predicted to exceed the criteria at each site;
- How many of the exposure and uptake scenarios result in exceedences; and
- How many sites exceed the criteria.

The majority of sites are predicted to have $[MeHg]_{rec}$ higher than the maximum $[MeHg]_{rec}$ in upstream reference sites: 18 sites for the minimum scenario, and 15 sites for the intermediate and

maximum scenarios. The critical outcome of the evaluation is whether or not the predicted $[MeHg]_{rec}$ values for exposed sites exceed the appropriate TRG as well as the reference site maximum $[MeHg]_{rec}$. A summary of the sites meeting this condition for all exposure and uptake scenarios for the fish receptors, and a summary is provided in Table 14. For the sucker, 1 site is predicted to result in such exceedences for the maximum scenario (site 6665 in Zone A). Perch $[MeHg]_{rec}$ predictions result in 3 sites for the minimum scenario, 7 exceedences for the intermediate scenario, and 14 exceedences for the maximum scenario. For the walleye, minimum scenario predictions result in 0 exceedences; the intermediate scenario predictions result in 14 exceedences, and maximum scenario predictions result in 15 exceedences. For the intermediate scenario, predicted $[MeHg]_{rec}$ for the walleye are just slightly above the TRG for several sites: 6667 (98 ng/g), 66M272 (100 ng/g), 66M80 (101 ng/g), 66M271 (105 ng/g) and 6666 (109 ng/g). The greatest exceedences are for sites 6665 and 66M76 (Zone A – 526 ng/g and 199 ng/g, respectively) and 6699 (Zone B – 269 ng/g). There are no benthic invertebrate MeHg data available for 2 sites in Zone A that show the greatest sediment Hg contamination (sites 6663 and 6664). However, considering the high [Hg] in sediment and the strong relationship between sediment [Hg] and benthic invertebrate [Hg], it is likely that [MeHg] in benthic invertebrates from these locations would be high enough to cause exceedences of the TRG for fish. The TRG applies to concentrations of MeHg in fishes, and are for the protection of wildlife consumers of fishes. Some data are available for direct evaluation of the predicted tissue mercury levels for heron and mink. Wolfe et al. (1998) reviewed THg and MeHg toxicity and tissue residue data associated with adverse effects for birds and mammals. (As noted above, nearly all mercury in fishes and higher trophic level animals should be in the methyl form.) For the Great Blue heron, liver concentrations > ~6000 ng THg/g ww correlated with chronic adverse effects. A conservative residue threshold for major toxic effects in water birds was concluded to be 5000 ng THg/g ww in liver. For mink, a similar criterion of 5000 ng MeHg/g ww in muscle or brain was suggested. This value of 5000 ng/g corresponds to 3.7 on the log-scales in Figure 9. For the great blue heron receptor, the highest predicted $[MeHg]_{rec}$ in any of the scenarios is 3906 ng/g ww (site 6665), and for the mink, the highest $[MeHg]_{rec}$ prediction is 5745 ng/g ww for site 6665 (Table 13). Thus, $[MeHg]_{rec}$ is not predicted to exceed the tissue residue benchmarks suggested by Wolfe et al. (1998) for heron, whereas it is predicted to exceed at one site for mink under the maximum exposure and uptake scenario.

5.5.2 Uncertainty in the prediction of mercury concentrations in receptors

The prediction of the potential transfer of MeHg from benthic invertebrates to the trophically linked receptor species involves several simplifying assumptions, each of which is associated with some degree of uncertainty in its relevance to conditions in St. Clair River. While it is beyond the scope of this study to quantify these uncertainties, those considered most important are identified here.

Assumptions regarding the modelling of Hg biomagnification include those dealing with the exposure of the receptors to Hg, and those dealing with the effects of Hg on the receptors. Regarding the latter category, some of the sources of uncertainty discussed by USEPA (1997c) could apply to the present study:

- validity of the biomagnification model,
- variability of the calculated BMFs and FCMs,
- selection of the receptors of concern,
- trophic levels at which receptors feed,
- limitations of the toxicity database (with respect to the determination of TRGs), and
- effects of environmental cofactors and multiple stressors.

Among these sources, the greatest contributor to uncertainty in predicting the trophic transfer of mercury could be the large ranges in the selected BMF and FCM values. These range over 1-1.5 orders of magnitude between lowest and highest, and include all BMFs judged to be potentially applicable to the St. Clair River. Further validation of their relevance would require field studies beyond the scope of this assessment. Owing to limitations of the available data and the desire to minimize assumptions about the distributions of the data, a probabilistic approach was not applied to predict receptor mercury concentrations. Rather, low, medium and high FCMs were used to define the range of possible outcomes and intermediate values that "balance" the minimum and maximum rates of biomagnification. Another problem inherent in the literature-derived BMF data is the difficulty in assigning prey and predator species to discrete trophic levels due to omnivory. When omnivory is integrated with a continuous measurement of trophic position (e.g., using stable isotope methods), estimates of BMFs will generally be higher for each discrete trophic level (Vander Zanden and Rasmussen 1996). Correct determination of trophic

levels is also limited by how well the composition of a predator's diet is quantified. Often the information necessary to clearly establish this is not available in the published studies.

Another potentially large source of uncertainty in predictions of $[MeHg]_{rec}$ relates to the exposure of receptors to Hg. These assumptions (listed in Section 2.2) are recognized as being conservative and limited in their representation of natural conditions. Spatial (and perhaps temporal) heterogeneity in the distribution of THg and MeHg throughout the study area, and aspects of receptor ecology challenge the maximum exposure scenario. A particularly important source of uncertainty could be the assumption of 100% residency of all consumers in the food chain on each site. The degree to which this assumption is unrealistic is proportional to the size of the foraging areas of the receptor species relative to the area of contaminated sediment. Given that the sampling sites could be on the order of 10 × 10 m to 100 × 100 m (= 0.01 to 1.0 ha), the 100% residency assumption is likely unrealistic. According to data compiled in the Wildlife Exposure Factors Handbook (USEPA 1993), feeding territory sizes for great blue heron range from 0.6 ha to 0.98 km^2, and distances they travel from heronry to foraging grounds range from 1.8 to 8 km. Home range sizes of mink are reported as 7.8 to 1626 ha, and 1.85 to 5.9 km of stream/river. These foraging/home range areas substantially exceed the site boundaries. If areas outside of the Hg-contaminated zones of the St. Clair River are not equally Hg-contaminated, the actual $[MeHg]_{rec}$ would be lower than those predicted by the models.

5.5.3 Observed mercury levels in receptors from the St. Clair River

Comparing the predicted $[MeHg]_{rec}$ values to actual [Hg] in fishes, heron and mink sampled from the St. Clair River AOC is a potential means of validating the model. Although fish and wildlife receptors may not feed as assumed by the prediction model (i.e., focus on single sites), and exposure histories can be difficult to determine, sources of mercury from beyond the St. Clair River should be low and contribute little to receptor mercury burdens, because expected foraging areas (at least for the fishes) are likely smaller than the St. Clair River area for most fish. (This may not be the case for some fish such as Walleye) (Grapentine et al. 2003a estimated the maximum individual foraging areas of the Longnose Sucker and Lake Trout to be 428 m^2 and 3459 m^2, respectively, based on models of Minns et al. (1996).) Measured [Hg] in recently sampled receptors indicate actual, as opposed to potential, biomagnification.

A 1999 survey of sport fish contaminant levels included collections of white sucker, yellow perch and walleye, from the upper, middle and lower St. Clair River (MOE 2003b). Throughout the river, [Hg] in boneless, skinless fillets are similar for each species. For white sucker (n= 1 or 2; 39 – 47 cm length), [THg] reportedly range from 80 to 430 ng/g ww (mean of 240 ng/g), higher than predicted under the worst case (maximum) exposure and uptake scenario, with the exception of one site (6665) (Table 13). Therefore the prediction model underestimates [Hg] in sucker; however, actual [Hg] are based on a very small sample size (only 1 or 2 fish per area of river). For yellow perch (n = 4 to 16, 15 – 32 cm length), [THg] reportedly range from 90 to 570 ng/g ww (mean of 250 ng/g), which generally falls within both the intermediate and maximum exposure and uptake scenarios (Table 13). For walleye (n = 8 to 15; 29 – 62 cm length), [THg] range from 100 to 970 ng/g ww, which also falls within both the intermediate and maximum uptake scenarios (Table 13). Mean [Hg] are higher in walleye collected from the lower portion of the river (mean of 360 ng/g Hg) compared to middle (mean of 270 ng/g Hg) and upper (mean of 140 ng/g Hg) portions of the river (MOE 2003b). Thus, the observed values for the sucker are high relative to the predicted [Hg], whereas the observed values for the perch and walleye are within predicted values for the intermediate-maximum scenarios.

Observations of [Hg] in receptor species residing in the St. Clair AOC demonstrate that mercury accumulates in tissues of higher trophic level members of the aquatic food web, and above the CCME TRG. It is also evident that the receptor methyl Hg concentrations predicted from the screening level approach of this assessment are not overestimating actual tissue levels for the intermediate and the highest level fish predator (perch and walleye) when using the intermediate (average) scenario. The methyl Hg predictions are, however, underestimating actual tissue levels for the adult benthivorous fish (sucker).

5.6 Potential Risk of Adverse Effects of Mercury due to Biomagnification

Concluding that mercury originating from contaminated sediment could concentrate in the food web at levels that can cause adverse effects depends on establishing that:

(1) mercury in invertebrates from sites exposed in the past to industrial effluents is elevated relative to concentrations in invertebrates from (upstream) reference sites;

(2) mercury in invertebrates is related to mercury in sediment; and

(3) predicted levels of mercury in receptors at exposed sites that exceed levels in receptors at

reference sites also exceed the TRG.

Most sites located in Zones A and B have invertebrate [Hg] significantly higher than concentrations for the upstream reference sites (Figures 5 and 6). Measured mercury concentration in invertebrates is related to mercury concentration in sediment for both THg and, importantly, the more biologically available MeHg (Figure 8, Table 12). Regarding the trophic transfer modelling, based on outcomes for perch and walleye under the intermediate mercury exposure and uptake scenario, up to 14 sites could be considered "of concern" because of predicted $[MeHg]_{rec}$ exceeding the maximum reference site concentration and the TRG.

Regarding the overall assessment of sediment conditions based on four lines of evidence, the potential for biomagnification line of evidence can differ from the other three lines of evidence. If fish and wildlife receptors are the concern, the appropriate spatial and temporal boundaries for assessing potential biomagnification are not the same as those for assessing sediment contaminant concentrations, sediment toxicity and benthic invertebrate communities. Activities of fishes, birds and mammals are not limited to individual sites to the same degree as contaminants and invertebrates. Whereas incorporating invertebrate contaminant bioaccumulation information into the framework works well on a site-by-site basis, fish and wildlife data require some form of spatial averaging or weighting to reflect realistic contaminant exposure conditions. On a per site basis, fish and wildlife biomagnification predictions remain "theoretical" or overly conservative.

One way of addressing the problem is to assess exposure to contaminants across areas of sediment comparable to the foraging areas of the receptors, as suggested by Freshman and Menzie (1996). Their "average concentration with area curve" exposure model involves determining the average concentration of a contaminant for increasing areas of soil, starting with the most contaminated site up to and beyond the foraging area of the receptor of interest. The average contaminant concentration for a section of soil corresponding to the foraging area is then compared to appropriate benchmark adverse effect levels. Exceedence of the benchmark by the average contaminant concentration is considered a potential impact to the receptor individual.

Application of this method requires a grid-type or other statistically suitable array of sampling sites designed to representatively quantify contaminant conditions across the study area. An example where this model was employed was for a study performed in Jellicoe Cove, Peninsula Harbour in 2002 (Grapentine et al. 2003b).

The application of tissue Hg residue data that are associated with adverse effects in other studies to evaluate potential risks to the receptors in the present study carries some uncertainty. The data come from different tissues, species, environmental conditions and study types (e.g., field vs. lab). In addition, Hg detoxification and a possible ameliorative effect of dietary selenium may contribute further uncertainty in the extrapolation of results from one set of conditions to another (USEPA 1997c). The TRGs also typically include uncertainty factors. For example, the MeHg reference concentration (92 ng/g wet wt) incorporates an uncertainty factor of 5 (Environment Canada 2002). Considering these uncertainties and the generally conservative ("worst case") assumption of the trophic transfer model, quantifying the probability that mercury from sediments in the St. Clair River could cause adverse effects to receptors is difficult.

5.7 Canada-Ontario Decision-Making Framework

A risk-based, decision-making framework for the management of sediment contamination was recently developed under the Canada/Ontario Agreement respecting the Great Lakes Basin Ecosystem using four lines of evidence (sediment chemistry, sediment toxicity, benthic invertebrate community and the potential for contaminant biomagnification). This decision framework was developed from the Sediment Triad and BEAST frameworks, and is described in Grapentine et al. (2002) and Chapman and Anderson (2005). The overall assessment of a test site is achieved by integrating the information obtained both within and among the four lines of evidence and the assessment allows for three possibilities (Chapman and Anderson 2005), where contaminated sediments:

1. Pose and environmental risk
2. May pose and environmental risk – further assessment is required
3. Pose a negligible environmental risk

The decision matrix for the weight of evidence categorization of St. Clair River sites is shown in Table 15. For the sediment chemistry column, sites with exceedences of a sediment quality guideline (SQG) – high (e.g., the Severe Effect Level) are indicated by "●", and sites with exceedences of a SQG – low (e.g., the Lowest Effect Level) by "◐". For the toxicity and benthos alteration columns, sites determined from BEAST analyses as toxic/severely toxic or different/very different from reference, respectively, are indicated by "●"; and sites determined as potentially toxic or possibly different from reference by "◐". For the biomagnification potential column, a "◐"occurs when there is a risk to consumers of benthic invertebrates and their predators determined through the conservative modelling exercise. The intermediate uptake and exposure scenario is used because it represents the average condition (actual sport fish contaminant concentrations also fall within this scenario). Predicted receptor contaminant values that are > TRG and > the predicted maximum reference concentration result in a "◐" for that site. (Note: a "●" in the biomagnification potential column would occur if there was significant evidence of risk based on additional or extensive studies including fish consumption advisories; Chapman and Anderson 2005.) Sites with no SQG exceedences, no sediment toxicity, benthic communities that are equivalent to reference conditions, or no Hg biomagnification potential are indicated by "O". Interpretation of the overall assessment for management implications also considers the degree of degradation for each line of evidence. Benthic community was not assessed in 2004. The potential for mercury biomagnification was not assessed at three sites because benthic invertebrates tissues samples could not be collected. Some sites show benthos alteration or potential toxicity but are not recommended for further action; in these cases, the benthos alteration is not judged to be detrimental, or toxicity is minimal (limited to 1 of 10 endpoints measured).

Sediment mercury

The SEL for Hg is exceeded at 11 sites (●); the LEL (but not the SEL) is exceeded at 8 sites (◐). Results from Flett Laboratories were considered (e.g., Table 6) with the exception of sites 6660, 6663 and 6664 (see section 4.1 for further explanation).

Overall toxicity

Three sites fall in Band 2 (potentially toxic) and are indicated by "◘". However, since only one endpoint was affected for each of these sites (i.e., *Hexagenia* survival or *Tubifex* cocoon production), and correlation to Hg was very weak or non existent, these sites are not recommended for further action with respect to toxicity.

Benthos Alteration

Benthic invertebrate community samples were collected at 16 sites in 2001 only. Eleven of the 16 sites fall in either of Bands 3 or 4 (●) (including 4 of the 5 upstream sites); however, 6 of these 11 sites have low (<60%) probabilities of belonging to any of the Great Lakes reference groups and therefore caution was used in interpretation of these data. Most sites have high taxon diversity with enriched tubificid and chironomid abundances compared to Great Lakes reference; however, this is also indicative of the upstream conditions. Some test sites also contain species that are normally found in relatively clean environments (e.g., enchytraeid and some naidid worms, trichopterans, mayflies, amphipods). Additionally, ANOVAs revealed no significant differences between upstream and downstream sites with respect to community composition. Thus all sites are not considered to be impaired with the exception of 6662 (Zone A). Site 6662 has low taxon diversity (2 taxa) and is highly enriched in tubificids and thus is considered to be impaired. (Site 6662 also has a relatively high probability (68%) of belonging to reference Group 3.)

Biomagnification Potential

Fourteen sites have predicted [MeHg] in the top level fish receptor (walleye) that are above the CCME TRG of 92 ng/g ww and above the predicted reference maximum under average conditions (intermediate exposure and uptake scenario) (◘). Actual Hg concentrations in walleye collected in 1999 from the river fall within the intermediate scenario for the most part (4 of the 15 fish collected from the lower river fall within the maximum scenario predictions). The 14 sites include 2 of the 3 sites (where tissue was collected) in Zone A, 11 of the 13 sites in Zone B, and 1 downstream site (66101). Benthic invertebrates were not collected for tissue analysis at 6660, 6663 and 6664 (see Section 3.1); therefore, biomagnification potential could not be determined for these sites. However, for sites 6663 and 6664 (Zone A), the likelihood of

potential risk of biomagnification is high due the high [Hg] in the sediment and the strong relationship between [MeHg] in the sediment and [MeHg] in the benthic invertebrates. Thus, a total of 16 sites are predicted to show Hg biomagnification potential.

6 CONCLUSIONS

Sediment mercury

Most test sites have sediment mercury levels elevated above upstream reference sites. The highest sediment mercury concentrations are found along the industrial sector (Zone A; up to 25× the SEL), and elevated concentrations extend to the bottom of Stag Island (Zone B; up to 1.9× the SEL).

Benthic invertebrate community

Most sites where benthic communities were assessed (2001 sites) show strong evidence of different communities compared to Great Lakes reference, primarily due to enriched Tubificidae and Chironomidae and high taxon diversity. However, about half these sites have low probabilities (<60%) of belonging to a single Great Lakes reference group; therefore, results were interpreted with caution. Comparison of benthic communities in the river indicates no differences between upstream controls and test sites. Correlation between the benthic community composition and sediment [Hg] is weak except perhaps for some sites in Zone B ($r^2 = 0.44$).

Sediment toxicity

There is no evidence of severe sediment toxicity at any site; however, there is reduced *Hexagenia* survival at two sites (Zones A and B) and reduced *Tubifex* cocoon production at one site (Zone B). Elevated sediment mercury is not correlated with observed toxicological response.

Mercury biomagnification potential

The purpose of the biomagnification component of the study was to determine if deleterious amounts of Hg could potentially be transferred from sediments through benthic invertebrates to fish or wildlife in the St. Clair River AOC. This was addressed by:

A. Determining if THg and MeHg are bioaccumulated by benthic invertebrates to higher concentrations in sites that were exposed to Hg-containing industrial effluents than in

upstream reference sites;

B. Determining if concentrations of THg and MeHg in invertebrates are related to concentrations in sediment; and

C. Predicting if concentrations of MeHg in consumers of benthic invertebrates and their predators (i.e., trophically linked receptor species) reach levels associated with adverse effects.

The main findings are:

A. Total and methyl mercury concentrations in sediment and invertebrates (chironomids, oligochaetes) at the majority of sites exposed to historical industrial discharges (Zones A and B) are elevated above those at upstream reference sites. This indicates that Hg is bioaccumulated by benthic invertebrates in Zones A and B of the St. Clair River to a greater degree than in upstream reference sites.

B. Concentrations of total and methyl mercury in sediment are significantly predictive of concentrations in oligochaetes and chironomids. This suggests that sediment [Hg] affects invertebrate [Hg]. Adjusting for effects of other sediment covariables (e.g., iron and manganese) improves the sediment-invertebrate relationship for MeHg.

C. Under the intermediate (average) exposure and uptake scenario, the number of sites predicted to have receptor [MeHg] higher than the maximum reference site receptor [MeHg] ***and*** to exceed the TRG for the protection of fish-consuming wildlife are:

- White sucker - 0 sites
- Yellow perch - 7 sites
- Walleye - 14 sites

Receptor [MeHg]s for up to 14 sites are consistently indicated to exceed both reference site conditions and TRGs. However, to what degree mercury might be biomagnified is not clear, due to uncertainties associated with predicting receptor [MeHg] values and conservative assumptions of the assessment. Reducing uncertainty in the predictions of mercury biomagnification in the St. Clair River AOC would be best achieved by identifying a more narrow range of appropriate BMFs, and by quantifying the actual exposures of receptors to dietary mercury.

Decision making framework for sediment contamination

Using the rule-based, weight of evidence approach described in Grapentine et al. (2002) and Chapman and Anderson (2005), where all four information components are available, a total of 16 sites require the risk of Hg biomagnification to be fully assessed. In two cases (sites 6663 and 6664), there were missing benthic invertebrate Hg tissue data. However, due to the high [Hg] in the sediment at these sites and the strong relationship observed between sediment mercury and benthic invertebrate mercury concentrations, it was determined that these two sites would likely require the need to fully assess the risk of biomagnification. One site (6662- Zone A) requires the need to determine reasons for benthos alteration and the remaining 9 sites require no further action.

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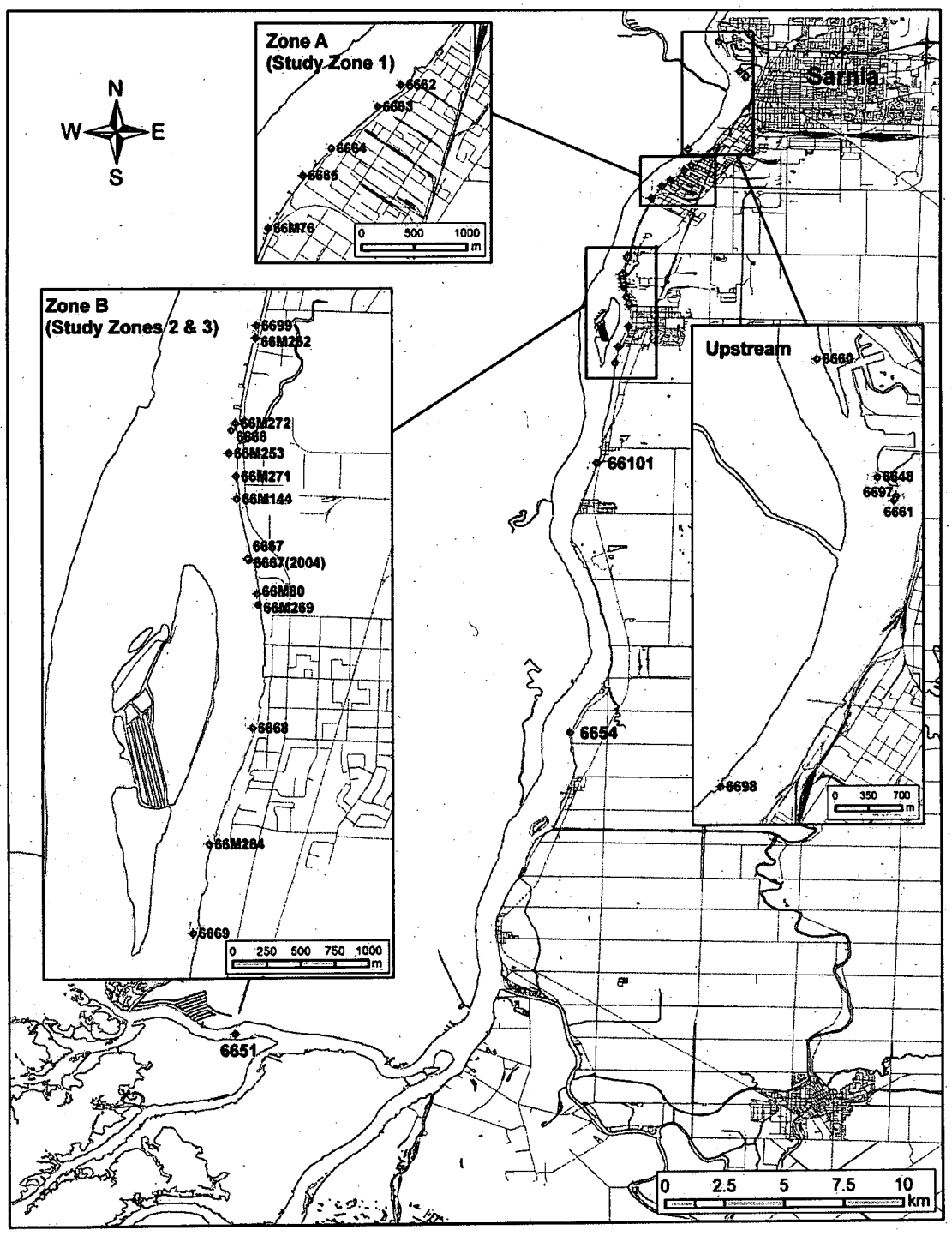


Figure 1. Location of sampling sites in the St. Clair River (2001 and 2004).

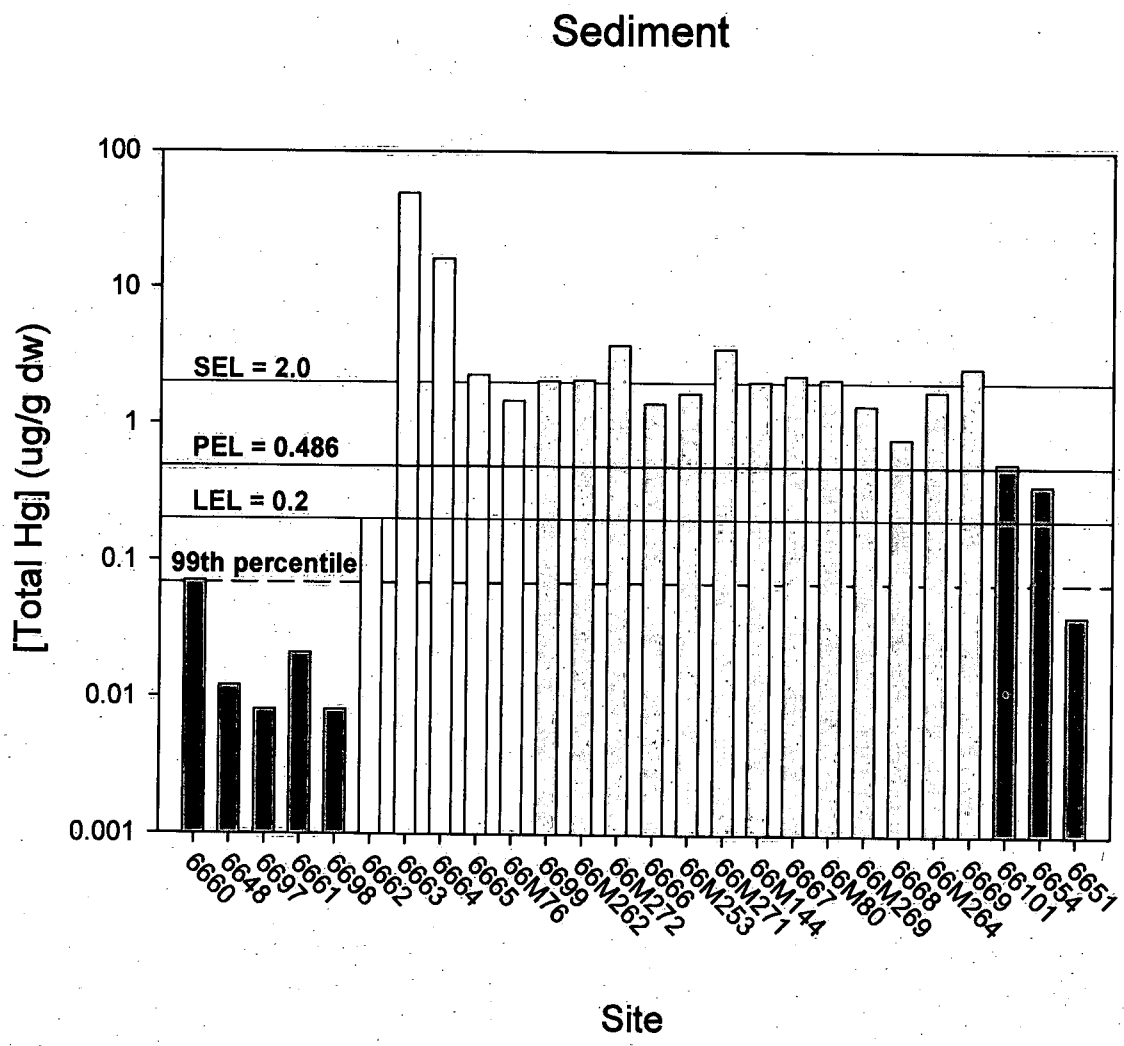


Figure 2. Total mercury in sediment (from Flett Laboratory) from exposed (yellow-Zone A; grey-Zone B; blue-downstream) and upstream reference sites (green) in the St. Clair River. The dashed line indicates the 99th percentile for upstream (reference sites). Sediment quality guidelines for Hg are also indicated: provincial lowest effect level (LEL) and severe effect level (SEL); federal probable effect level (PEL). Sites are ordered from upstream to downstream.

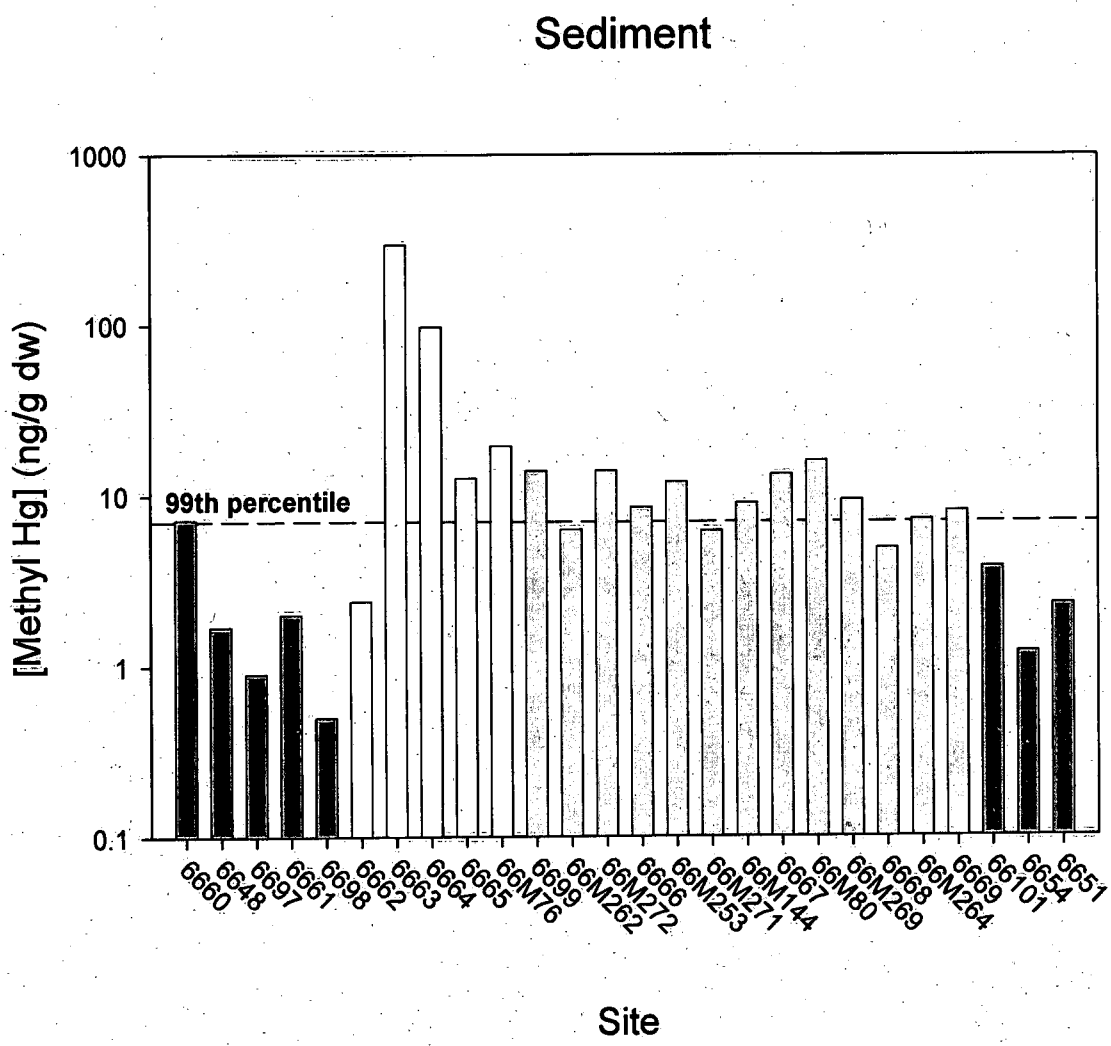


Figure 3. Methyl mercury in sediment from exposed (yellow-Zone A; grey-Zone B; blue-downstream) and upstream reference sites (green) in the St. Clair River. The dashed line indicates the 99th percentile for upstream (reference) sites. Values for Sites 6660, 6663 and 6664 are estimated based on mean percentages of methyl mercury to total mercury fro other sites (see text).

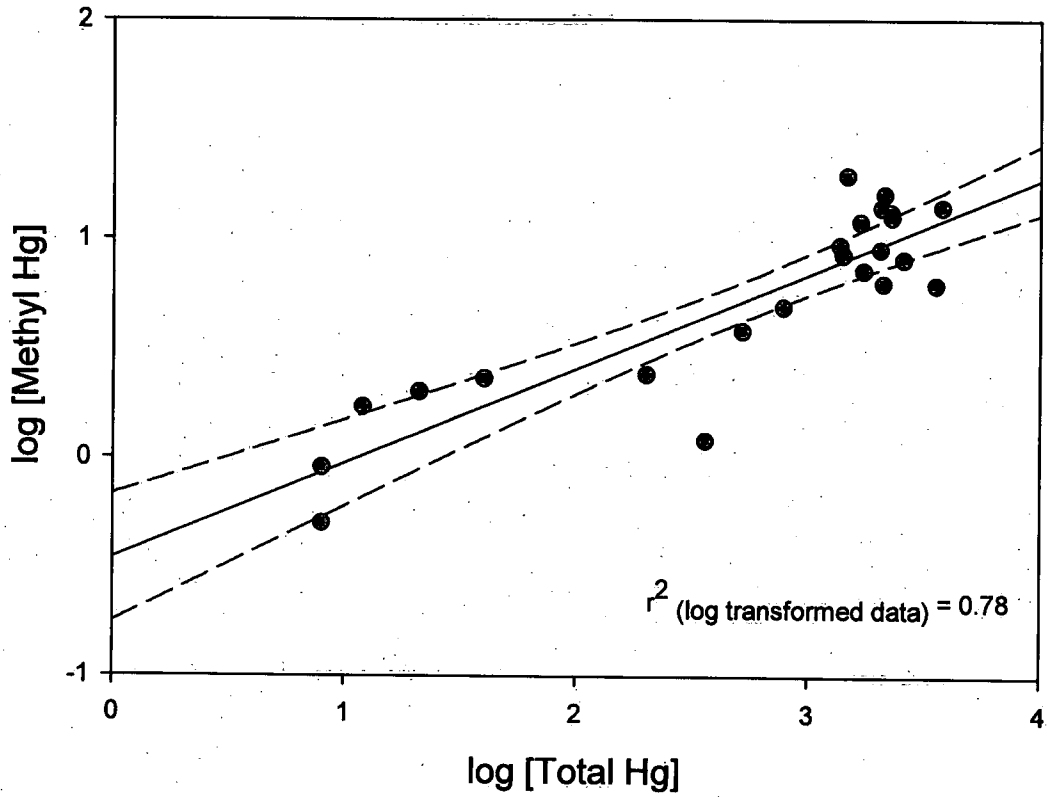


Figure 4. Log scatter plot of methyl Hg versus total Hg in sediment. The 95% confidence interval for the regression equation is shown by the dashed lines.

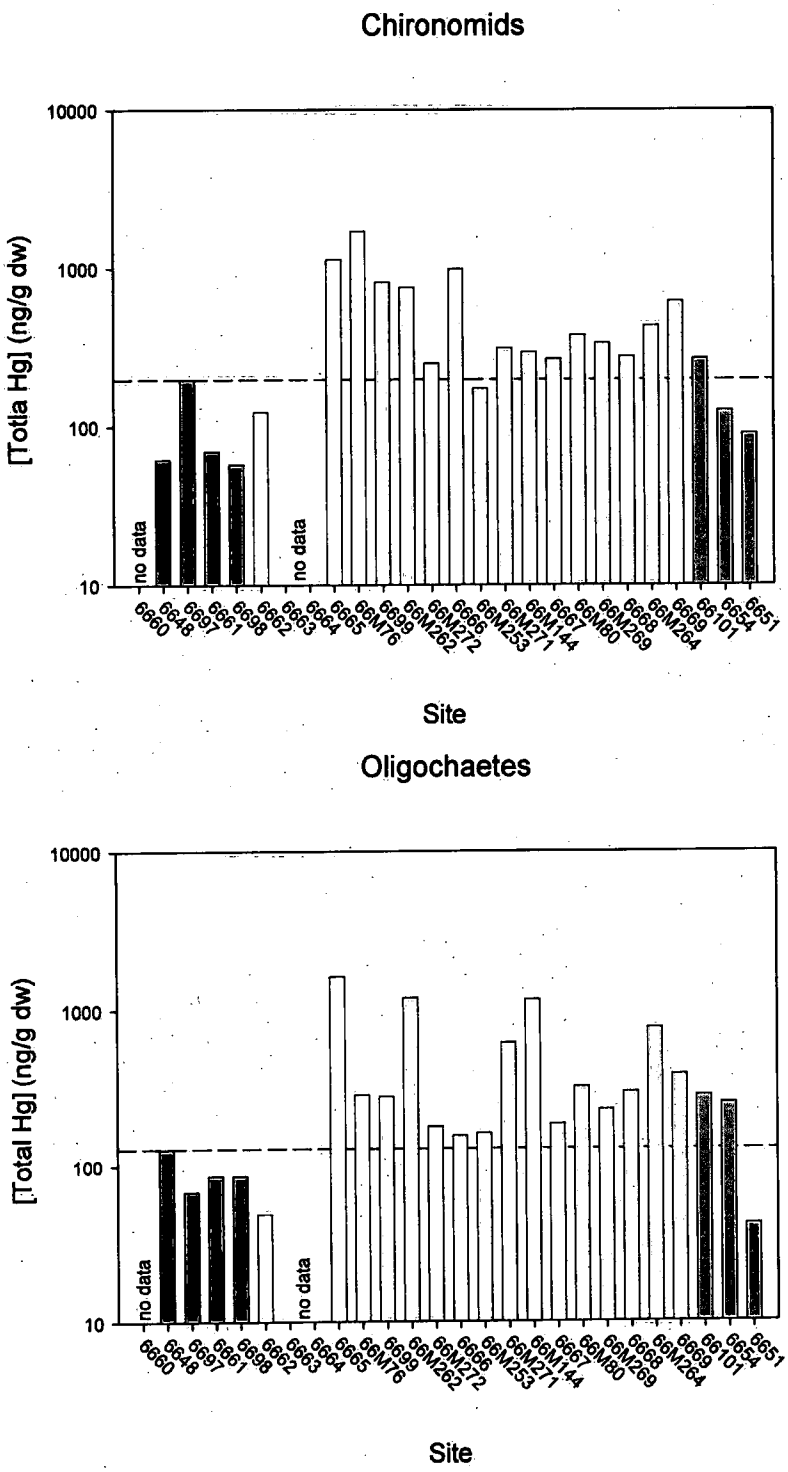


Figure 5. Total mercury (ng/g) in chironomids [top] and oligochaetes [bottom] in exposed (grey) and reference sites (green) in the St. Clair River. The dashed line indicates the 99th percentile for upstream (reference) sites.

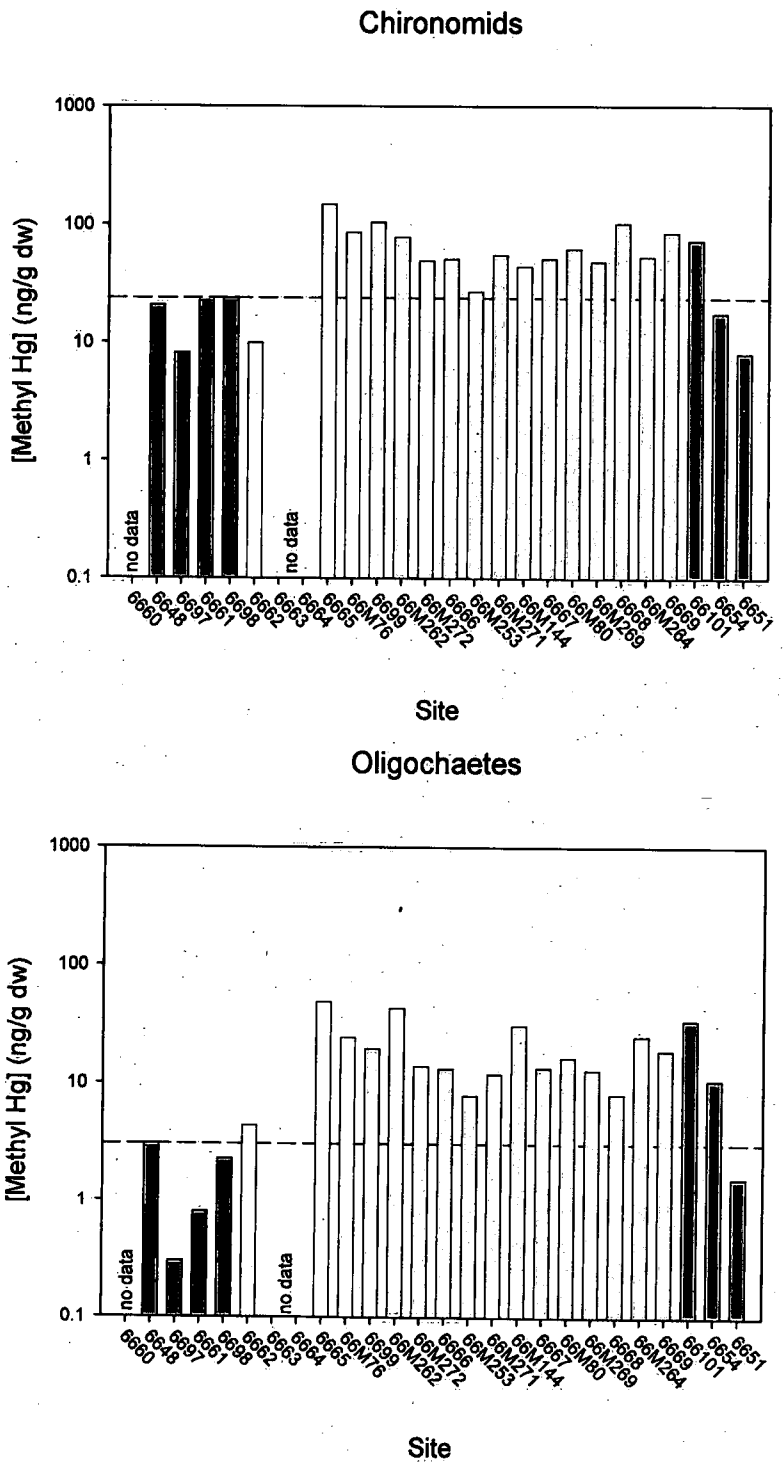


Figure 6. Methyl mercury (ng/g) in chironomids [top] and oligochaetes [bottom] from exposed (grey) and reference sites (green) in the St. Clair River. The dashed line indicates the 99th percentile for upstream (reference) sites.

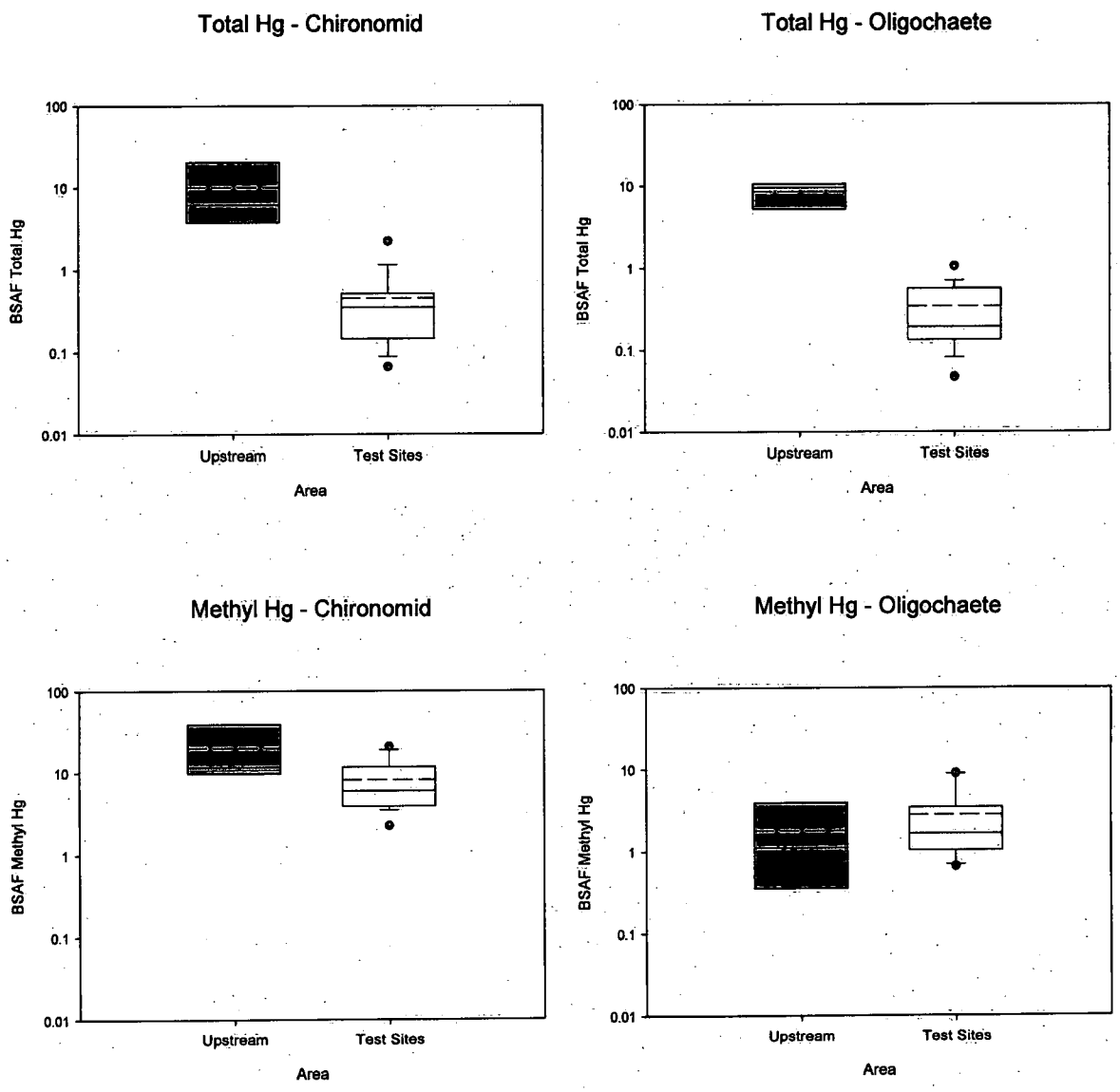
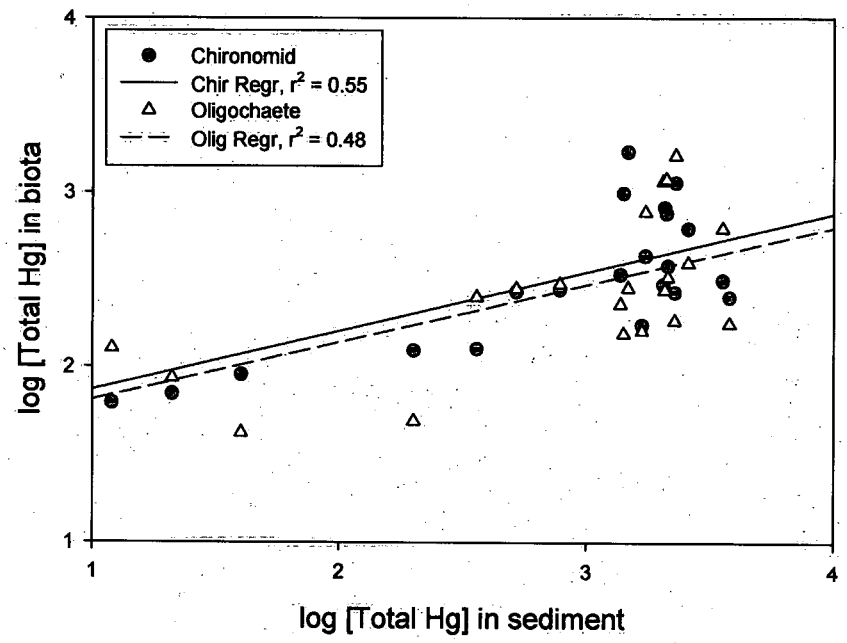


Figure 7. Biota-sediment accumulation factors for invertebrate taxa collected from exposed (grey) and reference sites (green) in the St. Clair River. Boxplots of BSAFs (=$[Hg]_{inv}$ / $[Hg]_{sed}$) for each taxon within areas show 90th and 10th percentile (whiskers above and below boxes for test sites only), inter-quartile ranges (box boundaries closest and farthest from zero), median (horizontal line within boxes), mean (dotted line) and outliers (solid circles for test sites only). (For upstream sites, the 10th and 90th percentiles could not be computed due to insufficient number of data points.)



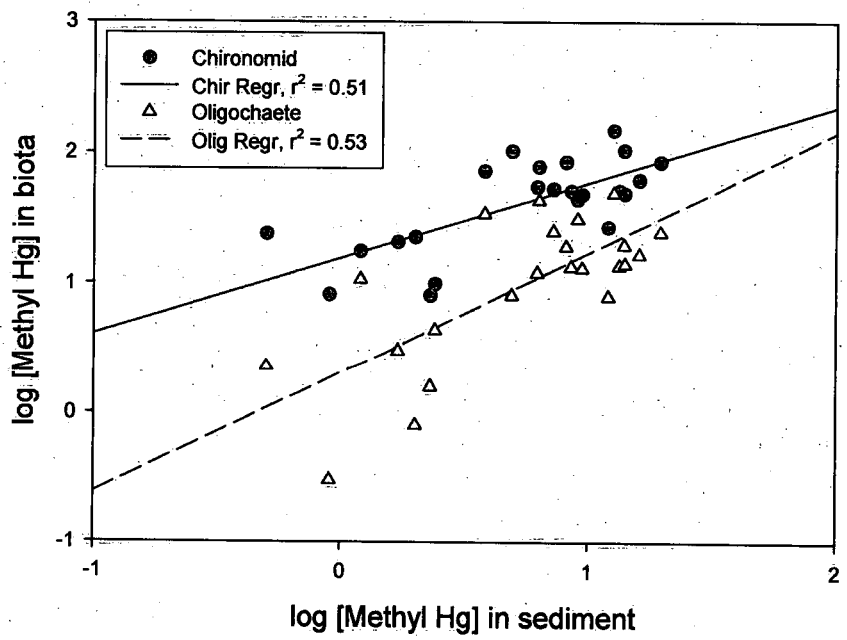
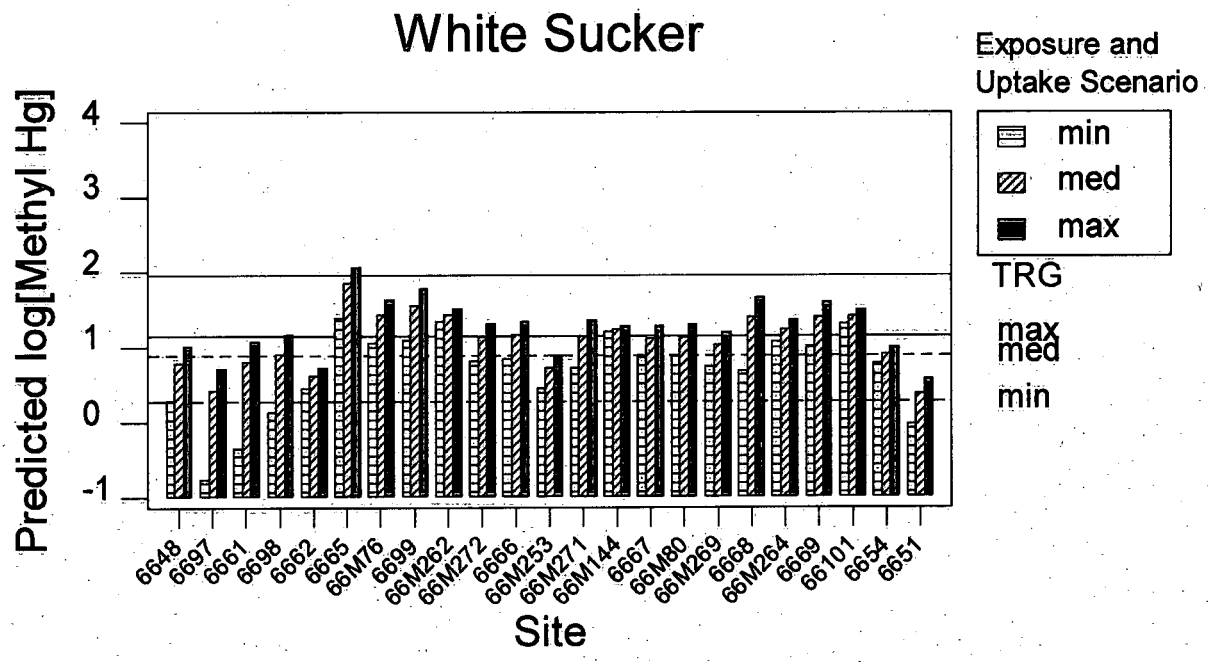


Figure 8. Relationships between total [top] and methyl mercury [bottom] in chironomids and oligochaetes to that in sediment for St. Clair River sites. Separate regression lines are shown for each taxon.



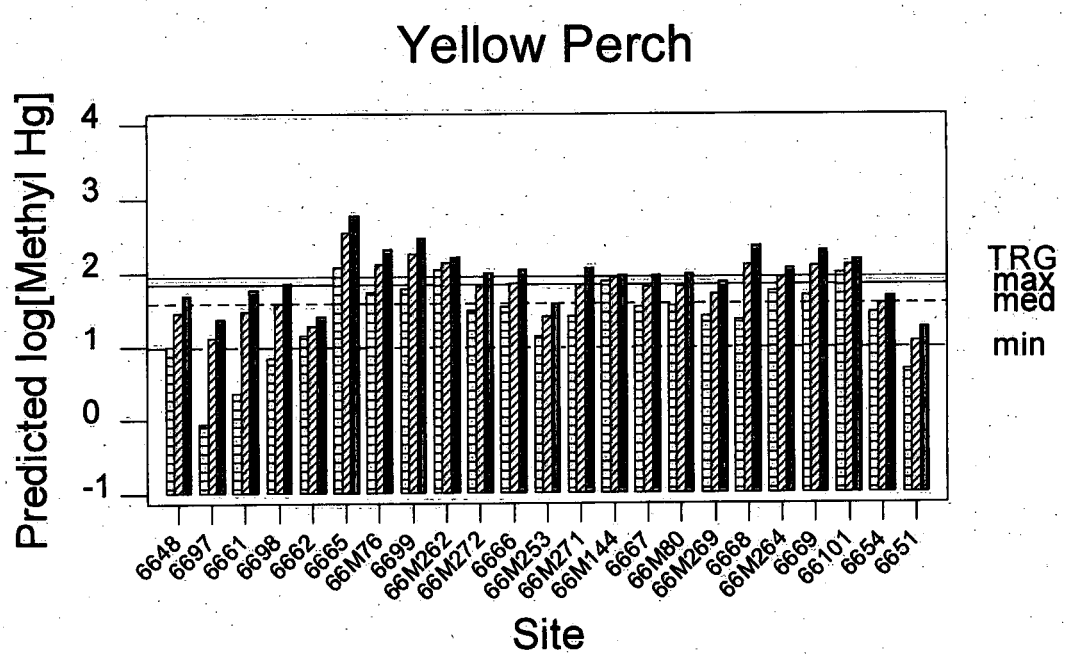
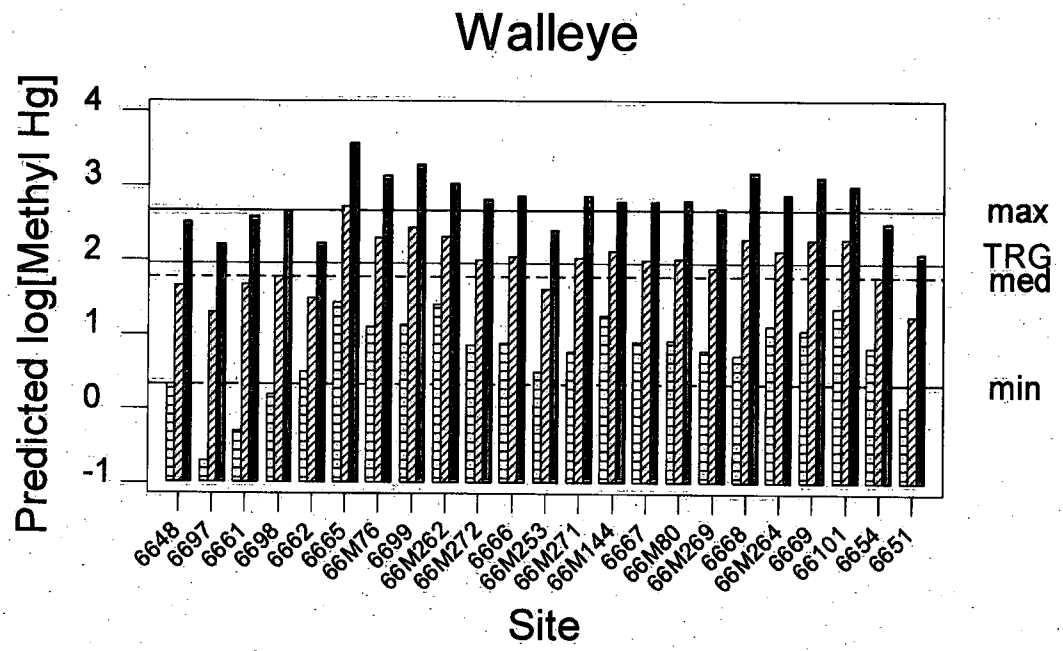


Figure 9. Predicted (minimum, intermediate, and maximum) concentrations of methyl mercury (ng/g ww) in five receptor species for St. Clair River sites. Charts compare predicted [MeHg] among receptors and between reference (6648, 6697, 6661, 6698) and test sites. Highest predicted [MeHg] for reference sites for each scenario is indicated on the chart (min, med, max). The tissue residue guideline (92 ng/g ww, Environment Canada), applicable to fishes only, is indicated is shown by the red line. (Note: no results for sites 6660, 6663 and 6664 – see text for explanation.)



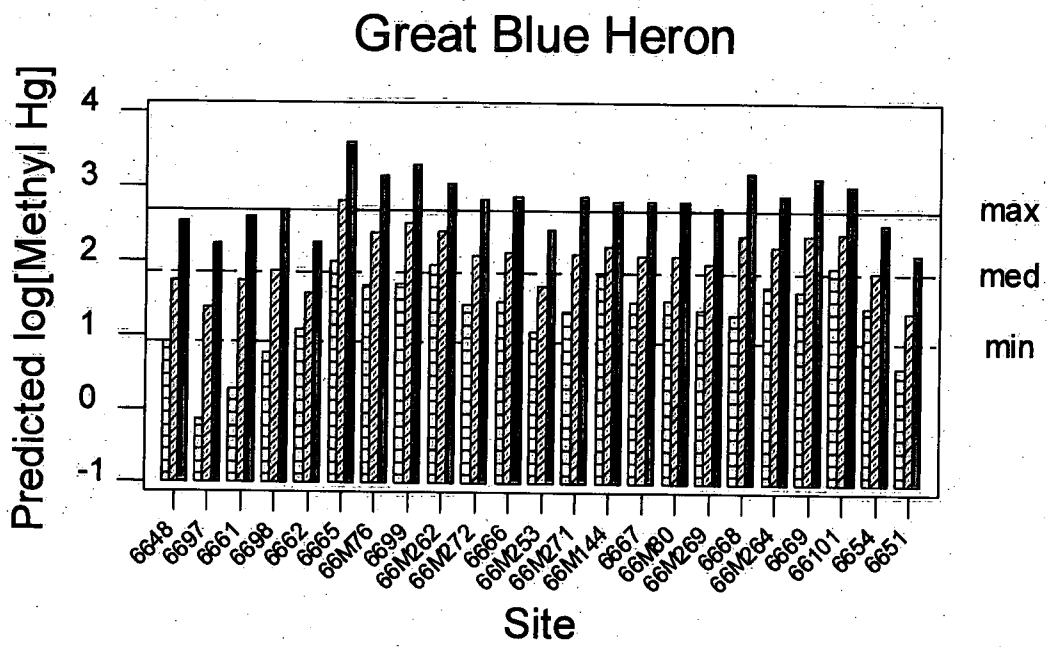


Figure 9. Continued.

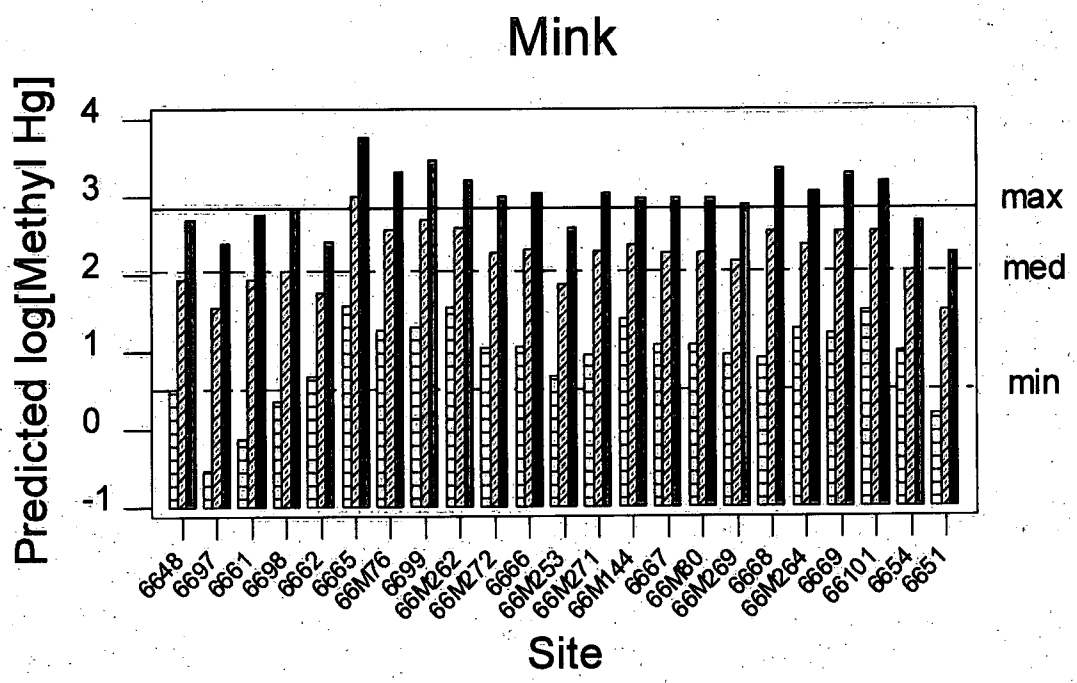


Figure 9. Continued.

Table 1. St. Clair River site positions (UTM NAD83) and depths. Overlapping Ontario Ministry of the Environment (MOE) stations from previous studies (Pope 1993; Thorburn et al. 2003) are indicated next to the site code.

Site	Location	Easting	Northing	Site Depth (m)
6660	Upstream (Pt. Edward)	384057.0	4760813.0	8.6
6648 (MOE 6A)	Upstream (Sarnia Bay)	384684.0	4759583.0	8.5
6697	Upstream (Sarnia Bay)	384878.7	4759384.7	2.3
6661 (MOE 263)	Upstream (Sarnia Bay)	384854.0	4759340.2	14.4
6698	Upstream (US)	383036.6	4756382.9	2.8
6662 (MOE 47)	Zone A	383125.0	4755719.7	4.0
6663	Zone A	382906.9	4755515.5	4.3
6664	Zone A	382468.4	4755126.0	3.3
6665 (MOE 75)	Zone A	382201.4	4754875.2	5.8
66M76	Zone A	381872.0	4754387.0	3.3
6699 (MOE 115)	Zone B	381104.7	4752016.2	2.3
66M262	Zone B	381099.5	4751924.0	0.6
66M272	Zone B	380950.1	4751304.9	1.6
6666 (MOE 143)	Zone B	380918.1	4751253.2	1.0
66M253	Zone B	380901.0	4751087.0	2.6
66M271	Zone B	380953.8	4750921.4	0.8
66M144	Zone B	380958.8	4750760.6	1.0
6667 (MOE 100)[a]	Zone B	381039.8 / 381046.0	4750328.9 / 4750320.0	2.1 / 1.5
66M80	Zone B	381106.4	4750074.3	2.0
66M269	Zone B	381195.5	4749996.0	2.3
6668 (MOE 147)	Zone B	381070.3	4749103.4	3.3
66M264	Zone B	380750.0	4748263.0	1.2
6669 (MOE 148)[a]	Zone B	380631.4 / 380627.5	4747605.5 / 4747603.3	0.7 / 0.9
66101	Mouth of Baby Creek	379976.8	4743454.1	0.5
6654 (MOE 58)	Stokes Pt Wharf	378941.2	4732335.2	0.6
6651 (MOE 74)	Delta - North Channel (US)	368342.1	4720012.9	2.3

[a] collected in 2001 and 2004

Table 2. Environmental variables measured at each site

Field	Water	Sediment	Biota
Northing	Alkalinity	Trace Metals	Total Hg
Easting	Conductivity	Major Oxides	Methyl Hg
Site Depth	Dissolved Oxygen	Total Phosphorus	
	Nitrates/Nitrites, Ammonia	Total Nitrogen	
	pH	Total Organic Carbon, Loss on Ignition	
	Temperature	Percents Clay, Silt, Sand, & Gravel	
	Total Kjeldahl Nitrogen	Total and Methyl Hg	
	Total Phosphorus	Polycyclic Aromatic Hydrocarbons, Total Polychlorinated Biphenyls, Organochlorine Pesticides	

Table 3. Literature derived BMFs for the receptors of concern. For each receptor, the number of trophic levels removed from benthic invertebrates (Level 1) is indicated. For each transfer between trophic levels, the lowest and the highest estimated BMFs (from Table A1) are used in calculating the food chain multipliers. See text for further details.

Methyl Hg				
Receptor	**Predator Type**	**Trophic levels of transfer**	**BMFs (low | med | high) of transfer**	**Food chain multipliers (low | med | high)**
White Sucker / Forage fish	benthivorous / planktivorous fish	1 - 2	3.43	3.43
Adult Yellow Perch	small piscivorous fish	1 - 2 - 3	3.43 x 5	17.15
Walleye	large piscivorous fish	1 - 2 - 3	3.43 x (1.12 | 3.20 | 32.40)	3.84 | 10.98 | 111.1
		1 - 2 - 3 - 4	3.43 x 5 x 2.40	41.16
Great Blue Heron	piscivorous bird	1 - 2 - 3	3.43 x 6.80	23.32
		1 - 2 - 3 - 4	3.43 x 5 x (0.85 | 2.37 | 6.80)	14.58 | 40.65 | 116.6
Mink	piscivorous mammal	1 - 2 - 3	3.43 x (1.70 | 5.20 | 22.64)	5.83 | 17.84 | 77.66
		1 - 2 - 3 - 4	3.43 x 5 x (1.70 | 4.70 | 10.00)	29.16 | 80.61 | 171.5

Table 4. St. Clair River overlying water characteristics (values in mg/L unless otherwise noted).

Site	Alkalinity	Conductivity (µS/cm)	Dissolved O_2	NO_3/NO_2	NH_3	pH	Total Phosphorus µg/L	Total Kjeldahl Nitrogen	Temp (°C)
6660	79.4	203	8.63	0.300	-[a]	8.01	5	0.15	19.7
6648	79.9	200	8.62	0.303	-[a]	7.98	6	0.15	19.9
6697	81.1	221	9.19	0.286	-[a]	8.01	8	0.15	18.9
6661	79.9	221	8.78	0.299	-[a]	8.01	7	0.15	18.8
6698	81.5	224	9.60	0.306	-[a]	8.01	7	0.15	19.4
6662	80.2	222	9.31	0.321	-[a]	8.05	19	0.21	19.4
6663	82.3	221	9.46	0.313	-[a]	8.04	8	0.14	19.4
6664	82.3	223	9.67	0.317	-[a]	8.03	13	0.15	19.7
6665	80.7	222	9.51	0.309	-[a]	8.02	7	0.15	19.6
66M76	79.5	211	9.07	0.345	0.014	8.19	6	0.17	18.6
6699	81.4	224	8.33	0.304	-[a]	7.99	7	0.14	19.2
66M262	79.9	210	7.65	0.332	0.023	8.02	13	0.22	17.1
66M272	80.3	218	7.33	0.334	0.025	8.08	13	0.30	17.4
6666	80.6	223	8.81	0.314	-[a]	7.98	11	0.15	19.1
66M253	78.6	215	8.47	0.342	0.014	8.26	7	0.20	18.5
66M271	80.7	220	8.15	0.333	0.044	8.10	36[c]	0.29	20.7
66M144	80.5	221	8.01	0.334	0.015	7.99	15	0.15	19.0
6667[b]	82.4 / 78.8	225 / 215	7.61 / 8.90	0.322 / 0.442	0.020	8.02 / 8.24	10 / 5	0.15 / 0.17	19.3 / 18.4
66M80	80.2	225	8.00	0.385	0.018	8.00	29[c]	0.17	17.7
66M269	79.2	220	8.40	0.370	0.016	8.16	11	0.18	18.2
6668	82.7	229	8.67	0.315	-[a]	7.98	17	0.17	19.3
66M264	91.1	220	8.95	0.346	0.011	8.22	7	0.22	18.1
6669[b]	82.5 / 79.4	225 / 206	8.93 / 8.56	0.310 / 0.350	0.023	8.08 / 8.12	15 / 6	0.18 / 0.19	19.2 / 18.0
66101	79.9	209	8.39	0.336	0.023	8.08	13	0.18	17.4
6654	79.4	225	9.31	0.346	-[a]	7.98	11	0.26	19.0
6651	80.4	222	8.96	0.316	-[a]	7.98	8	0.15	19.1

[a] not measured; [b] 2001 and 2004 results; [c]exceeding the interim water quality objective (total phosphorus should not exceed 20µg/L to avoid nuisance concentrations of algae in lakes, MOE 1994b)

Table 5. Physical characteristics of St. Clair River sediment (top 10 cm).

Site	% Sand	% Silt	% Clay	% Gravel
6660	98.38	1.62	0.00	0.00
6648	89.73	10.27	0.00	0.00
6697	89.88	10.12	0.00	0.00
6661	90.07	9.93	0.00	0.00
6698	87.43	9.63	0.00	2.94
6662	92.86	6.75	0.00	0.39
6663	66.67	1.52	0.00	31.81
6664	60.76	0.93	0.00	38.31
6665	95.11	1.73	0.00	3.16
66M76	92.52	7.48	0.00	0.00
6699	71.93	20.95	7.11	0.00
66M262	93.81	5.83	0.00	0.36
66M272	84.96	15.04	0.00	0.00
6666	93.39	6.23	0.00	0.38
66M253	50.72	29.97	19.3	0.00
66M271	97.43	1.63	0.00	0.95
66M144	51.31	7.18	13.9	27.61
6667[a]	73.96 / 90.43	16.10 / 9.57	9.94 / 0.00	0.00 / 0.00
66M80	83.58	3.64	0.00	12.78
66M269	80.69	3.01	0.00	16.3
6668	88.30	5.60	0.00	6.10
66M264	83.29	4.10	0.00	12.61
6669[a]	57.01 / 91.64	28.81 / 5.38	14.18 / 0.00	0.00 / 2.99
66101	98.96	0.88	0.00	0.16
6654	98.94	1.06	0.00	0.00
6651	56.89	28.90	14.21	0.00

[a] 2001 and 2004 results

Table 6. Total and methyl mercury sediment concentrations (recovery-corrected, Flett Laboratory). Values exceeding the provincial Severe Effect Level are highlighted.

Location	Site	Total Hg (µg/g dry weight)	Methyl Hg (ng/g dry weight)
Upstream (Pt. Edward)	6660	0.07[a]	7[b]
Upstream (Sarnia Bay)	6648	0.01	1.7
Upstream (Sarnia Bay)	6697	0.01	0.9
Upstream (Sarnia Bay)	6661	0.02	1.8 (2.2)[c]
Upstream (US)	6698	0.01	0.5
Zone A	6662	0.23 (0.17)[c]	2.4
Zone A	6663	49.30[a]	296[b]
Zone A	6664	16.20[a]	97[b]
Zone A	6665	2.29	12.6
Zone A	66M76	1.47	18.0 (20.0)[c] (20.0)[e]
Zone B	6699	2.07	13.9
Zone B	66M262	2.10	6.3
Zone B	66M272	3.78	14.0
Zone B	6666	1.41	8.5
Zone B	66M253	1.44 (1.91)[c]	12.0
Zone B	66M271	3.55	6.2
Zone B	66M144	1.72 (2.36)[c]	9.0
Zone B	6667	1.46 (3.08)[d]	12.3 (10.8)[c] (16.0)[d] (13.0)[c] (15.0)[e]
Zone B	66M80	2.13	16.0
Zone B	66M269	1.37	9.4
Zone B	6668	0.78	4.9
Zone B	66M264	1.87 (1.59)[c]	7.2
Zone B	6669	1.65 (1.79)[c] (3.52)[d] (3.87)[f] (2.89)[f]	7.5 (5.0)[d] (7.1)[f] (14.0)[f]
Mouth of Baby Creek	66101	0.52	3.8
Stokes Pt Wharf	6654	0.36	1.2
Delta - North Channel (US)	6651	0.04	2.3

[a] data not available from Flett Laboratory - results shown are from Caduceon laboratory; [b] estimated; [c] laboratory duplicate; [d] 2004 repeat; [e] laboratory repeat; [f] field replicate

Table 7. Trace metal and nutrient concentrations in St. Clair River sediment (top 10 cm) (Caduceon Laboratory) (values in µg/g dry weight unless otherwise noted). Values exceeding the provincial Severe Effect Level (SEL) are highlighted.

Site	Total Kjeldahl Nitrogen	Total Organic Carbon (%)	Total phosphorus	Loss on Ignition (%)	Al_2O_3 (%)	As	Cd	Co	Cr	Cu
Detection limit	*10*	*0.1*	*3*	*0.05*	*0.01*	*5.0 / 1.0*	*1.0 / 0.5*	*1.0*	*1.0*	*1.0*
6660	247	1.2	133	9.7	6.7	6.9	<1	1.0	4.1	6.8
6648	957	1.8	222	10.6	5.8	<5	<1	3.2	6.4	12.7
6697	407	1.4	181	10.6	7.1	<5	<1	2.0	5.3	8.1
6661	678	0.3	255	8.9	5.8	<5	<1	2.7	6.4	13.1
6698	450	2.3	191	7.1	5.8	<5	<1	1.7	5.3	11.8
6662	585	2.5	236	8.4	5.9	<5	1.0	1.7	5.8	21.4
6663	420	3.2	194	12.9	7.1	<5	1.0	2.9	18.8	17.6
6664	274	0.5	123	7.5	5.1	<5	<1	1.1	5.5	21.9
6665	386	0.6	168	7.9	4.1	<5	<1	1.8	6.1	10.4
66M76	440	1.9	375	13.9	5.32	3.0	<0.5	3.0	15.0	19.0
6699	1170	1.9	351	12.6	6.1	<5	<1	2.7	8.2	27.6
66M262	580	0.8	203	10.1	5.2	4.0	<0.5	3.0	12.0	12.0
66M272	1250	1.5	355	14.2	5.56	3.0	0.6	4.0	15.0	22.0
6666	391	1.5	237	8.6	5.8	<5	1.0	2.6	6.5	14.9
66M253	2610	2.5	772	18.2	5.83	4.0	0.6	5.0	16.0	33.0
66M271	490	1.1	312	5.65	5.19	2.0	0.5	3.0	16.0	19.0
66M144	790	0.7	346	7.58	7.27	6.0	0.6	6.0	21.0	16.0
6667[a]	930 / 1360	2.3 / 1.7	239 / 353	10.9 / 13.1	5.9 / 5.6	<5 / 4.0	<1 / 0.9	3.9 / 5.0	7.9 / 18.0	20.1 / 29.0
66M80	840	0.8	274	10.2	5.14	3.0	0.7	4.0	14.0	18.0
66M269	750	1.1	277	11.8	5.46	3.0	0.6	3.0	22.0	16.0
6668[b]	534	0.9	202	9.2	5.5	<5	<1	2.8	7.1	13.3
66M264	750	1.1	241	9.18	5.36	4.0	<0.5	3.0	16.0	14.0
6669[a,b]	1330 / 953	2.0 / 1.0	387 / 321	11.9 /10.7	6.4 / 5.5	<5 / 3.0	1.0 / 0.8	3.0 / 4.0	9.9 / 27.0	21.0 / 17.0
66101	190	0.6	144	5.06	5.29	1.0	<0.5	2.0	6.0	4.0
6654	342	0.4	153	5.2	3.5	<5	<1	1.4	3.8	5.9
6651	834	1.6	266	9.9	6.4	<5	<1	3.5	7.7	22.7
LEL	550	1	600	-	-	6.0	0.6	-	26	16
SEL	4800	10	2000	-	-	33.0	10	-	110	110

[a] 2001 and 2004 results; [b] QA/QC site, values represent the average of three field replicates

Table 7. Continued.

Site	Fe (%)	Mg (%)	Mn	Na (%)	Ni	P_2O_5 (%)	Pb	SiO_2 (%)	V	Zn
Detection limit	*0.01*	*0.01*	*1.0*	*0.01*	*1.0*	*0.03*	*1.0*	*0.01*	*1.0*	*1.0*
6660	0.47	1.3	163	0.029	10.9	0.07	20.1	67.6	6.5	14.1
6648	0.71	1.8	207	0.030	15.3	0.15	25.8	65.8	9.5	33.8
6697	0.57	1.7	185	0.030	12.6	0.10	19.8	64.5	8.9	20.1
6661	0.65	1.5	206	0.029	13.8	0.10	24.0	70.2	8.8	37.9
6698	0.55	1.5	145	0.029	12.9	0.11	17.3	73.7	8.6	41.9
6662	0.98	1.7	154	0.028	15.6	0.09	22.5	65.8	9.7	63.4
6663	1.22	1.7	172	0.031	34.2	0.08	22.9	57.6	15.1	88.8
6664	0.56	1.0	125	0.025	12.5	0.09	16.3	71.3	7.8	35.7
6665	0.69	1.0	142	0.027	13.9	0.09	14.7	74.6	8.9	49.7
66M76	0.87	1.5	206	.009	11.0	0.04	11.0	61.3	20.0	69.0
6699	0.81	1.9	209	0.032	18.3	0.13	24.6	63.0	10.9	56.8
66M262	0.75	1.4	173	.008	9.0	<0.03	8.0	68.6	18.0	59.0
66M272	0.89	1.7	219	.011	17.0	0.04	9.0	61.8	25.0	82.0
6666	0.74	1.8	185	0.028	14.5	0.12	24.4	67.3	9.5	43.7
66M253	1.07	1.5	237	.010	15.0	0.12	15.0	57.9	23.0	94.0
66M271	0.58	1.1	129	.006	7.0	<0.03	6.0	77.7	15.0	86.0
66M144	1.35	1.1	242	.010	20.0	0.04	10.0	69.7	27.0	61.0
6667[a]	0.85 / 0.95	1.9 / 1.6	221 / 230	0.030 / 0.011	20.2 / 14.0	0.12 / 0.04	35.5 / 21.0	63.8 / 60.6	17.8 / 24.0	49.0 / 83.0
66M80	0.75	1.3	183	.010	9.0	<0.03	47.0	66.9	17.0	68.0
66M269	0.82	1.5	210	.010	10.0	0.03	39.0	64.8	19.0	68.0
6668[b]	0.71	1.7	180	0.029	17.8	0.11	31.7	69.7	9.4	45.1
66M264	0.81	1.3	177	.008	10.0	<0.03	23.0	70.6	16.0	72.0
6669[a,b]	0.94 / 0.84	1.9 / 1.4	218 / 177	0.028 / 0.010	19.7 / 11.0	0.12 / 0.03	38.0 / 41.3	62.3 / 67.7	12.7 / 19.0	55.7 / 70.0
66101	0.44	1.0	101	.006	4.0	<0.03	7.0	78.6	11.0	34.0
6654	0.38	0.7	68	0.025	9.0	0.05	11.1	81.1	6.9	14.0
6651	0.95	1.9	238	0.029	20.6	0.17	25.2	67.7	12.5	68.6
LEL	2%	-	460	-	16	-	31	-	-	120
SEL	4%	-	1100	-	75	-	250	-	-	820

[a] 2001 and 2004 results; [b]QA/QC site, values represent the average of three field replicates

Table 8. Probabilities of test sites belonging to 1 of 6 Great Lakes faunal groups using a revised BEAST Model (2001 sites only). Highest probability for each site is bolded.

Site	Probability of Group Membership (%)					
	Gp 1	Gp 2	Gp 3	Gp 4	Gp 5	Gp 6
6660	0.330	0.131	**0.504**	0.032	0.001	0.001
6648	0.245	0.112	**0.623**	0.019	0.001	0.000
6697	0.402	0.127	**0.431**	0.039	0.001	0.000
6661	0.311	0.092	**0.503**	0.092	0.002	0.001
6698	0.212	0.046	**0.733**	0.009	0.000	0.000
6662	0.225	0.090	**0.677**	0.008	0.000	0.000
6663	0.357	0.120	**0.510**	0.013	0.001	0.000
6664	0.320	0.067	**0.423**	0.190	0.000	0.000
6665	0.193	0.062	**0.701**	0.044	0.000	0.000
6699	0.346	0.084	**0.530**	0.039	0.000	0.000
6666	0.301	0.086	**0.586**	0.027	0.000	0.000
6667	0.305	0.070	**0.604**	0.020	0.000	0.000
6668	0.321	0.073	**0.549**	0.056	0.000	0.000
6669	0.413	0.064	**0.469**	0.054	0.000	0.000
6654	0.172	0.024	**0.771**	0.032	0.000	0.000
6651	**0.488**	0.035	0.411	0.066	0.000	0.000

Table 9a. Mean abundance of dominant macroinvertebrate families (per m^2), taxon diversity, and BEAST difference-from-reference band for 2001 St. Clair River sites predicted to reference Group 3: Upstream reference sites. Families expected to be at test sites that are absent are highlighted.

Family	Ref. Gp. 3 Mean	Ref. Gp. 3 % Occurrence	% of total Abundance	6660	6648	6697	6661	6698
Probability (%) of ref. Group 3 membership	-	-	-	50.4	62.3	43.1	50.3	73.3
No. Taxa (SD)	*8.6 (5)*	-	-	*9*	*18*	*10*	*8*	*23*
Chironomidae	1211.9	100	37.7	6838.3	20812.1	3015.7	16948.1	15686.4
Tubificidae	620.3	94.1	19.3	2451.2	45819.0	12123.0	19722.6	15876.4
Sphaeriidae	402.7	82.4	12.5	0.0	0.0	0.0	0.0	0.0
Naididae	208.4	66.7	6.5	101.2	775.8	180.9	422.2	2237.5
Valvatidae	75.6	45.1	2.4	0.0	0.0	120.6	0.0	0.0
Sabellidae	160.2	41.2	5.0	0.0	0.0	0.0	0.0	0.0
Asellidae	82.7	31.4	2.6	0.0	0.0	0.0	0.0	9.0
Ephemeridae	44.3	31.4	1.4	0.0	9.0	60.3	60.3	9.0
BEAST BAND	-	-	-	**2**	**4**	**3**	**4**	**4**

Table 9b. Mean abundance of dominant macroinvertebrate families (per m^2), taxon diversity, and BEAST difference-from-reference band for 2001 St. Clair River sites predicted to reference Group 3: Zone A sites. Families expected to be at test sites that are absent are highlighted.

Family	Ref. Gp. 3 Mean	Ref. Gp. 3 % Occurrence	% of total Abundance	6662	6663	6664	6665
Probability (%) of ref. Group 3 membership	-	-	-	67.7	51.0	42.3	70.1
No. Taxa (SD)	*8.6 (5)*	-	-	*2*	*16*	*17*	*8*
Chironomidae	1211.9	100	37.7	1990.3	3258.6	4828.4	8158.3
Tubificidae	620.3	94.1	19.3	56152.0	944.5	5385.8	1248.1
Sphaeriidae	402.7	82.4	12.5	0.0	16.5	24.7	8.2
Naididae	208.4	66.7	6.5	0.0	236.1	213.6	33.7
Valvatidae	75.6	45.1	2.4	0.0	0.0	26.9	0.0
Sabellidae	160.2	41.2	5.0	0.0	0.0	0.0	0.0
Asellidae	82.7	31.4	2.6	0.0	0.0	0.0	0.0
Ephemeridae	44.3	31.4	1.4	0.0	0.0	9.0	0.0
BEAST BAND	-	-	-	**4**	**1**	**2**	**2**

[a]QA/QC site. Numbers represent the mean of three field replicates.

Table 9c. Mean abundance and diversity of macroinvertebrate families (per m^2), and BEAST summary results for 2001 St. Clair River sites predicted to reference Group 3: Zone B sites and site near Stokes Pt. Wharf. Families expected to be at test sites that are absent are highlighted.

Family	Ref. Gp. 3 Mean	Ref. Gp. 3 % Occurrence	% of total Abundance	6699	6666	6667	6668[a]	6669	6654
Probability (%) of ref. Group 3 membership	-	-	-	53.0	58.6	60.4	54.9	46.9	77.1
No. Taxa (SD)	*8.6 (5)*	-	-	*14*	*13*	*6*	*16*	*18*	*16*
Chironomidae	1211.9	100	37.7	1326.9	4523.5	7358.3	2564.8	11037.4	4768.9
Tubificidae	620.3	94.1	19.3	47165.3	47647.8	25271.4	9711.0	59650.2	1394.2
Sphaeriidae	402.7	82.4	12.5	0.0	0.0	0.0	5.5	1085.6	0.0
Naididae	208.4	66.7	6.5	60.3	1447.5	1930.0	37.5	301.6	4610.0
Valvatidae	75.6	45.1	2.4	603.1	965.0	0.0	9.0	1326.9	0.0
Sabellidae	160.2	41.2	5.0	0.0	0.0	0.0	0.0	0.0	0.0
Asellidae	82.7	31.4	2.6	0.0	0.0	0.0	0.0	0.0	0.0
Ephemeridae	44.3	31.4	1.4	0.0	0.0	0.0	0.0	0.0	0.0
BEAST BAND	-	-	-	**4**	**4**	**3**	**3**	**4**	**3**

[a]QA/QC site. Numbers represent the average of three field replicates.

Table 9d. Mean abundance of dominant macroinvertebrate families (per m^2), taxon diversity, and BEAST difference-from-reference band for 2001 St. Clair River site predicted to reference Group 1: delta site. Families expected to be at the test site that are absent are highlighted.

Family	Ref. Gp. 1 Mean	Ref. Gp. 1 % Occurrence	% of total Abundance	6651
Probability (%) of ref. Group 1 membership	-	-	-	48.8
No. Taxa (SD)	*6.8 (2.0)*	-	-	*5*
Tubificidae	8860.9	100	53.8	21954.2
Chironomidae	2702.1	97.1	16.4	22195.4
Sphaeriidae	2016.2	82.9	12.3	301.6
Naididae	677.2	74.3	4.1	0.0
Dreissenidae	661.7	48.6	4.0	0.0
Valvatidae	101.7	42.9	0.6	0.0
BEAST BAND	-	-	-	**2**

Table 10. Mean percent survival, growth (mg dry weight per individual) and reproduction in sediment toxicity tests, and BEAST difference from-reference band. Toxicity is highlighted yellow; potential toxicity italicized.

Site	*Chironomus* Growth	*Chironomus* %Survival	*Hyalella* Growth	*Hyalella* %Survival	*Hexagenia* Growth	*Hexagenia* %Survival	*Tubifex* No. Cocoons/Ad.	*Tubifex* %Hatch	*Tubifex* %Survival	*Tubifex* No. Young/Ad.	**BEAST BAND**
GL ref. mean	*0.35*	*87.1*	*0.50*	*85.6*	*3.03*	*96*	*9.9*	*57*	*98*	*29.0*	-
6660	0.46	94.7	0.49	90.7	3.22	100	12.3	62	100	27.8	**1**
6648	0.34	85.3	0.69	93.3	9.82	100	12.2	54	100	30.5	**1**
6697	0.38	82.7	0.56	97.3	6.03	98	12.0	57	100	27.7	**1**
6661	0.36	86.7	0.64	76.0	7.14	98	12.5	59	100	36.7	**1**
6698	0.58	94.7	0.70	84.0	8.32	96	13.3	53	100	35.7	**1**
6662	0.46	92.0	0.62	94.7	7.20	100	12.2	44	100	25.6	**1**
6663[a]	-	-	-	-	-	-	-	-	-	-	-
6664	0.37	96.0	0.69	98.7	3.20	**78**	11.1	55	100	24.2	**2**
6665	0.49	97.3	0.86	98.7	5.06	100	12.3	59	100	26.9	**1**
66M76	0.37	96.0	0.53	91.7	8.24	100	11.5	53	100	28.7	**1**
6699	0.48	94.7	0.69	93.3	6.62	100	11.6	53	100	25.7	**1**
66M262	0.48	88.0	0.42	94.7	1.59	100	9.3	56	100	22.0	**1**
66M272	0.32	92.0	0.38	86.7	7.49	100	10.8	53	100	25.4	**1**
6666	0.38	90.7	0.67	94.7	2.13	**76**	10.6	53	100	19.8	**2**
66M253	0.39	84.0	0.60	97.8	7.65	100	10.5	52	100	27.9	**1**
66M271	0.39	92.0	0.34	92.0	1.00	92	10.4	51	100	34.8	**1**
66M144	0.30	85.3	0.26	81.3	2.52	98	**4.7**	53	100	***6.1***	**2**
6667[b]	0.38/0.39	97.3/93.3	0.77/0.37	98.3/80.0	8.00/8.58	96/100	12.5/11.6	57/53	100/100	24.1/30.0	**1**
66M80	0.36	93.3	0.69	94.7	7.69	100	12.5	54	100	33.9	**1**
66M269	0.26	89.3	0.55	90.7	9.08	98	11.3	48	100	23.2	**1**
6668	0.46	73.3	0.61	97.3	6.79	100	12.0	56	100	23.5	**1**
66M264	0.45	89.3	0.47	94.7	7.17	100	7.8	48	100	15.4	**1**
6669[b]	0.40/0.39	93.3/90.0	0.67/0.52	98.3/89.3	7.01/8.83	98/100	10.9/10.5	57/54	100/100	26.6/37.3	**1**
66101	0.27	82.7	0.29	77.3	3.79	100	11.3	57	100	26.5	**1**
6654	0.48	92.0	0.49	90.7	3.65	100	12.8	62	100	32.3	**1**
6651	0.32	97.3	0.50	97.3	7.24	100	13.1	58	100	27.9	**1**
Non-toxic[c]	0.49 – 0.21	67.7	0.75 – 0.23	67.0	5.00 – 0.90	85.5	12.4 – 7.2	78 – 38	88.9	46.3 – 9.9	-
Potentially toxic	0.20 – 0.14	67.6 – 58.8	0.22 – 0.10	66.9–57.1	0.80 – 0	85.4 – 80.3	7.1 – 5.9	38 – 28	88.8– 84.2	9.8 – 0.8	-
Toxic	**< 0.14**	**< 58.8**	**< 0.10**	**< 57.1**	**negative**	**< 80.3**	**< 5.9**	**< 28**	**< 84.2**	**< 0.8**	-

[a]No toxicity tests performed (see Section 3.1 for details); [b] 2001/2004 results; [c]Upper limit for non-toxic category is set using 2 × standard deviation of the mean and indicates excessive growth or reproduction.

Table 11. Total and methyl mercury concentrations (ng/g dry weight) in resident benthic invertebrates.

Site	Total Hg		Methyl Hg	
	Chironomid	Oligochaete	Chironomid	Oligochaete
6660	-[a]	-[a]	-[a]	-[a]
6648	62	137 (117)[b]	21.3 (20)[c]	3.1
6697	181 (214)[b]	68	8.2	0.3
6661	70	86	22.6	0.8
6698	58	86	25.4 (21.1)[b] (23.3)[d]	2.3
6662	124	49	9.9	4.4
6663	-[a]	-[a]	-[a]	-[a]
6664	-[a]	-[a]	-[a]	-[a]
6665	1141	1626	148	49.0
66M76	1710	283	85	25 (24)[c]
6699	819	258 (293)[b]	105 (104)[c]	15.6 (22.9)[c] (19.8)[b]
66M262	757	1190	78	43
66M272	251	177	49	14
6666	991	155	51.1	14.0 (12.7)[c]
66M253	174	161	27	7.9
66M271	288 (338)[b]	618	55	12
66M144	296	1100 (1220)[b]	44	31
6667	223 (312)[e]	143 (227)[e] (222)[b]	59.7 (43)[e]	13.1 (14)[e]
66M80	379	325	62	17 (16)[b]
66M269	338	228	48	13
6668	277	297	103 (102)[c]	8.1
66M264	433	769	60(46)[b]	25
6669	476 (763)[e]	326 (458)[e]	102 (80)[b] (78.9)[d] (91.8)[f] (79)[e]	16.1 (22)[e]
66101	269	279	73(72)[b]	34
6654	127	251	17.6	10.7
6651	90	42	8.1	1.2 (2.0)[c]

[a] no data; [b] laboratory duplicate; [c] repeat analysis; [d] duplicate repeat analysis; [e] 2004 repeat; [f] laboratory triplicate

Table 12. Prediction of whole body concentrations of total and methyl Hg in resident invertebrate taxa based on sediment Hg concentration alone ("A" models), and sediment Hg concentration + other sediment physico-chemical variables ("B" models). The groups of multiple predictors listed are from the models that best predicted $[Hg]_{inv}$ using sediment and water variables. $[Hg]_{sed}$ was retained in all models.

Response ($[Hg]_{inv}$)	Model	Predictor ([X])	Coefficient	P (predictor)	R^2	R^2_{adj}	P (regression)
Total Hg Chironomids	A	Total Hg	0.33688	<0.001	0.552	0.531	<0.001
	B	Total Hg	0.44247	<0.001	0.910	0.876	<0.001
		Dissolved O_2	5.993	<0.001			
		Total Kjeldahl N (water)	-1.5317	<0.001			
		%Sand	1.5503	<0.001			
		Manganese	2.4361	<0.001			
		Depth	-0.4607	0.002			
Total Hg Oligochaetes	A	Total Hg	0.32939	<0.001	0.479	0.454	<0.001
	B	Total Hg	0.33720	<0.001	0.707	0.642	<0.001
		%Silt	-2.6292	0.003			
		%Sand	-1.1265	0.040			
		NO_3/NO_2 (water)	-5.0760	0.044			
Methyl Hg Chironomids	A	Methyl Hg	0.5788	<0.001	0.513	0.490	<0.001
	B	Methyl Hg	0.7743	<0.001	0.657	0.623	<0.001
		Iron	-1.3130	0.009			
Methyl Hg Oligochaetes	A	Methyl Hg	0.9219	<0.001	0.526	0.504	<0.001
	B	Methyl Hg	1.1848	<0.001	0.746	0.721	<0.001
		Manganese	-2.2096	<0.001			

Table 13. Predicted methyl mercury concentrations (ng/g wet weight) in receptor species. Highlighted values in fish receptors exceed the Environment Canada (2002) tissue residue guideline (92 ng/g ww) applicable for fishes.

	White Sucker			Yellow Perch			Walleye		
Site	min	med	max	min	med	max	min	med	max
6660	-	-	-	-	-	-	-	-	-
6648	1.9	6.0	10.0	9.6	29.8	50.1	2.2	45.4	324.4
6697	0.2	2.6	5.0	0.9	12.9	24.9	0.2	19.6	161.1
6661	0.4	6.1	11.7	2.2	30.4	58.7	0.5	46.3	380.0
6698	1.4	7.8	14.3	6.9	39.2	71.5	1.5	59.6	463.3
6662	2.8	4.0	5.2	14.1	20.2	26.2	3.1	30.6	170.0
6663	-	-	-	-	-	-	-	-	-
6664	-	-	-	-	-	-	-	-	-
6665	23.6	69.2	114.9	117.8	346.2	574.5	26.4	526.2	3721.9
66M76	11.2	26.2	41.3	55.9	131.1	206.3	12.5	199.3	1336.5
6699	12.1	35.4	58.8	60.4	177.2	294.0	13.5	269.3	1904.3
66M262	21.8	26.9	32.0	109.2	134.6	160.0	24.5	204.6	1036.6
66M272	6.4	13.2	19.9	31.9	65.8	99.6	7.1	100.0	645.5
6666	6.9	14.4	21.8	34.6	71.8	108.9	7.8	109.1	705.5
66M253	2.8	5.3	7.8	13.9	26.3	38.8	3.1	40.0	251.1
66M271	5.2	13.8	22.4	26.2	69.2	112.2	5.9	105.2	726.6
66M144	15.7	17.2	18.7	78.5	85.9	93.3	17.6	130.6	604.4
6667	7.0	12.9	18.8	35.2	64.5	93.8	7.9	98.1	607.7
66M80	7.3	13.3	19.3	36.4	66.5	96.7	8.1	101.2	626.6
66M269	5.3	10.3	15.3	26.6	51.5	76.5	6.0	78.3	495.5
6668	4.7	24.9	45.1	23.7	124.6	225.5	5.3	189.4	1461.0
66M264	11.6	17.1	22.7	57.8	85.6	113.4	12.9	130.1	734.4
6669	10.0	24.7	39.4	49.8	123.4	197.0	11.2	187.6	1276.0
66101	20.1	25.3	30.5	100.7	126.7	152.6	22.5	192.5	988.8
6654	6.0	7.8	9.6	30.0	39.1	48.2	6.7	59.4	312.2
6651	0.9	2.3	3.7	4.6	11.7	18.7	1.0	17.7	121.1

	Great Blue Heron			Mink		
Site	min	med	max	min	med	max
6660	-	-	-	-	-	-
6648	8.2	55.7	340.5	3.3	85.7	500.8
6697	0.7	24.0	169.1	0.3	36.9	248.7
6661	1.9	56.8	398.8	0.8	87.4	586.5
6698	5.8	73.1	486.2	2.3	112.5	715.2
6662	12.0	37.6	178.4	4.8	57.8	262.4
6663	-	-	-	-	-	-
6664	-	-	-	-	-	-
6665	100.2	645.7	3906.1	40.1	993.7	5745.3
66M76	47.5	244.6	1402.7	19.0	376.4	2063.1
6699	51.3	330.5	1998.5	20.5	508.5	2939.5
66M262	92.9	251.1	1087.9	37.1	386.5	1600.1
66M272	27.1	122.7	677.4	10.8	188.8	996.4
6666	29.5	133.9	740.4	11.8	206.0	1089.0
66M253	11.8	49.1	263.5	4.7	75.6	387.6
66M271	22.3	129.1	762.6	8.9	198.6	1121.6
66M144	66.8	160.3	634.3	26.7	246.6	933.0
6667	30.0	120.4	637.8	12.0	185.2	938.1
66M80	30.9	124.1	657.6	12.4	191.0	967.3
66M269	22.6	96.1	520.0	9.0	147.9	764.9
6668	20.1	232.4	1533.3	8.0	357.7	2255.2
66M264	49.1	159.6	770.7	19.6	245.7	1133.6
6669	42.4	230.2	1339.2	16.9	354.2	1969.7
66101	85.6	236.2	1037.7	34.2	363.6	1526.4
6654	25.5	72.9	327.6	10.2	112.2	481.9
6651	3.9	21.8	127.1	1.6	33.5	186.9

fishes [MeHg] > 92 ng/g

wildlife [MeHg] > 5000 ng/g

Table 14. Exceedences of criteria for predicted mercury concentrations in receptors based on three exposure and uptake scenarios for the St. Clair River study. The tissue residue guidelines (TRGs) are 92 ng/g ww for fishes and >5000 ng/g ww for wildlife (see text) (n = 19 for St. Clair River sites; n = 4 for reference sites).

Receptor	Scenario	Number of sites where $[Hg]_{rec}$ > TRG **and** reference maximum
Sucker	Minimum	0
Perch	Minimum	3
Walleye	Minimum	0
Heron	Minimum	0
Mink	Minimum	0
Sucker	Intermediate	0
Perch	Intermediate	7
Walleye	Intermediate	14
Heron	Intermediate	0
Mink	Intermediate	0
Sucker	Maximum	1
Perch	Maximum	14
Walleye	Maximum	15
Heron	Maximum	0
Mink	Maximum	1

Table 15. Decision matrix for weight-of-evidence categorization of St. Clair River sites. For the sediment chemistry column, sites with exceedences of the Severe Effect Level (SEL) for mercury (Flett Laboratory) are indicated by "●", and sites with exceedences of the Lowest Effect Level (LEL) by "◉". For the toxicity and benthic alteration columns, sites determined from BEAST analyses as toxic/severely toxic or different/very different are indicated by "●"; and sites determined as potentially toxic or possibly different from reference by "◉". Sites with no SQG exceedences, no sediment toxicity, or benthic communities equivalent to reference conditions are indicated by "O". Some sites show potential toxicity or benthic alteration but are not recommended for further action; in these cases, toxicity is minimal (limited to 1 of 10 endpoints measured) and does not appear related to sediment Hg and benthic communities are not deemed impaired.

Site (priority zone)	Sediment Total Hg	Toxicity	Benthos Alteration (2001 only)	Hg Biomagnification Potential	Assessment
6660 (Upstream)	O	O	◉	-[a]	No further actions needed
6648 (Upstream)	O	O	●	O	No further actions needed
6697 (Upstream)	O	O	●	O	No further actions needed
6661 (Upstream)	O	O	●	O	No further actions needed
6698 (Upstream)	O	O	●	O	No further actions needed
6662 (Zone A)	O	O	●	O	Determine reasons for benthos alteration
6663 (Zone A)	●	-[a]	O	-[a]	Fully assess risk of biomagnification[b]
6664 (Zone A)	●	◉	◉	-[a]	Fully assess risk of biomagnification[b]
6665 (Zone A)	●	O	◉	◉	Fully assess risk of biomagnification
66M76 (Zone A)	◉	O	-	◉	Fully assess risk of biomagnification
6699 (Zone B)	●	O	●	◉	Fully assess risk of biomagnification
66M262 (Zone B)	●	O	-	◉	Fully assess risk of biomagnification
66M272 (Zone B)	●	O	-	◉	Fully assess risk of biomagnification
6666 (Zone B)	◉	◉	●	◉	Fully assess risk of biomagnification
66M253 (Zone B)	◉	O	-	O	No further actions needed
66M271 (Zone B)	●	O	-	◉	Fully assess risk of biomagnification
66M144 (Zone B)	●	◉	-	◉	Fully assess risk of biomagnification
6667 (Zone B)	●	O	●	◉	Fully assess risk of biomagnification
66M80 (Zone B)	●	O	-	◉	Fully assess risk of biomagnification
66M269 (Zone B)	◉	O	-	O	No further actions needed
6668 (Zone B)	◉	O	●	◉	Fully assess risk of biomagnification
66M264 (Zone B)	◉	O	-	◉	Fully assess risk of biomagnification
6669 (Zone B)	●	O	●	◉	Fully assess risk of biomagnification
66101 (Downstream)	◉	O	-	◉	Fully assess risk of biomagnification
6654 (Downstream)	◉	O	●	O	No further actions needed
6651 (Delta)	O	O	◉	O	No further actions needed

[a]no data; [b]risk of biomagnification was determined from the high sediment [Hg] and the strong relationship between Hg in the sediment and Hg in the benthic invertebrates (see Sections 5.5.1 & 5.7 for details).

APPENDIX A. Literature Review of Biomagnification Factors

1.0 Introduction

This literature review was carried out to provide supporting information for the assessment of risk of biomagnification of mercury from contaminated sediments in the St. Clair River, Ontario. Biomagnification factors (BMFs), predator-prey factors (PPFs), and trophic transfer coefficients (TTCs) were obtained or derived from the literature for the calculation of total mercury and methylmercury concentrations in different trophic levels of a simple benthic freshwater food chain model (Figure A1).

The search was focused on the period 1996-2002, as a thorough review of the literature was carried out in 1997 by USEPA (1997a,b,c). Obtaining the information required to estimate mercury concentrations in receptors involved reviewing published literature, unpublished reports, databases, web pages and any other sources of data on BMFs relevant to the benthic invertebrate taxa and receptors; assessing the quality of the BMF data; and tabulating BMFs and estimates of their variability, together with information on the BMF's determination (e.g., location of study, organisms involved, proportion of receptor's diet that is invertebrates, effects of cofactors (if any), assumed ingestion rates and home ranges). The following criteria were applied to screen literature to obtain either BMFs or candidate datasets for calculating BMFs, after Suedel et al. (1994) and Gobas and Morrison (2000):

- If organisms that were presented were not from a logical food chain, or no evidence was presented that the feeding relationship between predator and prey was a functional feeding relationship, the data were not used. One exception to this rule was made in selecting a study of mink fed diets of different proportions of contaminated and uncontaminated fish (Halbrook et al., 1997), since there was a reasonable likelihood that these fish species would have been part of their diet.
- Mean concentrations of total Hg or MeHg needed to be presented for both predator and prey, and in comparable units.
- BMFs involving Hg concentrations in feathers or fur of predators were excluded.
- Unless evidence of comparability could be found, studies from non-freshwater systems or with non-comparable species were not used. More information is presented below on the assessment of comparability of different systems and species.

There were few studies that quoted BMF estimates specifically for the receptor species and feeding relationships defined in Figure A1. Of the small number of studies that calculated BMFs that were directly comparable in part to the food chain model, most were from freshwater pelagic foodwebs. Some were also studies in different ecosystems (marine, temperate montane freshwater, tropic freshwater). Thus, it was necessary to use the most relevant studies to obtain BMFs and document the relative comparability of different species and ecosystems to those presented in the study design for this assessment. Information to support substitutions of receptor with comparable species from the literature (in applying BMF estimates) is presented in Tables A3 - A12. Species were considered the most qualitatively similar when they occupied similar habitats, had similar feeding habits and dietary composition, similar range, similar feeding substrate, and similar food ingestion:body weight ratio. Sources for this information were CCME (1999), CWS (2002), Sample and Suter (1999), Scott and Crossman (1973), and USEPA (1997c). A breakdown of the number of BMFs obtained/calculated per feeding relationship, and the range of corresponding BMF values is presented in Table A1.

1.1 Terminology

Biomagnification is the process at by which the chemical concentration in an organism exceeds that in the organism's diet, due to dietary absorption (Gobas and Morrison 2000). The biomagnification factor (BMF) is an empirically-derived measure of the rate of contaminant transfer between the organism's diet and the organism, and is expressed as the ratio of chemical concentration in the organism to the concentration in its diet (Gobas and Morrison 2000). The synonymous terms predator-prey factor (PPF) and trophic transfer coefficient (TTC) are also found in the literature (USEPA 1997a; Suedel et al. 1994). A food chain multiplier (FCM) is used to quantify the increase in contaminant body burden through uptake from the food chain, but is defined as the factor by which a

substance at higher trophic levels exceeds the bioconcentration factor (BCF) at trophic level 1 (NCASI, 1999; USEPA, 1997a). Therefore, it does not necessarily apply to a specific trophic transfer, and may be a multiple of more than one BMF. BMFs, TTCs, and PPFs are unitless, and the concentrations used to derive them are usually expressed in units of mass of chemical per kg of the organism, and mass of chemical per kg of food, respectively (Gobas and Morrison 2000). These concentrations can be expressed on a wet weight or dry weight basis (Gobas and Morrison, 2000). BMFs, TTCs, and PPFs can be applied to specific trophic levels, as well as individual species in a food chain (USEPA, 1997b). The term BMF will be used in this document in reference to biomagnification factors, predator-prey factors, and trophic transfer coefficients acquired from the literature.

2.0 Methods

2.1 Literature Search

The literature search was done using typical methods of electronic database and chain-of-citation searches as well as consultation with leading researchers in the field of mercury ecotoxicology and risk assessment. The following electronic databases were used to search primary literature, secondary literature, grey literature, and internet resources:

- ISI Current Contents Connect
- CSA Aquatic Sciences and Fisheries Abstracts (ASFA)
- CSA TOXLINE
- MEDLINE
- National Research Council of Canada (NRC) Research Press database
- US Environmental Protection Agency (USEPA)- various databases of government publications
- US Army Corp. of Engineers (USACE)- various databases of government publications
- Integrated Risk Information System (IRIS)
- Environmental Fate Database (EFDB)
- Oak Ridge National Laboratory (ORNL) publications

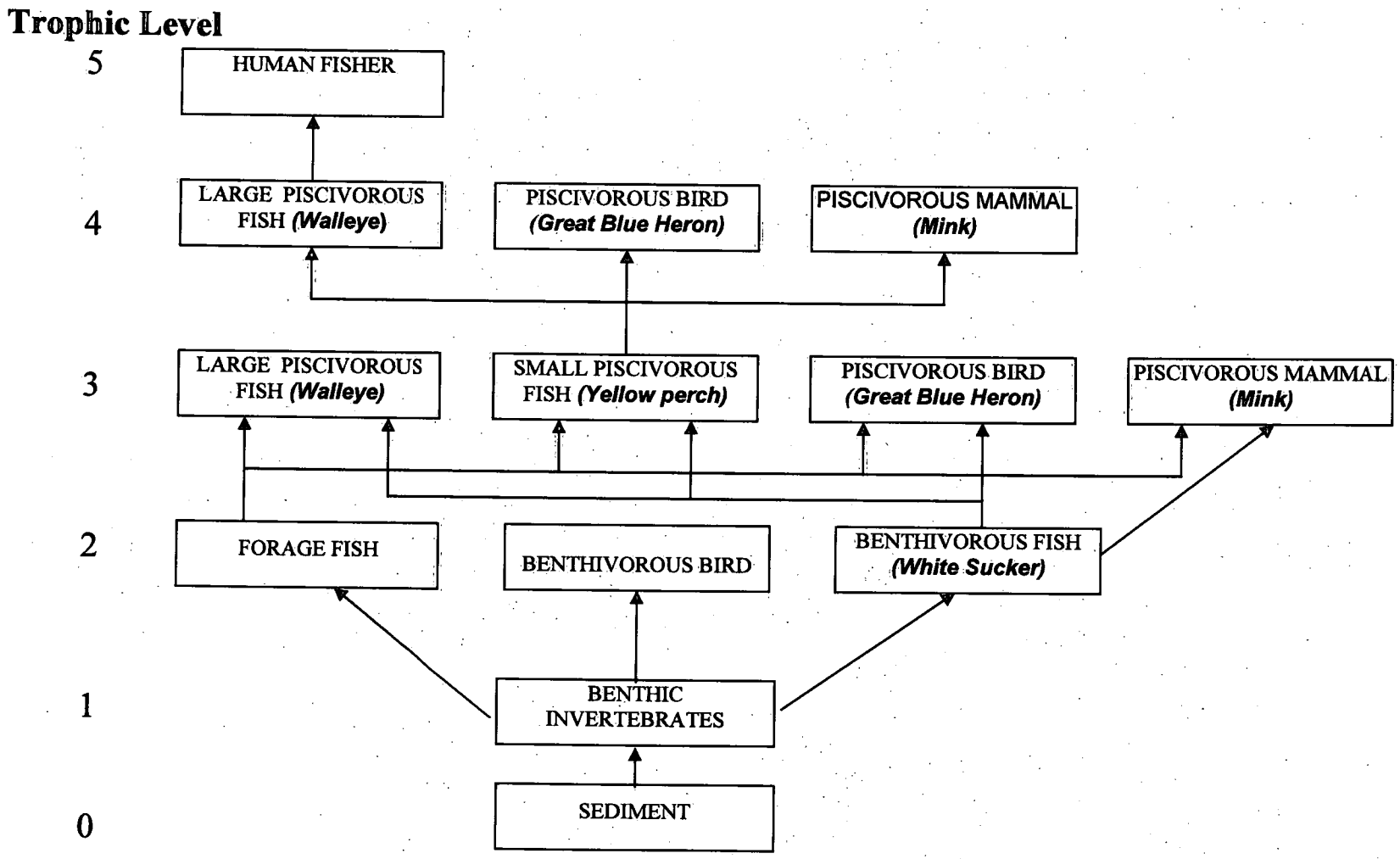


Figure A1. Generalized foodweb model for the assignment of trophic level to biomagnification factor estimates.

In addition, the following journals were individually searched for recent and upcoming articles:

- *Archives of Environmental Contamination and Toxicology*
- *Archives of Environmental Health*
- *Bulletin of Environmental Contamination and Toxicology*
- *Canadian Journal of Fisheries and Aquatic Sciences*
- *Chemosphere*
- *Environmental Pollution*
- *Environmental Research*
- *Hydrobiologia*
- *Journal of Great Lakes Research*
- *Science of the Total Environment*
- *Water, Air, and Soil Pollution*
- *Water Research*

Several researchers active in mercury bioaccumulation studies were also contacted as part of the literature search.

The search was focused on the period 1996-2002, as a thorough review of the literature was carried out in a 1997 USEPA document entitled "Mercury Study Report to Congress" document (USEPA, 1997a,b,c).

2.2 Assigning Trophic Levels to Receptor Species

Discrete trophic levels were applied using the food chain model (Figure A1). This was done to allow comparison of BMFs from different systems/foodwebs, as well as to conceptualize the transfer and magnification of mercury in the St. Clair River scenario. However, the use of discrete trophic levels may lead to lower estimates of BMFs. An excellent discussion about the effects of omnivory on trophic position is found in Vander Zanden and Rasmussen (1996). In short, omnivory is common in aquatic communities (for example, up to 50% in pelagic food webs), and the use of discrete variables to represent trophic position will not adequately account for omnivory. When omnivory is integrated with the use of a continuous measurement of trophic position (ie- using stable isotope methods), estimates of BMFs will generally be higher for each discrete trophic level (Vander Zanden and Rasmussen, 1996). Unfortunately, this literature survey did not yield any stable isotope studies on benthic freshwater food webs, and therefore system-specific BMFs based on continuous trophic position could not be obtained for lower trophic levels. Two such estimates for trophic levels 3 and 4 respectively, were obtained from pelagic foodweb studies.

2.3 Selecting Biomagnification Factor Estimates or Candidate Datasets from the Literature

The following criteria were applied to screen literature to obtain either BMFs or candidate datasets for calculating BMFs, after Suedel et al. (1994) and Gobas and Morrison (2000):

- If organisms that were presented were not from a logical food chain, or no evidence was presented that the feeding relationship between predator and prey was a functional feeding relationship, the paper was not used. One exception to this rule was made in selecting a study of mink fed diets of different proportions of contaminated and uncontaminated fish (Halbrook et al., 1997), since there was a reasonable likelihood that these fish species would have been part of their diet.
- Mean concentrations of total Hg or MeHg needed to be presented for both predator and prey, and in comparable units.
- Unless evidence of comparability could be found, studies from non-freshwater systems or with non-comparable species were not used. More information is presented below on the assessment of comparability of different systems and species.

2.4 Calculation of Biomagnification Factors from Candidate Datasets

Biomagnification factors were calculated from mean concentrations of total mercury and/or methylmercury from the literature using the equation (Gobas and Morrison 2000):

$$BMF = C_B/C_D$$

where:
C_B= mean contaminant concentration in the consumer (receptor) species
C_D= mean contaminant concentration in the diet of the organism

In all cases where BMFs were calculated from mean concentrations, the calculation was for the mean concentrations from two trophic levels with a functional feeding relationship which was defined and demonstrated in the study. Where results were presented for a number of different locations (ie- several different lakes), BMFs were calculated for each location and then averaged, as opposed to averaging the mean concentrations from all locations to calculate a BMF. In three cases (Hughes, 1997; Neumann and Ward, 1999; Suedel et al., 1994), a mean BMF was calculated by averaging several reported BMFs. Summaries of these calculations are presented in Tables A3 - A12.

2.5 Comparability of Species and Systems

There were very few studies which quoted BMF estimates for the receptor species and feeding relationships defined in Figure A1. Of the small number of studies which calculated BMFs that were directly comparable in part to the food chain model, most were from freshwater pelagic foodwebs. Some were also studies in quite different ecosystems (marine, temperate montane freshwater, tropic freshwater). Thus, it was important to document the relative comparability of different species and ecosystems to those presented in the study design for this assessment. Information to support substitutions of receptor species for comparable species from the literature (in applying BMF estimates) is presented in Tables A3 - A12. Species were considered the most qualitatively similar when they occupied similar habitats, had similar feeding habits and dietary composition, similar range, similar feeding substrate, and similar food ingestion:body weight ratio. Sources for this information were CCME (1999), CWS (2002), Sample and Suter (1999), Scott and Crossman (1973), and USEPA (1997c).

Applying BMFs calculated from one system to another is controversial, since rates of trophic transfer of mercury are thought to vary due to abiotic and biotic factors (USEPA, 2001). The USEPA, in developing national bioaccumulation factors to assess the risk to human health of mercury exposure, indicated that these factors are poorly understood and are likely to be system and site-specific (USEPA, 1997b; USEPA, 2001). Abiotic factors which may influence the chemistry of mercury include pH, temperature, and dissolved organic carbon in the waterbody, and these are usually determined by watershed characteristics which in turn affect inputs, bioavailability, speciation, and methylation of mercury in the sediments and water column (Downs et al., 1998; Greenfield et al., 2001; Meyer, 1998; Mason et al., 2000; USEPA, 2001; Watras et al., 1998). Biotic factors include food chain length, horizontal food web structure, feeding mechanisms of organisms at lower trophic levels, and the age/size/weight or metabolic rates of individuals in the sample used to calculate a given BMF (Environment Canada, 1997; Power et al., 2002; USEPA, 2000). However, no single factor has been correlated with extent of bioaccumulation in all cases examined (USEPA, 2001).

It was also suggested (as discussed above) that much of the uncertainty around applying BMFs from different systems may be due to an oversimplification of predator-prey relationships by using discrete trophic levels (Vander Zanden and Rasmussen, 1996). One stable isotope study was found from Papua, New Guinea whose results indicated similar magnitude of biomagnification to temperate and arctic foodwebs (Bowles et al., 2000). Another stable isotope study from an arctic foodweb indicated that age did not affect bioaccumulation of mercury in the muscle of ringed seals or clams (Atwell et al, 1997). A third from a subarctic lake found a higher rate of biomagnification (BMF=5.4 versus 3.0) than for a comparable freshwater temperate system (Power et al., 2002).

Unless the relative comparability to temperate freshwater systems was demonstrated, studies from marine, arctic marine, and tropic freshwater were not used to select or derive BMFs.

3.0 Results

A total of 80 references were examined in detail to yield BMFs, datasets to calculate BMFs, or to provide supporting information in applying BMFs. Results are broken down as follows:

- Primary literature- 61 references

- Secondary literature- 5 references
- Grey literature- 14 references

Of those 80, only 11 yielded appropriate BMFs or datasets, following guidelines set out in section 2 above. However, a number of the references (Cantox Environmental Inc., 2001; Suedel et al., 1994; USEPA, 1997a) were reviews which synthesized BMFs from several sources. Along with BMF estimates, the following supporting information was gathered:

- Range, standard deviation, or standard error of BMF estimates
- Trophic level of predator/receptor
- Type of study (field, laboratory, modeling, review)
- Prey species
- Predator species
- Mercury parameter (total Hg or MeHg)
- Scope of study (ie- number of lakes sampled)
- Location of study
- Biological medium sampled
- Relative age/size of organisms sampled
- Reference from which BMF or dataset came from
- Comments

These results are reported in Table A2.

A breakdown of the number of BMFs obtained/calculated per feeding relationship, and the range of corresponding BMF values is presented in Table A1.

Table A1- Breakdown of results of literature review for each hypothetical feeding relationship

Feeding Relationship	Trophic levels of transfer	# of Estimates	Total and Methyl Hg BMFs			Comments
			Low	Medium *	High	
Benthic invertebrates to forage or benthivorous fish	1 - 2	1	3.43	3.43	3.43	High BMF calculated from benthos [THg] values which are below DL excluded.
Benthivorous or forage fish to small piscivorous fish	2 - 3	1	5	5	5	
Benthivorous or forage fish to large piscivorous fish	2 - 3	8	1.12	3.20	32.4	
Benthivorous or forage fish to piscivorous bird	2 - 3	1	6.80	6.80	6.80	High THg value from heron with ambiguous feeding relationship dropped.
Benthivorous or forage fish to piscivorous mammal	2 - 3	10	1.70	5.20	22.64	High THg value from fur/hair excluded. Hg form given as total and methyl for most values.
Small piscivorous fish to large piscivorous fish	3 - 4	1	2.40	2.40	2.40	
Small piscivorous fish to piscivorous bird	3 - 4	6	0.85	2.37	6.80	High THg values from plumage excluded.
Small piscivorous fish to piscivorous mammal	3 - 4	9	1.70	4.7	10.00	Hg form given as total and methyl for most values.

* "Medium" = datum if n = 1, median if n > 2

Table A2. Summary of literature-derived biomagnification factors by trophic level.

Table B2- Summary of Literature-Derived Biomagnification Factors by Trophic Level

Value	Range	Trophic Level	Type of Study	Prey Species	Predator Species	Hg Parameter	Scope	Location	Sample Medium	Age/Size of Sample	Reference	Comments
2.14	0.3-7	2	Review	"Primary consumers" (aquatic)	"Secondary consumers" (aquatic)	Total Hg					Suedel et al., 1994.	Values reported as TTCs
3.43	0.5-10.5	2	Review	"Primary consumers" (aquatic)	"Secondary consumers" (aquatic)	MeHg					Suedel et al., 1994	Values reported as TTCs
27.13	Not calculated	2	Field	Benthos	Carp and bullhead	Total Hg	One estuary	Old Woman Creek, Lake Erie	Skinless fillets (carp), whole body (bullhead)	>30 cm in length	Francis et al., 1998	BMFs calculated from mean concentrations and feeding relationships reported in paper
1.12	0.2-1.9	3	Review	"Secondary consumers" (aquatic)	"Top predators" (aquatic)	Total Hg					Suedel et al., 1994	Values reported as TTCs
1.51	Not calculated	3	Field	Lake chubsucker	Redfin pickerel	Total Hg	Nine wetlands	Savannah River Site, South Carolina	Whole body	Chubsucker mean length/weight=79 mm/4g Pickerel mean length/weight= 106 mm/3g	Snodgrass et al., 2000	Mean BMF calculated from individual wetland BMFs, which were calculated from geometric mean concentrations in each species for each wetland Feeding relationship implied by results cited from other studies from that area
1.55	1.3-1.8	3	Field	Groove-snouted catfish (omnivore) and seven-spotted archerfish (insectivore)	Barramundi, giant freshwater anchovy, Sepik gurjeke	MeHg	One lake	Papua, New Guinea	Whole body		Bowles et al., 2001	Stable isotope (δ15N) study. Results suggest that the biomagnification power of the food web is similar to that of temperate-lake and arctic-marine systems Range of BMFs based on BMFs calculated from +/- 1 SD from mean MeHg concentrations
1.70	Not reported	3	Review	Only reported as "concentration of MeHg in diet"	Otter	Total Hg and MeHg	Pooled results of twelve studies	Ontario (3 studies), Georgia (3), Louisiana (1), Manitoba (2), Wisconsin (2), Norway (1)	Muscle	Not reported	Cantox Environmental Inc., 2001	Sampling details from Wren et al., 1986 BMF calculated by Cantox Environmental Inc
2.40	1.4	3	Field	Bluegill, black crappie, yellow perch	Chain pickerel, largemouth bass	Total Hg	Two lakes	Connecticut	Axial muscle (whole fillets)	Fish aged 2-5 years	Newmann and Ward, 1999	
2.70	Not reported	3	Review	Fish (species not reported)	Otter	Total Hg and MeHg	Not reported	Georgia	Muscle	Not reported	Cantox Environmental Inc., 2001	BMF calculated by Cantox Environmental Inc
3.60	Not reported	3	Review	Only reported as "concentration of MeHg in diet"	Otter	Total Hg and MeHg	One lake, N=20 for fish sample, N=4 for otter sample	Tadenac Lake, Muskoka, Ontario	Muscle	Not reported	Cantox Environmental Inc., 2001	Sampling details from Wren et al., 1983 BMF calculated by Cantox Environmental Inc
3.40	Not reported	3	Review	Fish (species not reported)	Otter	Total Hg and MeHg	Not reported	Not reported	Liver	Not reported	Cantox Environmental Inc., 2001	BMF calculated by Cantox Environmental Inc.
4.00	Not reported	3	Modelling	Pelagic forage fish (smelt, ciscoes, coregonids, shiners, ninespine stickleback)	Lake trout	Total Hg	56 lakes, >10 individuals/species, period 1975-84 (source= MOE sportfish contaminants monitoring)	Canadian Shield lakes, Ontario	Whole skinless fillets (smaller fish), axial muscle (larger fish)	Pooled results	Vander Zanden and Rasmussen, 1996	BMF corrected by authors for omnivory from original value of 2.0 defined by Cabana et al., 1994 Correction based on results of δ15N stable isotope study of trophic position and effects of omnivory on trophic position Sampling details from Cabana et al
4.70	Not reported	3	Review	Only reported as "concentration of MeHg in diet"	Otter	Total Hg and MeHg	Pooled results of twelve studies	Ontario (3 studies), Georgia (3), Louisiana (1), Manitoba (2), Wisconsin (2), Norway (1)	Liver	Not reported	Cantox Environmental Inc., 2001	Sampling details from Wren et al., 1986 BMF calculated by Cantox Environmental Inc
5.80	Geometric SD=1.47	3	Review	"Forage fish"	"Piscivorous fish"	MeHg.	14 studies	Michigan (2 studies), Ontario (5), Manitoba (1), Wisconsin (1), New York (1), Norway (1), Sweden (2), Brazil (1)	Various	Various	USEPA, 1997	BMF is geometric mean of values from literature review. Selected values from the literature used in the calculation of the average BMF are presented in attached "USEPA, 1997" worksheet
5.60	Not reported	3	Field	Forage fish (burbot, cisco, northern lake chub, round whitefish, threespine stickleback) and benthivores (longnose sucker, slimy sculpin)	Lake trout	Total Hg	One lake	Stewart Lake, northern Labrador	Dorsal muscle	All age classes	Power et al., 2002	BMF reported in study Stable isotope study of a subarctic freshwater lacustrine system
5.70	Not reported	3	Review	Fish (species not reported)	Otter	Total Hg and MeHg	Not reported	Georgia	Liver	Not reported	Cantox Environmental Inc., 2001	BMF calculated by Cantox Environmental Inc
6.00	Not reported	3	Review	Bluntnose minnow, rainbow smelt	Common loon	Total Hg	One lake, N=20 for fish sample, N=1 for loon sample	Tadenac Lake, Muskoka, Ontario	Whole skinless fillet (fish), breast muscle (birds)	Pooled sample of fish from beach seining (fish) Loon= 5 kg	Cantox Environmental Inc., 2001	Sampling details from Wren et al., 1983 BMF calculated by Cantox Environmental Inc.
10.00	Not reported	3	Review	Fish (species not reported)	Otter	Total Hg and MeHg	Not reported	Not reported	Not reported	Not reported	Cantox Environmental Inc., 2001	BMF calculated by Cantox Environmental Inc.
10.00	Not reported	3	Review	Fish (species not reported)	Otter	Total Hg and MeHg	Not reported	Not reported	Liver	Not reported	Cantox Environmental Inc., 2001	BMF calculated by Cantox Environmental Inc.
14.29	Not calculated	3	Field	Carp, bullhead, catfish (<30 cm length)	Bowfin, catfish (>30 cm length)	Total Hg	One estuary	Old Woman Creek, Lake Erie	Skinless fillets (carp, bowfin, catfish), whole body (bullhead)	Piscivores= >30 cm in length, benthivores= <30 cm length	Francis et al., 1998	BMFs calculated from mean concentrations and feeding relationships reported in paper.
32.40	0.1-141	3	Review	"Secondary consumers" (aquatic)	"Top predators" (aquatic)	MeHg					Suedel et al., 1994	Values reported as TTCs
85.56	Not calculated	3	Field	Carp, bullhead, catfish (<30 cm length); gizzard shad, black crappie	Great blue heron	Total Hg	One estuary	Old Woman Creek, Lake Erie	Skinless fillets (carp, catfish, crappie), whole body (bullhead, gizzard shad)	Benthivores= <30 cm length, heron (N=1) size not reported	Francis et al., 1998	BMFs calculated from mean concentrations and feeding relationships reported in paper
87.81	92-96	3	Field	Freshwater and intertidal fishes	Otter	Total Hg	One coastal creek and estuary (N= 32 otters)	Prince William Sound, Alaska	Fur	Juveniles to old adults (four age categories)	Ben-David et al., 2001	BMF calculated from mean concentrations and standard errors presented in paper. The feeding relationship with freshwater fishes was supported by stable isotope measurements
Liver- 13.92 Kidney- 22.64 Hair- 108.23	Liver- 12-17 Kidney- 20-25 Hair- 87-149	3	Controlled field	Benthivores	American mink	Total Hg	50 female farmed mink	Oak Ridge National Laboratory, Tennessee	Liver, kidney, and fur	Female adults	Halbrook et al., 1997	BMFs calculated from mean concentrations in different tissues and different specific dietary mixes of contaminated and uncontaminated fish

Table A2. Continued.

Table B2- Summary of Literature-Derived Biomagnification Factors by Trophic Level (continued)

Value	Range	Trophic Level	Type of Study	Prey Species	Predator Species	Hg Parameter	Scope	Location	Sample Medium	Age/Size of Sample	Reference	Comments
1.70	Not reported	4	Review	Only reported as "concentration of MeHg in diet"	Otter	Total Hg and MeHg	Pooled results of twelve studies	Ontario (3 studies), Georgia (3), Louisiana (1), Manitoba (2), Wisconsin (2), Norway (1)	Muscle	Not reported	Cantox Environmental Inc., 2001	Sampling details from Wren et al., 1986 BMF calculated by Cantox Environmental Inc.
1.83	1-4	4	Field	Yellow perch	Osprey	Total Hg (osprey), MeHg (yellow perch)	Five osprey nesting areas	St. Mary's R., Georgian Bay, Kawartha Lakes, New Jersey	Eggs	Freshly laid and addled eggs	Hughes, 1997	
2.40	1-4	3	Field	Bluegill, black crappie, yellow perch	Chain pickerel, largemouth bass	Total Hg	Two lakes	Connecticut	Axial muscle (whole fillets)	Fish aged 2-5 years	Neumann and Ward, 1999	
2.70	Not reported	4	Review	Fish (species not reported)	Otter	Total Hg and MeHg	Not reported	Georgia	Muscle	Not reported	Cantox Environmental Inc., 2001	BMF calculated by Cantox Environmental Inc.
3.00	Not reported	4	Review	Only reported as "concentration of MeHg in diet"	Otter	Total Hg and MeHg	One lake, N=20 for fish sample, N=4 for otter sample	Tadenac Lake, Muskoka, Ontario	Muscle	Not reported	Cantox Environmental Inc., 2001	Sampling details from Wren et al., 1983 BMF calculated by Cantox Environmental Inc.
3.40	Not reported	4	Review	Fish (species not reported)	Otter	Total Hg and MeHg	Not reported	Not reported	Liver	Not reported	Cantox Environmental Inc., 2001	BMF calculated by Cantox Environmental Inc.
4.20	Not reported	4	Review	Only reported as "concentration of MeHg in diet"	Otter	Total Hg and MeHg	Pooled results of twelve studies	Ontario (3 studies), Georgia (3), Louisiana (1), Manitoba (2), Wisconsin (2), Norway (1)	Liver	Not reported	Cantox Environmental Inc., 2001	Sampling details from Wren et al., 1986 BMF calculated by Cantox Environmental Inc.
5.70	Not reported	4	Review	Fish (species not reported)	Otter	Total Hg and MeHg	Not reported	Georgia	Liver	Not reported	Cantox Environmental Inc., 2001	BMF calculated by Cantox Environmental Inc.
6.00	Not reported	4	Review	Smallmouth bass, northern pike, lake trout	Common loon	Total Hg	One lake, N=20 for fish sample, N=1 for loon sample	Tadenac Lake, Muskoka, Ontario	Dorso lateral muscle (fish), breast muscle (birds)	Pooled sample of fish from gill netting (fish) Loons 5 kg	Cantox Environmental Inc., 2001	Sampling details from Wren et al., 1983 BMF calculated by Cantox Environmental Inc.
10.00	Not reported	4	Review	Fish (species not reported)	Otter	Total Hg and MeHg	Not reported	Not reported	Not reported	Not reported	Cantox Environmental Inc., 2001	BMF calculated by Cantox Environmental Inc.
10.00	Not reported	4	Review	Fish (species not reported)	Otter	Total Hg and MeHg	Not reported	Not reported	Liver	Not reported	Cantox Environmental Inc., 2001	BMF calculated by Cantox Environmental Inc.
10.00		4	Review	Predatory fishes	American mink	MeHg	Not reported	Not reported	Not reported	Not reported	USEPA, 2000	
14.58	12-16	4	Field	Yellow perch	Osprey	Total Hg (osprey), MeHg (yellow perch)	Five osprey nesting areas	St. Mary's R., Georgian Bay, Kawartha Lakes, New Jersey	Feathers- wing/mantle/tail	Pooled sample from chicks and adults	Hughes, 1997	
Liver 2.81 Kidney 3.81 Brain 0.85 Muscle 1.48 Feathers 95.7	Not calculated	4	Field	Northern pike, coregonids, walleye, suckers	Osprey	Total Hg	130 nests in three major watersheds in areas impacted and not impacted by hydroelectric development	James Bay/Hudson Bay areas, Quebec	Liver, kidney, brain, breast muscle, and feathers of osprey	Chicks and adults	Des Granges et al., 1998	BMFs calculated from mean concentrations in different tissues and weighted mean concentrations in main fish species consumed in the diet Evidence for feeding relationship established in the paper

Table A3- Data summary and calculations from Suedel et al., 1994

Parameter	Trophic Level 2	Trophic Level 3
BMF Total Hg	0.3	0.2
	0.3	0.4
	1.6	1
	1.7	1.4
	6.8	1.8
		1.9
Mean	**2.14**	**1.12**
BMF MeHg	0.5	0.1
	0.7	0.2
	2	0.3
	10.5	0.7
		4.5
		80
		141
Mean	**3.425**	**32.4**

Note- data from literature used to derive BMFs (reported as trophic transfer coefficients (TTCs)) were expressed in comparable units measured in organisms which were part of functional food chains/feeding relationships.

Table A4- Data summary and calculations from Hughes, 1997

Location	Feather/YP (4-5)	Feathers/YP (20)	Eggs/YP (4-5)	Eggs/YP (20)
St. Mary's River	12.33	15.74	1.07	1.36
Georgian Bay	12.00	21.71	2.05	3.71
Kawartha Lakes	13.58	11.64	1.83	1.57
Mean BMF	**14.50**		**1.93**	

Notes- YP=yellow perch. (4-5)=yellow perch aged 4-5 years, (20)= 20 cm yellow perch. Data presented are unitless BMFs. Mean BMFs are for mercury in feathers and eggs, averaged for both groups of prey each. Mercury concentrations used to derive BMFs were ug/g dry weight total Hg.

Table A5- Data summary and calculations from Neumann and Ward, 1999

		BMF @ age				
Lake	**Species**	**Age 2**	**3**	**4**	**5**	**Lake Average BMF**
Pickerel	Black crappie->TP	3.7	3.1	2.7	2.2	2.88
	Bluegill->TP	2.4	2.6	2.9	3.4	
Lillinonah	Yellow perch->TP	1.4	1.4	1.3	1.2	1.93
	Bluegill->TP	1.9	2.3	2.7	3.2	
					Mean	**2.40**

Notes- TP=top predators- largemouth bass, smallmouth bass, and chain pickerel. Mercury concentration values used to derive BMFs were expressed in ug/g dry weight total Hg.

Table A6- Data summary and calculations from Bowles et al., 2001

Species	Trophic Level	Mean [MeHg]	+1SD	-1SD
Arius bernyi	2	0.18	0.33	0.03
Toxotes chatareus	2	0.29	0.44	0.14
Mean [MeHg] TL2		0.24	0.38	0.09
Strongylura kreffti	3	0.38	0.63	0.14
Thryssa scratchleyi	3	0.34	0.66	0.02
Lates calcarifer	3	0.46	0.76	0.16
Mean [MeHg] TL3		0.39	0.68	0.10
BMFs	**2 --> 3**	**1.67**	**1.78**	**1.20**
Mean BMF		**1.55**		

Note-*A. bernyi*=groove-snouted catfish*T. chatareus*=seven-spotted archerfish*S. kreffti*=Sepik garpike,*T.scratchleyi*=giant freshwater anchovy, *L. calcarifer*=barramundi. All concentrations used to derive BMFs were expressed as ug/g wet weight MeHg.

Table A7- Summary of BMFs used in USEPA's (1997) PPF calculation

BMF	Predator	Prey	Location
2.75	lake trout	bloater	L. Michigan
3.5	northern pike, largemouth bass	yellow perch, white sucker	35 lake aggregate, upper michigan
3.6	northern pike, largemouth bass	rainbow smelt, whitefish	L. Tyrifjorden, Norway
4	northern pike, walleye	specific weighted diets	L. Simcoe
5	lake trout (60 cm)	rainbow smelt (15 cm)	9 lake aggregate, Ontario
5.06	northern pike, walleye	white sucker, cisco	average of 6 Canadian Shield lakes
5.22	walleye (age 5)	yellow perch (age 2)	10 lake aggregate, Wisconsin
5.63	smallmouth bass, walleye	gizzard shad, bluegill	Onandaga Lake, New York
6.8	northern pike	yellow perch	43 lake aggregate, Sweden
7.1	largemouth bass	silversides	Clear L., California
7.4	northern pike	yellow perch	25 lake aggregate, Sweden
9.8	northern pike	spottail shiner, yellow perch	4 lake average, Manitoba

Table A8- Data summary and calculations from Ben-David et al., 2001

Trophic Transfer	Mean [total Hg]	+1 SE	-1 SE	Comments
Jackpot Bay freshwater fishes	0.12	0.14	0.1	Dolly Varden, coastrange sculpin, sticklebacks
Jackpot Bay intertidal fishes	0.085	0.092	0.07	Rockfish, kelp greenling, crescent gunnels, intertidal sculpins,
Mean Jackpot Bay fishes	0.1025	0.116	0.085	
Jackpot Bay otters	9	9.5	8.2	River otter
BMF	**87.80**	**81.90**	**96.47**	

Note- all mercury concentrations used to calculate BMFs were expressed as mg/kg dry weight total Hg. Standard errors used were those reported in the study. Both intertidal and freshwater fish Hg concentrations were used due to stable isotope dietary analysis which indicated a significant portion of intertidal fish in diet.

Table A9- Data summary and calculations for Des Granges et al., 1998

Type of Habitat	mean [Fish]	mean [Liver]	mean [Kidney]	mean [Brain]	mean [Muscle]	mean [Feathers]
Developed	1.420	3.610	5.280	1.010	1.790	58.090
Natural	0.234	0.720	0.910	0.230	0.360	16.470

BMF per Habitat	Liver	Kidney	Brain	Muscle	Feathers
BMF Developed	2.542	3.718	0.711	1.261	40.908
BMF Natural	3.080	3.893	0.984	1.540	70.460
Mean BMF	**2.811**	**3.806**	**0.848**	**1.400**	**55.684**

Note- concentrations are expressed in mg/kg dry weight total Hg. "Developed" areas are nesting sites on hydroelectric reservoirs.

Table A10- Data summary and calculations from Halbrook et al., 1997

Diet	mean [Diet]	mean [Liver]	mean [Kidney]	mean [Hair]
B	0.05	0.61	1.25	7.43
D	0.15	1.93	3.47	13.44
E	0.22	3.67	4.35	19.03

Diet	BMF Liver	BMF Kidney	BMF Hair
B	12.20	25.00	148.60
D	12.87	23.13	89.60
E	16.68	19.77	86.50
Mean BMF	13.92	22.64	108.23
Range	12-17	20-25	87-149

Table A11- Data summary and calculations for Snodgrass et al., 2000

Wetland	Gmean[total Hg] benthivore	Gmean[total Hg] top predator
40	0.18	0.26
41	0.32	0.49
42	0.19	0.32
77	0.63	1.05
97	0.27	0.24
136	0.33	0.68
139	0.28	0.35
142	0.2	0.31
Mean		

Note- benthivore= lake chubsucker, top predator= redfin pickerel, Gmean=geometric mean. All concentrations are expressed in ug/g dry weight total Hg.

Table A12- Data summary and calculations from Francis et al., 1998

Receptor	Mean [Total Hg]	Mean [MeHg]	Cutoff
Benthos	0.003		
Carp Sm	0.019	0.015	<30 cm
Carp Lg.	0.100	0.101	>30 cm
Catfish Sm.	0.066	0.064	<30 cm
Catfish Lg.	0.199	0.199	>30 cm
Bullhead	0.003	0.003	
Bowfin	0.636	0.613	
Great Blue Heron	1.620		
Crappie	0.003	0.001	
Gizzard Shad	0.004	0.002	

Trophic Transfer	Trophic Level	BMF	Details
Benthos-Benthivores	2	17.128	mean[large carp+bullhead]/[benthos]
Benthivores-Large Piscivores	3	14.294	mean[bowfin+large catfish]/mean[small carp+bullhead+small catfish]
Benthivores-Piscivorous Birds	4	85.563	[heron]/mean[small carp+bullhead+small catfish+crappie+gizzard shad]

Note- Benthos= oligochaetes, larval Chironomids, Ceratopogonidae, Chaoboridae. Carp and catfish were grouped into small and large size classes to reflect their variable trophic level with size. Functional feeding relationships were defined in the study. BMFs were only derived for total Hg. Mercury concentrations were expressed as ug/g wet weight of total Hg and MeHg.

Table A13. Summary information to compare alternate species to receptor species.

Table B13- Summary information to compare alternate species to receptor species

Trophic Level	Latin Name	Common Name	Receptor Species Comparison	Habitat	Range Include Cornwall?	Food Type	Food Substrate	Feeding Technique	Food Ingestion: Body Weight Ratio	Food Size Class	Source	Other
2	*Bucephala clangula*	Common goldeneye	Common goldeneye	Lakes/ponds/rivers	Yes	Omnivore	Freshwater benthic	Bottom forager	0.3		CCME, 1999, CWS, 2002	
2	*Bucephala albeola*	Bufflehead	Common goldeneye	Lakes/ponds/rivers	No, but in Great Lakes	Omnivore	Freshwater benthic	Gleaner	0.36		CCME, 1999, CWS, 2002	
2	*Aythya valisineria*	Canvasback	Common goldeneye	Marshes	Yes	Omnivore	Freshwater benthic	Bottom forager			CWS, 2002	Regionally very rare
2	*Melanitta fusca*	White-winged scoter	Common goldeneye	Lakes/ponds/rivers	No, but in Great Lakes	Molluscovore/ crustaceovore	Freshwater benthic	Gleaner			CWS, 2002	Regionally rare.
2	*Aythya affinis*	Lesser scaup	Common goldeneye	Lakes/ponds/rivers	Yes	Omnivore	Freshwater benthic	Bottom forager	0.31		CCME, 1999, CWS, 2002	
2	*Catostomous commersoni*	White sucker	White sucker	Warmer, shallow lakes or warm, shallow bays, and tributary rivers of larger lakes. Generally found at depths <30 feet	Yes	Insectivore/molluscovore	Freshwater benthic				Scott and Crossman, 1973	
2	*Erimyzon sucetta*	Lake chubsucker	White sucker	Small, shallow, warm, weedy ponds	No, northern extreme of range is Lake Erie and Lake St. Clair	Insectivore	Freshwater benthic				Scott and Crossman, 1973	
2	*Cyprinus carpio*	Common carp	White sucker	Warm, turbid waters	Yes	Herbivore/insectivore/ Molluscovore	Freshwater benthic				Scott and Crossman, 1973	
3	*Coregonus artedi*	Cisco	Forage fish	Deeper waters of lakes.	Yes	Omnivore	Freshwater pelagic				Scott and Crossman, 1973	
3	*Couesius plumbeus*	Northern lake chub	Forage fish	Deeper waters of lakes and large rivers.	Yes	Omnivore	Freshwater pelagic				Scott and Crossman, 1973	
3	*Amia calva*	Bowfin	Walleye	Swampy, vegetated bays of warm lakes and rivers	Yes	Piscivore	Freshwater benthic				Scott and Crossman, 1973	
3	*Catostomous catostomous*	Longnose sucker	White sucker	Lakes/ponds/rivers (almost everywhere in clear, cold water)	Yes	Invertebrates	Freshwater benthic				Scott and Crossman, 1973	
3	*Cottus cognatus*	Slimy sculpin	White sucker	Deeper waters of lakes and cooler streams on rocky or gravelly substrate	Yes	Insectivore	Freshwater benthic				Scott and Crossman, 1973	
3	*Procopium cylindraceum*	Round whitefish	White sucker	Lakes at depths less than 150 feet	Yes	Omnivore	Freshwater benthic				Scott and Crossman, 1973	
2 and 3	*Lepomis macrochirus*	Bluegill	Forage fish	Shallow, weedy, warm water of large and small lakes, ponds, and heavily vegetated, slowly flowing areas of small rivers and large creeks. Shallow water, < 20 feet deep.	Yes	Insectivore/omnivore	Freshwater benthic				Scott and Crossman, 1973	
2 and 3	*Coregonus clupeaformis*	Lake whitefish	Forage fish	Cool water of lakes, spawns in shallower water. Depth range of 60 to 174 feet.	Yes	Omnivore	Freshwater benthic				Scott and Crossman, 1973	
2 and 3	*Ictalurus punctatus*	Channel catfish	Walleye/white sucker	Cool, clear, deeper waters of large lakes and rivers.	Yes	Omnivore	Freshwater benthic				Scott and Crossman, 1973	
2 and 3	*Perca flavescens*	Yellow perch	Yellow perch	Warm to cool water habitats of all types. Prefer clear water and abundant vegetation. Shallow water <30 feet deep.	Yes	Omnivore	Freshwater pelagic and benthic				Scott and Crossman, 1973	
2 and 3	*Pomoxis nigromaculatus*	Black crappie	Yellow perch	Clear, quiet, warm water of large ponds, small lakes, bays and shallower areas of larger lakes, and areas of low flow of larger rivers	Yes	Omnivore	Freshwater benthic				Scott and Crossman, 1973	
2 and 3	*Ictalurus nebulosus*	Brown bullhead	Yellow perch/white sucker	Shallow, warm-water areas of ponds/lakes/rivers. Depths of <40 feet	Yes	Omnivore	Freshwater benthic				Scott and Crossman, 1973	
3 and 4	*Lutra canadensis*	River otter	American mink	Lakes/ponds/rivers	Yes	Piscivore	Freshwater pelagic and benthic		0.10-0.17	>30 cm	Sample and Suter, 1999, CCME, 1999, USEPA, 1997	100% of diet is fish
3 and 4	*Mustela vison*	American mink	American mink	Lakes/ponds/rivers	Yes	Omnivore	Freshwater pelagic and benthic		0.14-0.24	0-20 cm	Sample and Suter, 1999, CCME, 1999, USEPA, 1997	33-90% of diet is fish or aquatic prey (mean=55%)
3 and 4	*Gavia immer*	Common loon	Great blue heron	Lakes/ponds/rivers (primary habitat)	Yes	Piscivore	Freshwater pelagic	Diver	0.18		CWS, 2002, CCME, 1999	
3 and 4	*Pandion haliaetus*	Osprey	Great blue heron	Lakes/ponds/rivers (tertiary habitat)	Yes	Piscivore	Freshwater pelagic	Foot plunger	0.2	0-40 cm	CWS, 2002, CCME, 1999, Sample and Suter, 1999	
3 and 4	*Ardea herodias*	Great blue heron	Great blue heron	Lakes/ponds/rivers (tertiary habitat)	Yes	Piscivore	Freshwater pelagic	Ambusher	0.21	0-30 cm	CWS, 2002, CCME, 1999, Sample and Suter, 1999	
3 and 4	*Stizostedion vitreum*	Walleye	Walleye	Shallow, turbid lakes; large streams or rivers	Yes	Piscivore	Freshwater pelagic and benthic				Scott and Crossman, 1973	
3 and 4	*Esox lucius*	Northern pike	Walleye	Heavily vegetated slow-moving rivers or weedy bays of lakes	Yes	Piscivore/Omnivore	Freshwater pelagic and benthic				Scott and Crossman, 1973	
3 and 4	*Micropterus salmoides*	Largemouth bass	Walleye	Shallow bays of larger lakes, more rarely large, slow-moving rivers	Yes	Omnivore	Freshwater pelagic and benthic				Scott and Crossman, 1973	Adult diet is 50-90% small fishes
3 and 4	*Esox niger*	Chain pickerel	Walleye	Sluggish streams and heavily vegetated lakes and ponds; water < 10 feet deep.	Yes	Piscivore	Freshwater pelagic and benthic				Scott and Crossman, 1973	
3 and 4	*Esox americanus americanus*	Redfin pickerel	Walleye	Sluggish, heavily vegetated acidic streams; less frequently in ponds and weedy backwaters/quiet bays of larger lakes/rivers	Yes	Piscivore	Freshwater pelagic and benthic				Scott and Crossman, 1973	
3 and 4	*Salvelinus namaycush*	Lake trout	Walleye	Deep lakes; less frequently in northern half of range in shallow lakes and in rivers	Yes	Omnivore	Freshwater pelagic				Scott and Crossman, 1973	
3 and 4	*Lota lota* (Linnaeus)	Burbot	Walleye	In central/southern Canada, the deep waters of lakes and rivers. Restricted to below hypolimnion in summer.	Yes	Omnivore	Freshwater pelagic and benthic				Scott and Crossman, 1973	

APPENDIX B. Mercury Concentrations in Biota (Wet Weight)

Table B1. Total mercury in benthic invertebrates (**converted to ng/g wet weight**).

Site	BIOTA – Total Hg	
	Chironomid	**Oligochaete**
6660	-[a]	-[a]
6648	8.78	23.01
6697	34.89	11.86
6661	10.61	14.30
6698	10.15	14.86
6662	19.11	9.13
6663	-[a]	-[a]
6664	-[a]	-[a]
6665	258.28	227.85
6699	134.34	49.73
6666	123.13	23.51
6667	24.81 (31.23)[b]	25.50 (28.41)[b]
6668	35.54	50.75
6669	70.53 (91.45)[b]	51.65 (67.92)[b]
6654	20.30	41.01
6651	12.10	7.11
66101	33.02	48.18
66M144	36.58	171.23
66M253	14.55	16.57
6M262	90.53	176.36
66M264	54.04	103.78
66M269	31.41	27.25
66M271	37.21	78.85
66M272	29.76	23.57
66M76	242.08	37.64
66M80	34.48	41.74

[a] no data; [b] 2004 repeat

Table B2. Methyl mercury in benthic invertebrates (**converted to ng/g wet weight**).

Site	BIOTA – Methyl Hg	
	Chironomid	**Oligochaete**
6660	-[a]	-[a]
6648	2.92	0.56
6697	1.45	0.05
6661	3.42	0.13
6698	4.17	0.40
6662	1.53	0.82
6663	-[a]	-[a]
6664	-[a]	-[a]
6665	33.50	6.87
6699	17.14	3.52
6666	6.35	2.02
6667	6.64 (4.30)[b]	2.34 (1.77)[b]
6668	13.15	1.38
6669	13.50 (9.47)[b]	2.55 (3.26)[b]
6654	2.81	1.75
6651	1.09	0.27
66101	8.90	5.87
66M144	5.44	4.58
66M253	2.26	0.81
6M262	9.33	6.37
66M264	6.61	3.37
66M269	4.46	1.55
66M271	6.54	1.53
66M272	5.81	1.86
66M76	12.03	3.26
66M80	5.64	2.12

[a] no data; [b] 2004 repeat

APPENDIX C. Total Mercury Data (Caduceon Laboratory)

Table C1. Total mercury concentrations in St. Clair River sediment (top 10 cm) (Caduceon Laboratory).

Location	Site	Total Hg (µg/g dry weight)
Upstream (Pt. Edward)	6660	0.07
Upstream (Sarnia Bay)	6648	1.04
Upstream (Sarnia Bay)	6697	0.06
Upstream (Sarnia Bay)	6661	0.04
Upstream (US)	6698	0.03
Zone A	6662	0.17
Zone A	6663	49.30
Zone A	6664	16.20
Zone A	6665	2.70
Zone A	66M76	2.99
Zone B	6699	2.98
Zone B	66M262	2.01
Zone B	66M272	2.56
Zone B	6666	1.35
Zone B	66M253	1.33
Zone B	66M271	4.38
Zone B	66M144	2.82
Zone B	6667[a]	1.71 / 2.96
Zone B	66M80	2.77
Zone B	66M269	1.65
Zone B	6668[b]	1.19
Zone B	66M264	2.37
Zone B	6669[a,b]	2.20 / 4.38
Mouth of Baby Creek	66101	0.64
Stokes Pt Wharf	6654	0.27
Delta - North Channel (US)	6651	0.06

[a] 2001 and 2004 results; [b]QA/QC site, values represent the average of three field replicates

APPENDIX D. Organic Contaminant Concentrations

Table D1. Organic contaminant concentrations (µg/g dry weight) (2001 sites).

Component	6648	6697	6661	6698	6662	6665	6699	6666	6667	6668	6669	6654	6651
1,2,3,4-tetrachlorobenzene	<	<	<	<	<	<	<	<	<	<	<	<	<
1,2,3,5-tetrachlorobenzene	<	<	<	<	<	0.004	0.002	<	0.003	<	0.002	<	<
1,2,3-trichlorobenzene	<	<	<	<	<	<	<	<	<	<	<	<	<
1,2,4,5-tetrachlorobenzene	<	<	<	<	0.009	0.01	0.019	0.011	0.008	0.01	0.012	0.009	<
1,2,4-trichlorobenzene	<	<	0.004	<	<	<	<	<	<	<	<	<	<
1,3,5-trichlorobenzene	<	<	<	<	0.056	0.058	0.026	0.016	0.02	0.022	0.028	0.01	<
2,3,6-trichlorotoluene	<	<	<	<	<	<	<	<	<	<	<	<	<
2,4,5-trichlorotoluene	<	<	<	<	<	<	<	<	0.01	<	<	<	<
2,6-dichlorobenzyl chloride	<	<	<	<	<	<	<	<	<	<	<	<	<
a-BHC (hexachlorocyclohexane)	<	<	<	<	<	<	<	<	<	<	<	<	<
a-Chlordane	<	<	<	<	<	<	<	<	<	<	<	<	<
Acenaphthene	<	<	<	<	0.14	0.06	0.04	0.06	<	<	<	<	<
Acenaphthylene	<	<	<	<	0.04	<	<	<	<	<	<	<	<
Aldrin	<	<	<	<	<	<	<	<	<	<	<	<	<
Anthracene	<	<	<	<	0.18	0.12	0.04	<	<	<	0.06	<	<
b-BHC (hexachlorocyclohexane)	<	<	<	<	<	<	<	<	<	<	<	<	<
Benzo(a)anthracene	<	<	<	<	0.6	0.1	0.08	0.1	0.12	0.1	0.1	<	<
Benzo(a)pyrene	<	<	<	<	0.52	<	<	<	0.08	<	<	<	<
Benzo(b)fluoranthene	<	0.04	<	0.04	0.82	0.08	0.08	0.1	0.14	0.12	0.1	<	0.04
Benzo(g,h,i)perylene	<	<	<	<	0.32	<	0.08	<	0.08	0.08	<	<	<
Benzo(k)fluoranthene	<	<	<	<	0.34	0.04	<	0.04	0.04	0.04	0.04	<	<
Chrysene	<	0.06	0.04	0.04	0.8	0.18	0.14	0.24	0.18	0.16	0.16	<	0.04
d10-phenanthrene	0.096	0.094	0.099	0.091	0.094	0.12	0.094	0.099	0.094	0.097	0.097	0.092	0.095
d12-chrysene	0.082	0.091	0.089	0.088	0.084	0.1	0.086	0.08	0.08	0.087	0.087	0.086	0.085
d8-naphthalene	0.11	0.1	0.11	0.11	0.11	0.12	0.099	0.096	0.093	0.089	0.11	0.099	0.098
Dibenzo(a,h)anthracene	<	<	<	<	0.08	<	<	<	<	<	<	<	<
Dieldrin	<	<	<	<	<	<	<	<	<	<	<	<	<
Endosulphan I	<	<	<	<	<	<	<	<	<	<	<	<	<
Endosulphan II	<	<	<	<	<	<	<	<	<	<	<	<	<
Endosulphan sulphate	<	<	<	<	<	<	<	<	<	<	<	<	<
Endrin	<	<	<	<	<	<	<	<	<	<	<	<	<
Fluoranthene	0.06	0.08	0.06	0.08	1.9	0.24	0.16	0.3	0.32	0.34	0.18	<	0.06
Fluorene	<	<	<	<	0.16	0.08	0.06	0.06	0.04	0.04	0.04	<	<
g-BHC (hexachlorocyclohexane)	<	<	<	<	<	<	<	<	<	<	<	<	<
g-Chlordane	<	<	<	<	<	<	<	<	<	<	<	<	<
Heptachlor	<	<	<	<	<	<	<	<	<	<	<	<	<
Heptachlor epoxide	<	<	<	<	<	<	<	<	<	<	<	<	<
Hexachlorobenzene	0.002	0.002	0.004	<	0.065	0.11	0.19	0.15	0.18	0.03	0.11	0.02	0.005
Hexachlorobutadiene	<	<	<	<	0.2	0.26	0.15	0.094	0.077	0.036	0.06	0.017	<
Hexachloroethane	<	<	<	<	0.016	0.008	0.005	0.003	0.003	<	0.005	<	<
Indeno(1,2,3-c,d)pyrene	<	<	<	<	0.44	<	<	<	<	0.08	<	<	<
Methoxychlor	<	<	<	<	<	<	<	<	<	<	<	<	<
Mirex	<	<	<	<	<	<	<	<	<	<	<	<	<
Naphthalene	<	<	<	<	0.3	0.14	0.12	0.06	0.06	<	0.04	<	<
Octachlorostyrene	<	<	<	<	0.11	0.036	0.093	0.054	0.053	0.02	0.038	0.011	<
op-DDT	<	<	<	<	<	<	<	<	<	<	<	<	<
Oxychlordane	<	<	<	<	<	<	<	<	<	<	<	<	<
PAHs; total	**0.16**	**0.3**	**0.2**	**0.28**	**9.94**	**1.68**	**1.36**	**1.8**	**1.68**	**1.54**	**1.18**	**0.08**	**0.28**
PCB; total	**<**	**0.06**	**0.08**	**<**	**0.06**	**0.14**	**0.1**	**0.04**	**0.16**	**0.1**	**0.2**	**<**	**0.06**
Pentachlorobenzene	<	<	<	<	0.017	0.013	0.016	0.008	0.01	0.006	0.011	0.003	<
Phenanthrene	0.06	0.06	0.06	0.06	1.7	0.34	0.32	0.42	0.32	0.28	0.22	0.04	0.08
pp-DDD	<	<	<	<	<	<	<	<	<	<	<	<	<
pp-DDE	<	<	<	<	<	0.004	0.004	<	<	<	0.002	<	<
pp-DDT	<	<	<	<	<	<	<	<	<	<	<	<	<
Pyrene	0.04	0.06	0.04	0.06	1.6	0.3	0.24	0.42	0.3	0.3	0.24	0.04	0.06
Toxaphene	<	<	<	<	<	<	<	<	<	<	<	<	<

Table D2. Organic contaminant concentrations (ug/g dry weight)s in St. Clair River sediment (2004 sites).

Component	SITE MDL	Units	66M76	66M262	66101	66M80	66M271	66M144	66M272	66M264	6667	66M253	66M269	6669-1	6669-2	6669-3
Aroclor-1016	0.038	ug/gm	<0.041	<	<	<	<	<	<	<	<	<0.045	<	<	<	<
Aroclor-1221	0.042	"	<0.045	<	<	<	<	<	<	<	<	<0.049	<	<	<	<
Aroclor-1232	0.058	"	<0.062	<	<	<	<	<	<	<	<	<0.068	<	<	<	<
Aroclor-1242	0.043	"	<0.046	<	<	<	<	<	<	<	<	<0.050	<	<	<	<
Aroclor-1248	0.032	"	<0.034	<	<	<	<	<	<	<	<	<0.038	<	<	<	<
Aroclor-1254	0.059	"	<	<	<	<	<	<	<	<	<	<	<	<	<	0.096
Aroclor-1260	0.031	"	<0.033	<	<	<	<	<	<	<	<	<0.036	<	<	<	0.083
Aroclor-1262	0.044	"	<0.047	<	<	<	<	<	<	<	<	<0.052	<	<	<	<
Aroclor-1268	0.054	"	<0.058	<	<	<	<	<	<	<	<	<0.063	<	<	<	<
Total PCBs	0.059	"	**<0.062**	<	<	<	<	<	<	<	<	**<0.068**	<	<	<	**0.18**
Hexachlorobutadiene	0.010	mg/kg	0.077	0.099	<0.011	0.03	0.022	0.017	0.031	0.032	0.037	0.043	0.044	0.053	0.082	0.028
Hexachlorobenzene	0.010	"	0.59	0.079	0.015	0.041	0.03	0.024	0.068	0.029	0.89	0.072	0.034	0.12	0.072	0.087
Octachlorostyrene	0.010	"	0.075	0.04	<0.011	0.028	0.013	0.013	0.026	0.015	0.027	0.026	0.025	0.048	0.053	0.043
Surrogate Recoveries		%														
4,4'-Dibromooctaflourobiphenyl			65	54	65	57	62	61	66	64	62	65	62	64	60	63
Decachlorobiphenyl			81	68	73	72	70	71	74	72	71	75	75	74	67	73
Surrogate Recoveries		%														
1,4-Dibromobenzene			90	81	77	70	56	42	57	63	72	71	65	59	69	66
1,3,5-Tribromobenzene			88	81	83	76	48	46	52	67	77	74	62	48	58	61
1,2,4,5-Tetrabromobenzene			97	94	96	106	67	54	73	69	99	101	80	70	77	77
Hexabromobenzene			107	102	103	97	77	66	103	91	117	94	105	102	99	95

Table D2. Continued.

	SITE		66M76	66M262	66101	66M80	66M271	66M144	66M272	66M264	6667	66M253	66M269	6669-1	6669-2	6669-3
Component	MDL	Units														
Naphthalene	0.010	mg/kg	0.25	0.1	<	0.049	0.28	0.039	0.13	0.044	0.075	0.061	0.047	0.039	0.049	0.044
Acenaphthylene	0.010	"	0.045	0.027	<	0.026	0.014	0.042	0.058	0.031	0.02	0.026	0.02	0.042	0.04	0.038
Acenaphthene	0.010	"	0.11	0.059	<	0.072	0.036	0.045	0.12	0.037	0.05	0.062	0.039	0.037	0.046	0.039
Fluorene	0.010	"	0.13	0.099	0.011	0.13	0.083	0.11	0.15	0.087	0.086	0.083	0.069	0.093	0.11	0.095
Phenanthrene	0.010	"	0.54	0.39	0.043	0.44	0.33	0.22	0.45	0.24	0.32	0.27	0.28	0.28	0.34	0.25
Anthracene	0.010	"	0.14	0.096	<	0.096	0.069	0.066	0.1	0.07	0.073	0.063	0.056	0.09	0.11	0.088
Fluoranthene	0.010	"	0.25	0.17	0.022	0.17	0.12	0.097	0.24	0.17	0.19	0.11	0.14	0.24	0.27	0.24
Pyrene	0.010	"	0.41	0.29	0.036	0.3	0.25	0.2	0.37	0.26	0.26	0.18	0.2	0.48	0.5	0.47
Benz(a)anthracene	0.010	"	0.13	0.087	<	0.11	0.074	0.05	0.14	0.075	0.11	0.059	0.086	0.15	0.17	0.15
Chrysene	0.010	"	0.19	0.12	0.021	0.15	0.12	0.076	0.19	0.11	0.15	0.12	0.11	0.19	0.21	0.2
Benzo(b)fluoranthene	0.010	"	0.12	0.064	<	0.076	0.041	0.034	0.15	0.068	0.097	0.064	0.072	0.12	0.15	0.13
Benzo(k)fluoranthene	0.010	"	0.029	0.011	<	0.012	<	<	0.027	0.011	0.026	0.011	0.015	0.028	0.031	0.03
Benzo(a)pyrene	0.010	"	0.16	0.077	<	0.085	0.042	0.036	0.17	0.066	0.11	0.069	0.08	0.15	0.16	0.15
Indeno(1,2,3-cd)pyrene	0.010	"	0.071	0.03	<	0.032	0.013	0.014	0.078	0.029	0.049	0.032	0.032	0.061	0.073	0.068
Dibenzo(ah)anthracene	0.010	"	0.044	0.024	<	0.021	0.01	<	0.041	0.017	0.027	0.023	0.024	0.037	0.039	0.04
Benzo(ghi)perylene	0.010	"	0.15	0.061	<	0.058	0.032	0.029	0.12	0.05	0.083	0.074	0.059	0.099	0.11	0.1
Total PAHs			**2.8**	**1.7**	**0.1**	**1.8**	**1.5**	**1.1**	**2.5**	**1.4**	**1.7**	**1.3**	**1.3**	**2.1**	**2.4**	**2.1**
Surrogate Recoveries		%														
Anthracene-2H10			86	85	89	83	81	83	82	84	85	87	83	84	84	82
Chrysene-2H12			79	80	81	82	82	81	78	78	80	79	78	80	82	79
Benzo(a)pyrene-2H12			96	96	99	98	99	97	94	96	96	95	94	97	98	96

APPENDIX E. Invertebrate Family Abundances

Table E1. Invertebrate families identified in the St. Clair River, 2001 (densities expressed as number/m^2).

	Upstream					Zone A				Zone B					Stokes Pt	Delta
Family	6660	6648	6697	6661	6698	6662	6663	6664	6665	6699	6666	6667	6668a	6669	6654	6651
Ancylidae	0.0	9.0	0.0	0.0	0.0	0.0	0.0	26.9	0.0	0.0	0.0	0.0	3.0	60.3	0.0	0.0
Arrenuridae	0.0	0.0	0.0	120.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Asellidae	0.0	0.0	0.0	0.0	9.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Baetidae	0.0	35.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Bosminidae	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	9.0	0.0
Brachycentridae	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	60.3	0.0	0.0	0.0	0.0	0.0	0.0
Caenidae	0.0	53.8	180.9	0.0	9.0	0.0	9.0	0.0	0.0	723.8	904.7	60.3	0.0	1146.0	1093.4	0.0
Candoniidae	0.0	35.9	0.0	0.0	44.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	904.7	9.0	60.3
Ceratopogonidae	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	60.3	9.0	0.0
Chironomidae	6683.6	20812.1	3015.7	16948.1	15686.4	1990.3	3246.7	4828.4	8158.3	1326.9	4523.5	7358.3	2564.8	11037.4	4768.9	22195.4
Chydoridae	9.0	233.0	0.0	723.8	0.0	0.0	259.9	0.0	9.0	60.3	60.3	0.0	0.0	180.9	475.0	0.0
Coenagrionidae	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	9.0	0.0
Crangonyctidae	0.0	0.0	0.0	0.0	80.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.0	0.0	26.9	0.0
Cuspidariidae	0.0	0.0	0.0	0.0	0.0	0.0	35.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cyclocyprididae	0.0	9.0	60.3	0.0	0.0	0.0	0.0	0.0	0.0	60.3	0.0	0.0	0.0	1507.8	134.4	0.0
Cyclopidae	9.0	0.0	0.0	60.3	9.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	301.6	26.9	0.0
Cyprididae	0.0	0.0	120.6	60.3	71.7	0.0	0.0	44.8	0.0	60.3	60.3	0.0	3.0	9288.3	188.2	0.0
Daphnidae	0.0	3468.5	0.0	60.3	9.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.0	0.0	0.0	0.0
Dreissenidae	9.0	179.3	0.0	0.0	197.2	0.0	0.0	44.8	17.9	301.6	0.0	0.0	0.0	0.0	0.0	0.0
Empididae	0.0	0.0	60.3	0.0	89.6	0.0	9.0	0.0	0.0	0.0	60.3	0.0	6.0	361.9	869.4	0.0
Enchytraeidae	0.0	33.7	60.3	0.0	303.6	0.0	11.2	11.2	0.0	0.0	180.9	60.3	37.5	2412.5	1754.1	60.3
Ephemeridae	0.0	9.0	60.3	60.3	9.0	0.0	0.0	9.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	180.9
Erpobdellidae	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	120.6	0.0	0.0
Gammaridae	9.0	44.8	60.3	0.0	188.2	0.0	9.0	9.0	0.0	0.0	1206.3	0.0	3.0	60.3	9.0	0.0
Glossiphoniidae	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	180.9	0.0	0.0
Hyalellidae	0.0	251.0	0.0	0.0	0.0	0.0	0.0	9.0	0.0	120.6	0.0	0.0	0.0	0.0	0.0	0.0
Hydridae	0.0	9.0	0.0	0.0	44.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hydrobiidae	0.0	0.0	120.6	0.0	179.3	0.0	125.5	44.8	0.0	4101.3	1507.8	0.0	23.9	3256.9	26.9	0.0
Hydropsychidae	0.0	98.6	0.0	301.6	1496.7	0.0	35.9	286.8	17.9	0.0	120.6	0.0	6.0	0.0	0.0	0.0
Hydroptilidae	0.0	9.0	0.0	0.0	53.8	0.0	0.0	17.9	0.0	0.0	60.3	0.0	3.0	0.0	286.8	0.0
Hydrozetiidae	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.0	0.0	0.0	0.0
Hygrobatidae	9.0	98.6	0.0	422.2	71.7	0.0	80.7	62.7	0.0	60.3	0.0	180.9	0.0	0.0	0.0	0.0
Lebertiidae	9.0	125.5	0.0	60.3	143.4	0.0	26.9	17.9	0.0	0.0	0.0	0.0	3.0	0.0	71.7	0.0
Leptoceridae	0.0	0.0	0.0	120.6	9.0	241.3	0.0	0.0	0.0	60.3	301.6	60.3	0.0	542.8	62.7	0.0
Limnesiidae	53.8	26.9	0.0	0.0	0.0	0.0	9.0	0.0	0.0	120.6	0.0	0.0	12.0	965.0	89.6	0.0
Limnocytheridae	0.0	44.8	0.0	301.6	98.6	0.0	0.0	0.0	0.0	0.0	0.0	241.3	0.0	0.0	0.0	0.0
Lumbriculidae	22.5	0.0	0.0	0.0	22.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	120.6	0.0	0.0
Lumbrineridae	0.0	0.0	0.0	0.0	26.9	0.0	170.3	35.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Lymnaeidae	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	60.3	0.0	0.0
Macrothricidae	0.0	26.9	0.0	361.9	17.9	0.0	0.0	0.0	0.0	0.0	0.0	180.9	0.0	0.0	0.0	0.0
Mactridae	0.0	0.0	0.0	0.0	0.0	0.0	9.0	35.9	9.0	0.0	0.0	0.0	3.0	0.0	80.7	0.0
Milnesiidae	0.0	71.7	0.0	0.0	17.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Muscidae	0.0	0.0	0.0	0.0	9.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Naididae	101.2	753.3	120.6	422.2	2237.5	0.0	191.1	213.6	33.7	60.3	241.3	1930.0	37.5	241.3	4598.8	0.0
Oxidae	0.0	9.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.0	60.3	0.0	0.0
Physidae	0.0	0.0	0.0	0.0	9.0	0.0	0.0	0.0	0.0	241.3	422.2	0.0	0.0	0.0	0.0	0.0
Pionidae	62.7	251.0	0.0	482.5	179.3	0.0	80.7	44.8	0.0	0.0	180.9	361.9	0.0	301.6	0.0	0.0
Planariidae	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	120.6	120.6	0.0	0.0	180.9	26.9	0.0
Planorbidae	0.0	0.0	60.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	60.3	0.0	0.0	0.0	0.0	0.0
Pleuroceridae	0.0	0.0	0.0	0.0	0.0	0.0	26.9	26.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Polycentropodidae	0.0	9.0	0.0	0.0	188.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Pyralidae	0.0	0.0	0.0	0.0	17.9	0.0	0.0	0.0	0.0	180.9	120.6	0.0	9.0	60.3	53.8	0.0
Sphaeriidae	0.0	0.0	0.0	0.0	0.0	0.0	16.5	24.7	8.2	0.0	0.0	0.0	5.5	1085.6	0.0	301.6
Spongillidae	295.8	3101.0	3920.4	2834.7	1819.4	0.0	9.0	421.2	0.0	9831.1	1206.3	15621.2	179.3	663.4	188.2	1930.0
Tetrastemmatidae	0.0	107.6	0.0	0.0	600.5	0.0	107.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	143.4	0.0
Torrenticolidae	0.0	9.0	0.0	0.0	9.0	0.0	35.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Trhypachthoniidae	9.0	17.9	0.0	60.3	0.0	0.0	0.0	17.9	0.0	60.3	60.3	0.0	6.0	60.3	9.0	0.0
Trochochaetidae	0.0	0.0	0.0	60.3	0.0	422.2	26.9	0.0	0.0	1930.0	361.9	1326.9	295.8	241.3	0.0	120.6
Tubificidae	2451.2	45819.0	12123.0	19601.9	15876.4	55488.5	910.8	5385.8	1248.1	45174.9	47044.6	23884.2	9340.0	59408.9	1394.2	21833.5
Unionidae	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	9.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Valvatidae	0.0	0.0	120.6	0.0	0.0	0.0	0.0	26.9	0.0	603.1	965.0	0.0	9.0	1326.9	0.0	0.0

[a] QA/QC site; value represents mean of three field replicates

Table E2. Relative densities (%) of major macroinvertebrate taxa in St. Clair River, 2001. Reference site data includes the mean of upstream sites in the St. Clair River (n=5) and the mean of the Great Lakes reference sites (Reference Group 3, n=51).

Relative Density (%)	Reference		Zone A				Zone B					Downstream	
	Upstream St. Clair River	Great Lakes Ref. Group 3	6662	6663	6664	6665	6699	6666	6667	6668	6669	Stokes Pt. 6654	Delta 6651
Tubificids	52.2	19.3	96.6	18.1	48.2	13.1	85.3	82.5	71.7	78.0	71.6	9.1	49.1
Chironomids	41.2	37.7	3.4	62.5	43.2	85.9	2.4	7.8	20.9	20.6	13.2	31.1	49.7
Sphaeriids	0.0	12.5	0.0	0.3	0.2	0.1	0.0	0.0	0.0	0.0	1.3	0.0	0.7
Naidids	2.1	6.5	0.0	4.5	1.9	0.4	0.1	2.5	5.5	0.3	0.4	30.0	0.0
Gastropods	0.7	3.5	0.0	6.2	1.4	0.0	10.3	5.1	0.0	0.3	5.7	0.5	0.0
Amphipods	0.2	2.3	0.0	0.2	0.2	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0
Mayflies	0.2	1.7	0.0	0.2	0.1	0.0	0.0	0.0	0.2	0.0	1.3	7.0	0.4
Trichopterans	1.1	1.0	0.0	0.9	3.0	0.3	0.2	0.8	0.0	0.1	0.7	2.6	0.0
Others	2.3	15.5	0.0	7.1	1.8	0.3	1.5	1.3	1.7	0.6	5.9	19.8	0.1

Table E3. Macroinvertebrate taxa identified in the St. Clair River, 2001 (densities expressed as number/33.16cm^2).

	UPSTREAM					DOWNSTREAM										
Site	6660	6648	6697	6661	6698	6662	6663	6664	6665	6699	6666	6667	6668	6669	6654	6651
P. Annelida																
Cl. Oligochaeta																
F. Enchytraeidae																
Enchytraeus	-	0.11	-	-	-	-	-	-	-	-	0.60	0.20	0.12	-	0.75	-
Mesenchytraeus	-	-	0.20	-	1.01	-	0.04	0.04	-	-	-	-	-	8.00	5.07	0.20
F. Lumbriculidae																
Eclipidrilus sp.	0.07	-	-	-	0.07	-	-	-	-	-	-	-	-	0.40	-	-
F. Naididae																
Allonais pectinata	-	-	-	-	-	-	0.15	-	-	-	-	-	-	-	-	-
Chaetogaster diaphanus	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.07	-
Chaetogaster diastrophus	-	-	-	-	-	-	-	-	-	-	-	0.20	-	-	-	-
Dero digitata	-	0.04	-	-	-	-	-	-	-	-	-	0.20	0.09	-	-	-
Dero furcata	-	-	-	-	-	-	-	0.11	-	-	-	-	-	-	-	-
Nais bretscheri	-	0.07	-	-	0.15	-	-	-	-	-	-	-	-	-	0.22	-
Nais communis	-	0.04	-	-	-	-	0.15	-	-	-	-	-	-	-	-	-
Nais elinguis	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.04	-
Nais simplex	-	-	-	-	0.89	-	0.04	-	-	-	-	-	-	-	0.22	-
Nais variabilis	-	1.60	-	-	2.68	-	-	0.34	-	0.20	0.40	-	-	0.20	14.02	-
Ophidonais serpentina	-	-	-	-	-	-	-	-	-	-	-	-	0.01	-	-	-
Paranais frici	-	-	-	-	-	-	-	-	-	-	-	5.80	0.02	-	-	-
Pristina acuminata	-	-	-	-	0.37	-	-	-	-	-	-	-	-	-	-	-
Pristina aequiseta	-	0.04	-	-	-	-	-	-	-	-	-	-	-	0.20	-	-
Pristina jenkinae	-	0.07	-	-	-	-	-	0.15	-	-	-	-	-	-	0.56	-
Pristina leidyi	-	-	-	-	0.07	-	-	-	-	-	-	-	-	0.40	-	-
Pristina osborni	-	0.07	-	-	1.08	-	-	-	-	-	-	0.20	-	-	0.04	-
Specaria josinae	0.04	0.52	0.40	1.20	0.15	-	-	0.04	-	-	0.20	-	-	-	0.04	-
Stylaria lacustris	-	-	0.20	-	-	-	-	-	-	-	4.00	-	-	0.20	0.04	-
Uncinais uncinata	0.30	0.04	-	0.20	1.83	-	0.41	0.04	0.11	-	0.20	-	-	-	0.04	-
Vejdovskyella comata	-	0.07	-	-	0.19	-	-	-	-	-	-	-	-	-	-	-
Vejdovskyella intermedia	-	-	-	-	-	-	0.04	0.04	-	-	-	-	-	-	-	-
F. Tubificidae																
Aulodrilus americanus	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.15	-
Aulodrilus limnobius	-	0.04	-	0.20	-	-	-	-	-	-	-	-	0.01	1.20	-	-
Aulodrilus pigueti	-	1.86	0.80	2.60	0.07	0.20	0.07	1.23	-	2.00	3.00	11.00	0.93	12.00	0.04	3.80
Aulodrilus pluriseta	-	0.04	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ilyodrilus templetoni	-	0.93	-	-	0.48	1.20	0.04	0.04	-	0.40	-	-	0.24	5.20	-	0.60
Limnodrilus cervix	-	-	-	0.20	-	0.40	-	-	-	-	-	-	-	-	-	-
Limnodrilus claparedianus	-	0.11	-	-	-	-	-	-	-	-	-	-	-	-	0.04	-
Limnodrilus hoffmeisteri	-	2.16	0.20	1.20	1.08	-	0.56	1.79	-	0.60	1.80	1.40	0.47	6.00	0.07	2.00
Limnodrilus maumeenis	-	0.37	0.40	0.20	0.04	1.80	-	0.04	-	0.20	-	-	0.01	0.80	-	0.80
Limnodrilus udekemianus	0.04	2.50	2.20	1.00	1.83	4.20	-	0.07	-	8.60	4.40	2.00	0.14	2.40	0.37	0.20
Potamothrix moldaviensis	0.15	0.30	0.80	0.40	1.86	1.20	0.07	0.22	0.26	0.40	0.40	-	0.14	-	0.22	1.40
Potamothrix vejdovskyi	0.15	0.07	-	0.40	0.30	-	0.07	-	0.26	-	-	-	-	-	-	-
Spirosperma ferox	0.04	-	-	-	0.52	-	0.04	0.11	-	-	-	-	-	4.40	0.30	-
Tasserkidrilus americanus	-	-	-	0.40	-	0.80	-	-	-	0.20	0.80	0.20	-	-	-	-
Tubifex tubifex	0.04	-	-	-	-	-	0.04	-	-	-	-	-	-	-	-	-
Quistradrilus multisetosus	-	-	-	0.20	-	1.40	0.12	-	-	6.40	1.20	4.40	1.23	0.80	-	0.40
Immature tubificids with cheatal hairs	0.48	39.75	14.00	6.80	3.73	132.8	1.90	13.94	3.58	105.80	119.40	52.00	24.07	127.40	2.98	54.20
Immature tubificids without cheatal hair	7.23	103.80	21.80	52.00	42.73	42.20	0.22	0.41	0.04	31.80	27.00	12.80	4.96	37.60	0.60	9.40
C. Hirudinea																
F. Glossiphoniidae																
Alboglossiphonia heteroclita	-	-	-	-	-	-	-	-	-	-	-	-	-	0.60	-	-
F. Erpobdellidae																
Nephelopsis obscura	-	-	-	-	-	-	-	-	-	-	-	-	-	0.40	-	-
P. Nemertea	-	0.36	-	-	1.99	-	0.36	-	-	-	-	-	-	-	0.48	-
P. Nemata	0.26	2.82	4.00	1.00	2.05	5.40	0.16	0.35	0.06	2.60	6.20	1.40	0.43	33.80	4.61	0.60
P. Platyhelminthes	-	0.45	-	-	0.18	-	0.03	-	-	0.40	0.40	-	-	0.60	0.09	-

Table E3. Continued.

	UPSTREAM					DOWNSTREAM										
Site	6660	6648	6657	6661	6698	6662	6663	6664	6665	6699	6666	6667	6668	6669	6654	6651
P. Arthropoda																
O. Amphipoda																
F. Hyalellidae																
Hyalella azteca	-	0.83	-	-	-	-	-	0.03	-	0.40	-	-	-	-	-	-
F. Gammaridae													0.01			
Gammarus lacustris	-	-	0.20	-	-	-	-	-	-	-	-	-	-	-	-	-
Gammarus sp.	0.03	0.15	-	-	0.62	-	0.03	0.03	-	-	-	-	-	-	-	-
O. Isopoda																
F. Asellidae																
Caecidotea	-	-	-	-	0.03	-	-	-	-	-	-	-	-	-	-	-
O. Acari		1.72	-			-							0.02		0.21	
Sub O. Prostigmata																
F. Arrenuridae																
Arrenurus sp.	-	-	-	0.40	-	-	-	-	-	-	-	-	-	-	-	-
F. Hygrobatidae																
Hygrobates sp.	0.03	0.33	-	1.40	0.24	-	0.27	0.21	-	0.20	-	-	-	-	-	-
F. Lebertiidae																
Lebertia sp.	0.03	0.45	-	0.20	0.48	-	0.09	0.06	-	-	-	-	0.01	-	0.24	-
F. Limnesiidae																
Limnesia sp.	0.18	0.09	-	-	-	-	0.03	-	-	0.40	-	-	0.03	3.20	0.30	-
F. Oxidae																
Oxus sp.	-	0.03	-	-	-	-	-	-	-	-	-	-	0.01	0.20	-	-
F. Pionidae																
Forelia sp.	-	0.62	-	1.60	-	-	-	-	-	-	-	1.20	-	-	-	-
Neotiphys	-	0.21	-	-	-	-	-	0.06	-	-	-	-	-	1.00	-	-
Piona sp.	0.21	-	-	-	0.59	-	0.27	0.09	-	-	0.60	-	-	-	-	-
F. Torrenticolidae	-	0.03	-	-												
Testudacarus sp.	-	-	-	-	0.03	-	-	-	-	-	-	-	-	-	-	-
Torrenticola sp.	-	-	-	-	-	-	0.12	-	-	-	-	-	-	-	-	-
O. Orbatida																
F. Trhypachthoniidae	0.03	0.06	-	-	-	-	-	0.06	-	0.20	0.40	-	0.02	0.20	-	-
F. Hydrozetidae																
Hydrozetes	-	-	-	-	-	-	-	-	-	-	-	-	0.01	-	-	-
Cl. Insecta																
F. Ceratopogonidae	-	-	-	-	-	-	-	-	-	-	-	-	-	0.20	0.03	-
F. Chironomidae																
Ablabesmyia	-	-	-	-	0.12	-	0.08	-	-	-	-	-	-	0.80	0.91	-
Chironomus	0.32	4.61	0.60	1.60	0.75	2.20	0.20	0.39	0.08	0.20	0.40	3.00	0.29	0.20	-	2.00
Cladopelma	-	-	0.40	-	-	-	-	-	-	-	-	-	-	-	-	-
Cladotanytarsus	-	0.04	-	0.60	-	-	0.28	0.18	0.20	-	-	-	-	-	0.04	-
Cricotopus	0.07	1.03	-	0.20	2.17	-	0.55	0.08	-	-	0.60	-	0.16	1.40	1.30	-
Cryptochironomus	0.83	0.08	0.40	0.40	0.32	-	0.35	0.21	1.03	-	0.20	1.00	0.09	1.00	0.59	1.20
Cryptotendipes	0.04	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Demicryptochironomus	0.04	0.04	-	-	0.32	-	0.20	0.16	-	-	-	-	-	-	0.04	-
Dicrotendipes	-	1.34	-	-	-	-	0.59	0.04	-	0.80	0.20	-	0.11	3.60	1.14	-
Eukiefferiella	-	-	-	-	-	-	-	-	-	-	-	0.20	-	-	-	-
Hamischia	-	-	-	-	-	-	0.04	-	-	-	-	-	-	-	-	-
Lopescladius	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.08	-
Microtendipes	-	0.28	-	-	0.04	-	0.08	0.04	-	-	0.20	-	-	-	-	-
Micropsectra	-	-	-	0.60	-	-	-	0.04	-	-	-	-	-	-	-	-
Monodiamesa	0.51	-	-	0.60	-	-	0.12	0.04	0.16	-	-	-	-	-	-	-
Nanocladius	0.04	-		-	-	-	-	-	-	-	-	-	-	-	-	-
Nilothauma	-	-	-	-	-	-	0.16	-	-	-	-	-	-	-	-	-
Orthocladius	-	-	-	-	-	-	-	0.04	-	-	-	-	-	-	-	-
Parachironomus	-	-	0.20	-	-	-	-	-	-	-	0.20	-	-	4.00	-	-
Paracladopelma	-	0.12	-	-	-	-	-	-	0.04	-	-	-	-	-	-	-
Parakiefferiella	-	0.20	-	-	0.32	-	0.47	0.20	-	-	-	-	-	-	-	-
Paralauterborniella	0.79	3.04	-	4.20	0.63	0.20	0.24	0.39	0.51	-	0.20	0.20	0.08	-	-	0.60
Paraphaenocladius	-	-	-	-	-	-	0.04	-	-	-	-	-	-	-	-	-
Paratanytarsus	-	0.35	0.40	-	0.04	-	0.59	0.35	-	-	1.00	-	0.09	1.80	1.30	-
Paratendipes	-	1.42	-	0.40	0.43	-	0.12	0.43	0.04	0.40	-	-	0.05	-	-	-
Procladius	0.07	11.28	0.80	5.20	3.51	0.60	0.12	0.47	0.20	1.80	5.00	6.00	0.16	10.80	-	1.00
Polypedilum	18.46	36.24	1.80	38.60	26.07	2.40	6.31	11.87	224.33	0.60	3.80	10.00	6.63	11.60	7.22	67.20
Potthastia longimana group	0.04	0.08	-	0.20	-	-	0.16	-	0.16	-	-	-	0.03	-	0.24	-
Psectrocladius	-	0.04	-	-	0.04	-	0.04	-	-	-	-	-	-	0.20	0.35	-
Pseudochironomus	-	-	-	-	-	-	-	0.08	-	-	-	-	-	-	-	-
Rheotanytarsus	0.04	2.33	-	0.40	3.08	-	0.12	0.32	-	-	1.40	-	0.25	0.60	1.85	-
Stempellina	-	-	-	-	0.12	-	0.04	-	-	-	-	-	-	-	-	-
Stictochironomus	0.07	1.89	0.20	1.60	0.16	0.40	0.28	0.32	0.20	-	-	-	-	-	0.63	0.80
Tanypus	-	-	-	-	0.04	-	-	-	-	-	-	-	-	0.20	-	-
Tanytarsus	0.20	1.22	-	1.00	0.12	-	0.24	0.16	-	-	-	0.20	-	0.40	0.04	-
Thienemanniella	-	0.04	-	-	-	-	-	-	-	-	-	-	0.01	-	-	-
Thienemannimyia	-	0.35	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Tribelos	0.04	3.00	5.20	0.60	13.76	0.80	0.24	0.55	0.12	0.80	1.80	6.80	0.55	28.40	0.08	0.80

Table E3. Continued.

	UPSTREAM					DOWNSTREAM										
Site	6660	6648	6697	6661	6698	6662	6663	6664	6665	6699	6666	6667	6668	6669	6654	6651
F. Empididae																
Chelifera	-	-	-	-	0.15	-	-	-	-	-	-	-	-	-	-	-
Hemerodromia sp.	-	-	0.20	-	0.15	-	0.03	-	-	-	0.20	-	0.02	1.20	2.88	-
F. Muscidae	-	-	-	-	0.03	-	-	-	-	-	-	-	-	-	-	-
O. Ephemeroptera																
F. Baetidae	-	0.12	-	-	-	-	-	-	-	-	-	-	-	-	-	-
F. Ephemeridae																
Hexagenia	-	0.03	0.20	0.20	-	-	-	-	-	-	-	-	-	-	-	0.60
Hexagenia limbata	-	-	-	-	0.03	-	-	-	-	-	-	-	-	-	-	-
F. Caenidae																
Caenis sp.	-	0.15	0.20	-	0.03	-	0.03	-	-	-	-	0.20	-	3.60	3.57	-
O. Trichoptera																
F. Brachycentridae																
Brachycentrus	-	-	-	-	-	-	-	-	-	0.20	-	-	-	-	-	-
Brachycentrus lateralis	-	-	-	-	-	-	0.03	0.12	0.03	-	-	-	0.01	-	0.27	-
F. Dipseudopsidae																
F. Hydropsychidae							0.12						0.02			
Cheumatopsyche sp.	-	0.03	-	-	0.12	-	-	0.03	-	-	-	-	-	-	-	-
Hydropsyche alhedra	-	-	-	-	4.84	-	-	0.92	0.06	-	-	-	-	-	0.00	-
Hydropsyche sp.	-	0.30	-	1.00	-	-	-	-	-	-	0.40	-	-	-	-	-
F. Hydroptilidae		0.03											0.01		0.95	
Hydroptila	-	-	-	-	0.18	-	-	0.06	-	-	-	-	-	-	-	-
Ochrotrichia sp.	-	-	-	-	-	-	-	-	-	-	0.20	-	-	-	-	-
F. Leptoceridae														0.40	0.06	
Nectopsyche sp.	-	-	-	-	0.03	-	-	-	-	-	-	-	-	-	-	-
Oecetis	-	-	-	-	-	-	-	-	-	-	-	-	-	1.20	0.03	-
Triaenodes	-	-	-	-	-	-	-	-	-	-	-	-	-	0.20	-	-
F. Polycentropodidae																
Neureclipsis	-	-	-	-	0.62	-	-	-	-	-	-	-	-	-	-	-
Polycentropus	-	0.03	-	-	-	-	-	-	-	-	-	-	-	-	-	-
O. Lepidoptera																
F. Pyralidae																
Acentria sp.	-	-	-	-	0.67	-	-	-	-	0.60	0.40	-	0.03	0.20	0.18	-
O. Odonata																
F. Coenagrionidae	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.03	-
P. Tardigrada																
F. Milnesiidae	-	0.24	-	-	0.06	-	-	-	-	-	-	-	-	-	-	-
P. Mollusca																
Cl. Bivalvia																
F. Cuspidariidae																
Cardiomyia pectinata	-	-	-	-	-	-	0.12	-	0.00	-	-	-	-	-	-	-
F. Dreissenidae		0.59	-	-												
Dreissena polymorpha	0.03	-	-	-	0.65	-	-	0.15	0.06	1.00	-	-	-	-	-	-
F. Mactridae																
Mulinia lateralis	-	-	-	-	-	-	0.03	0.12	0.03	-	-	-	0.03	-	0.27	-
F. Sphaeridae																
Sphaerium striatinum	-	-	-	-	-	-	-	0.08	-	-	-	-	-	-	-	-
Pisidium compressum	-	-	-	-	-	-	-	-	-	-	-	-	0.02	-	-	-
Pisidium fallax	-	-	-	-	-	-	0.05	-	0.03	-	-	-	-	-	-	-
Pisidium henslowanum	-	-	-	-	-	-	-	-	-	-	-	-	-	3.60	-	1.00
F. Unionidae																
Lampsilis fasciola	-	-	-	-	-	-	-	-	0.03	-	-	-	-	-	-	-
Cl. Gastropoda																
F. Ancylidae																
Ferrissia sp.	-	0.03	-	-	-	-	-	0.09	-	-	-	-	0.01	0.20	-	-
Ferrissia rivularis	-	-	-	-	0.27	-	-	-	-	-	-	-	0.01	-	0.09	-
F. Lymnaeidae																
Pseudosuccinea columella	-	-	-	-	-	-	-	-	-	-	-	-	-	0.20	-	-
F. Hydrobiidae																
Amnicola limosus	-	-	-	-	-	-	-	-	-	-	0.20	-	0.03	1.40	-	-
Lyogyrus walkeri	-	-	0.40	-	-	-	-	-	-	13.60	4.80	-	0.05	-	-	-
Probythinella emarginata	-	-	-	-	-	-	0.09	0.15	-	-	-	-	-	-	-	-
Pyrgulopsis lustrica	-	-	-	-	0.59	-	0.33	-	-	-	-	-	-	9.40	0.09	-
F. Physidae					0.03											
Physella sp.	-	-	-	-	-	-	-	-	-	0.80	1.40	-	-			
F. Planorbidae																
Gyraulus circumstriatus	-	-	-	-	-	-	-	-	-	-	0.20	-	-	-	-	-
Helisoma anceps	-	0.03	0.40	-	-	-	-	-	-	2.40	3.00	-	-	0.20	0.06	-
Micromenetus dilatatus	-	-	0.20	-	-	-	-	-	-	-	-	-	-	-	-	-
F. Pleuroceridae																
Elimia livescens	-	-	-	-	-	-	0.09	0.09	-	-	-	-	-	-	-	-
Pleurocera acuta	-	-	-	-	0.09	-	0.56	0.12	-	-	-	-	-	-	-	-
F. Valvatidae																
Valvata lewisi	-	-	-	-	-	-	-	-	-	-	-	-	-	4.40	-	-
Valvata piscinalis	-	-	0.40	-	-	-	-	0.09	-	2.00	0.40	-	0.03	-	-	-
Valvata sincera	-	-	-	-	-	-	-	-	-	-	2.80	-	-	-	-	-
P. Cnideria																
F. Hydridae																
Hydra polyps	-	0.03	-	-	0.15	-	-	-	-	-	-	-	-	-	-	-
Total Number of Taxa	31	68	26	34	65	15	59	55	22	28	38	21	45	50	53	18
Total Abundance per 33 cm²	31	233	57	129	128	198	18	38	232	186	200	121	42	339	56	149
Total Abundance per 1 m²	9316	70380	17250	38902	38620	59771	5556	11418	69844	56092	60314	36369	12587	102111	16921	44873

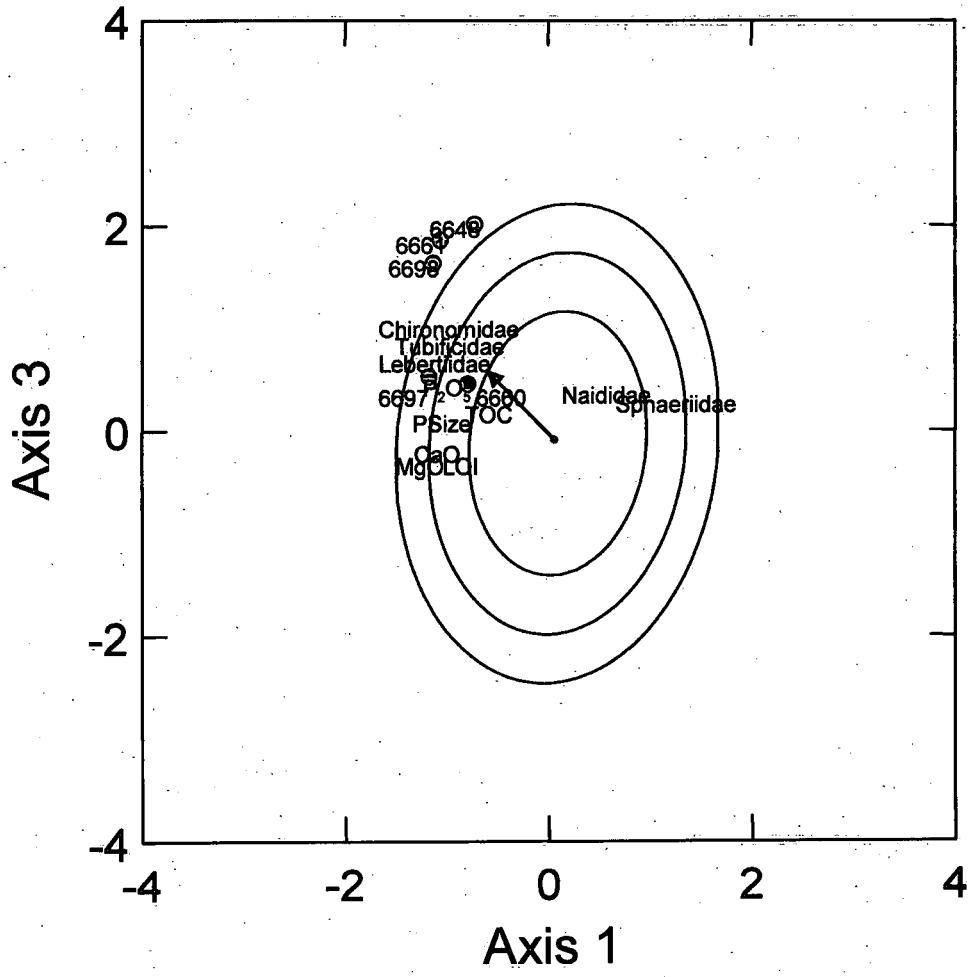


Figure F1. Ordination of subset of St. Clair River sites predicted to Reference Group 3 summarized on Axes 1 and 3 with 90%, 99%, and 99.9% probability ellipses around reference sites (not shown). Significant ($p \leq 0.05$) environmental variables and families are shown. Correlations of the most significant taxa and environmental variables are shown with arrows. Stress = 0.15.

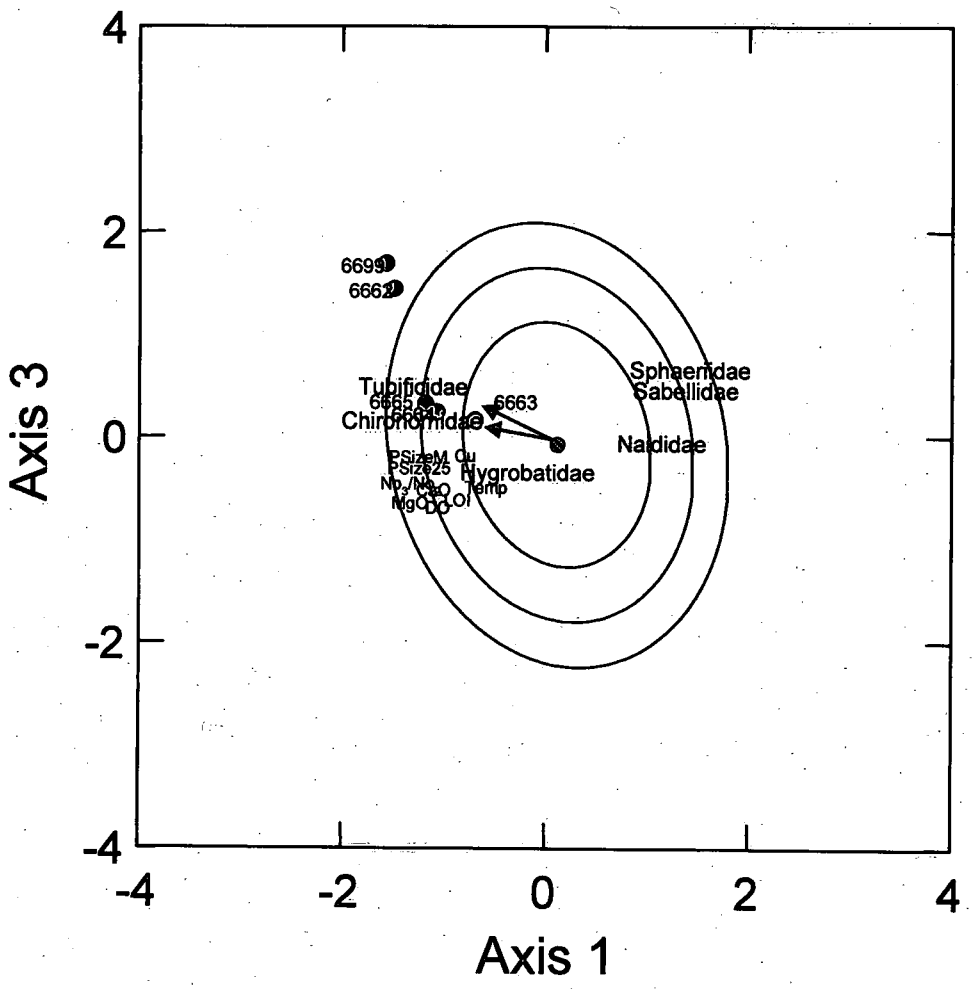
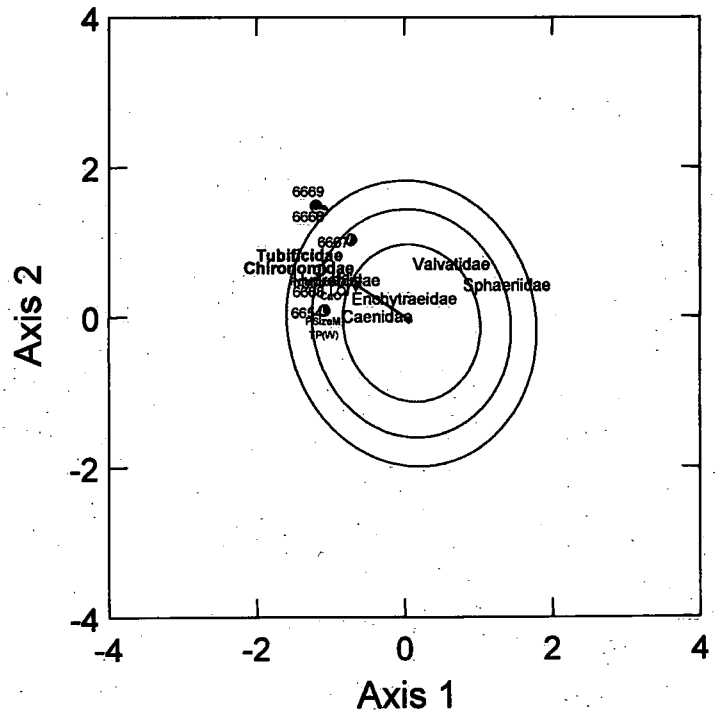


Figure F2. Ordination of subset of St. Clair River sites predicted to reference Group 3 summarized on Axes 1 and 3 with 90%, 99%, and 99.9% probability ellipses around reference sites (not shown). Significant ($p \leq 0.05$) environmental variables and families are shown. Correlations of the most significant taxa and environmental variables are shown with arrows. Stress = 0.16.



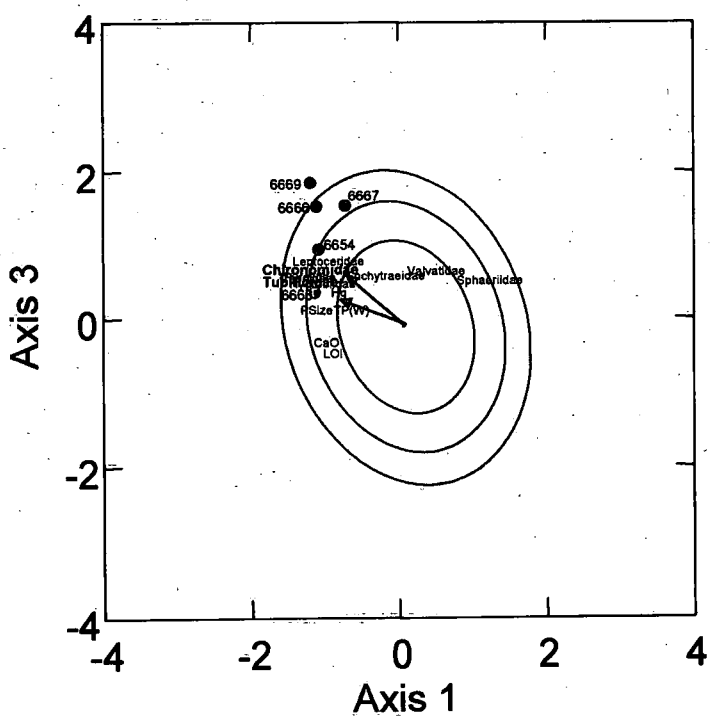


Figure F3. Ordination of subset of St. Clair River sites predicted to reference Group 3 with 90%, 99%, and 99.9% probability ellipses around reference sites (not shown). Two views of the same scores are shown. Significant ($p \leq 0.05$) environmental variables and families are shown. Correlations of the most significant taxa and environmental variables are shown with arrows. Stress = 0.15.

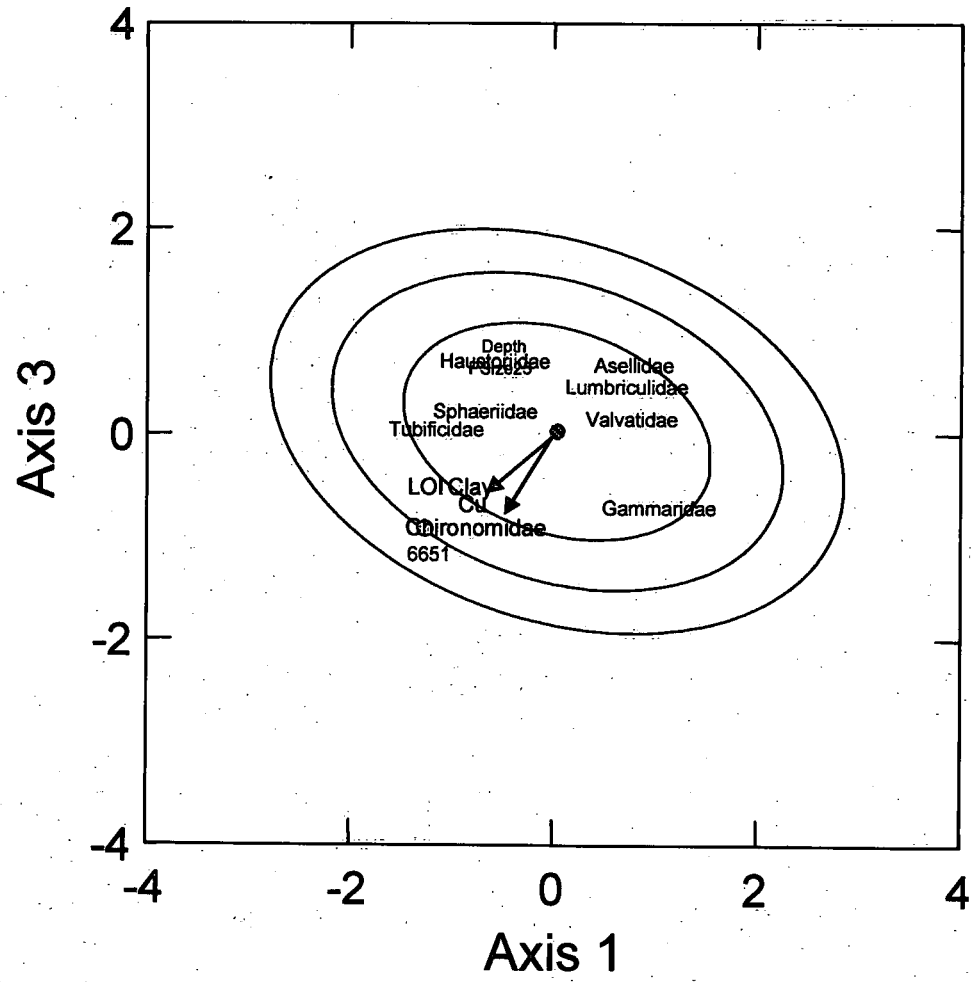


Figure F4. Ordination of site (6651) predicted to Reference Group 1 summarized on Axes 1 and 3 with 90%, 99%, and 99.9% probability ellipses around reference sites (not shown). Significant ($p \leq 0.05$) families and environmental variables are shown. Correlations of the most significant taxa and environmental variables are shown with arrows. Stress = 0.11.

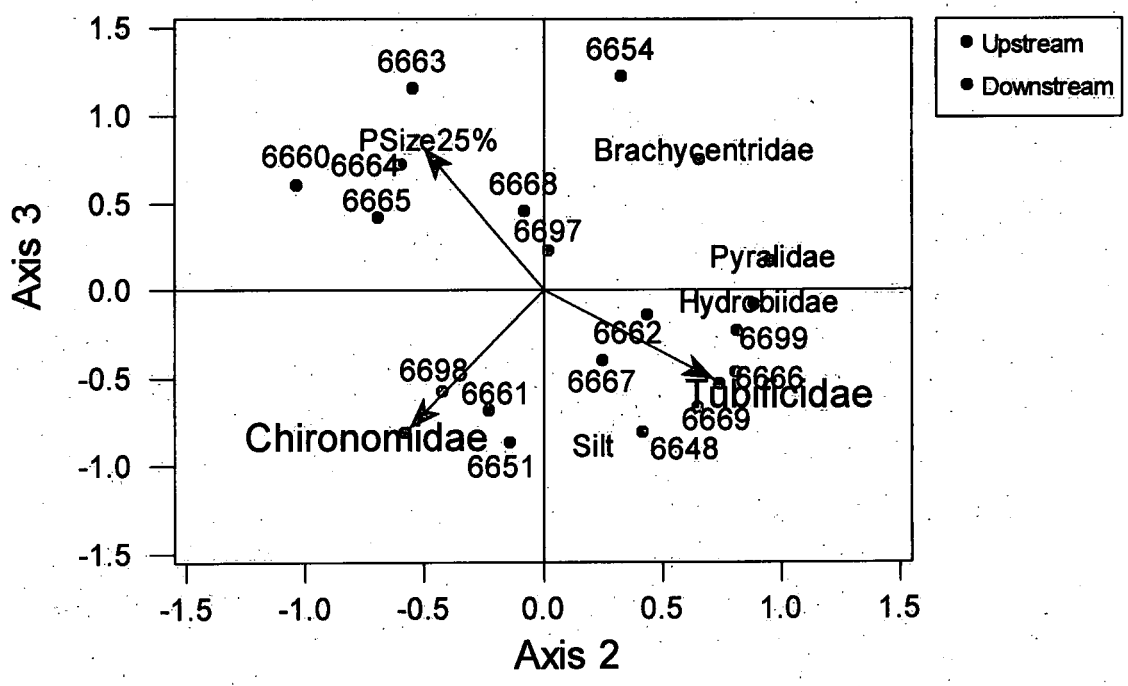


Figure F5. Hybrid multidimensional scaling of St. Clair River sites summarized on Axes 2 and 3. Stress level = 0.12. Site scores are indicated with green and red solid circles, taxon scores with blue solid circles, and environmental attributes with yellow solid circles. The most highly correlated significant families, Tubificidae (r^2=0.87) and Chironomidae (r^2=0.64), are shown as vectors. Only significantly correlated environmental variables are shown.

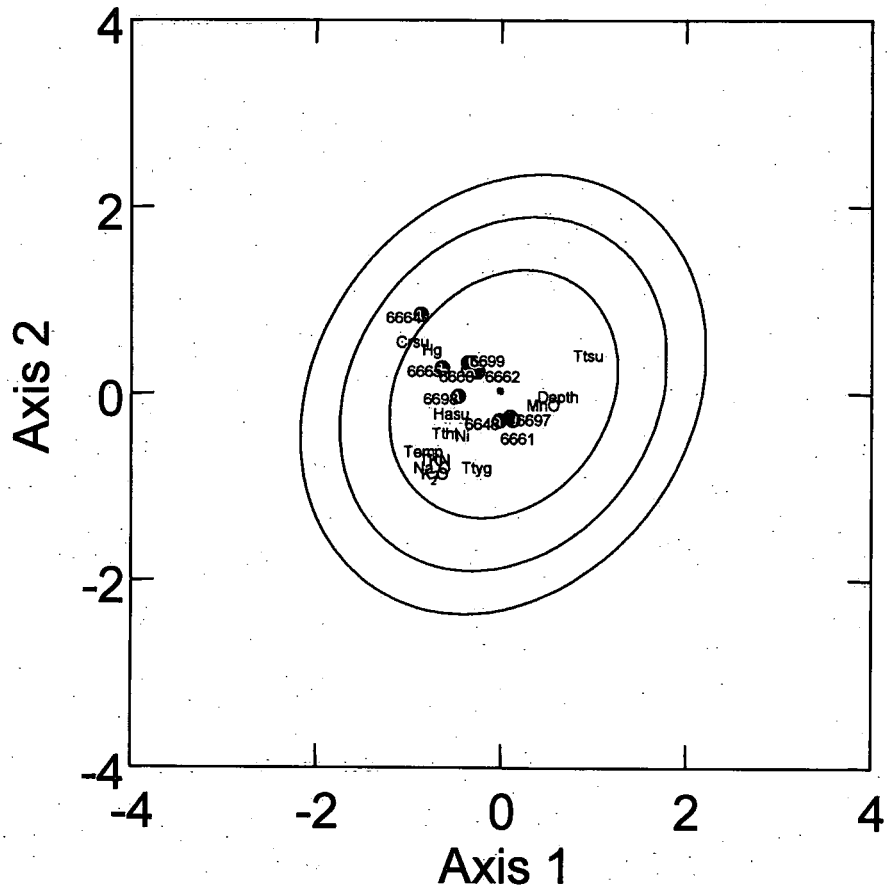


Figure G1. Ordination of subset of test sites using 10 toxicity test endpoints summarized on Axes 1 and 2, showing 90%, 99%, and 99.9% probability ellipses around reference sites (not shown). [*Chironomus* survival (Crsu) and growth (Crgw), *Hexagenia* survival (Hlsu) and growth (Hlgw), *Hyalella* survival (Hasu) and growth (Hagw), *Tubifex* survival (Ttsu), cocoon production (Ttcc), percent cocoon hatch (Ttht) and young production (Ttyg)]. Stress level = 0.089. Scores for correlated environmental variables are also plotted.

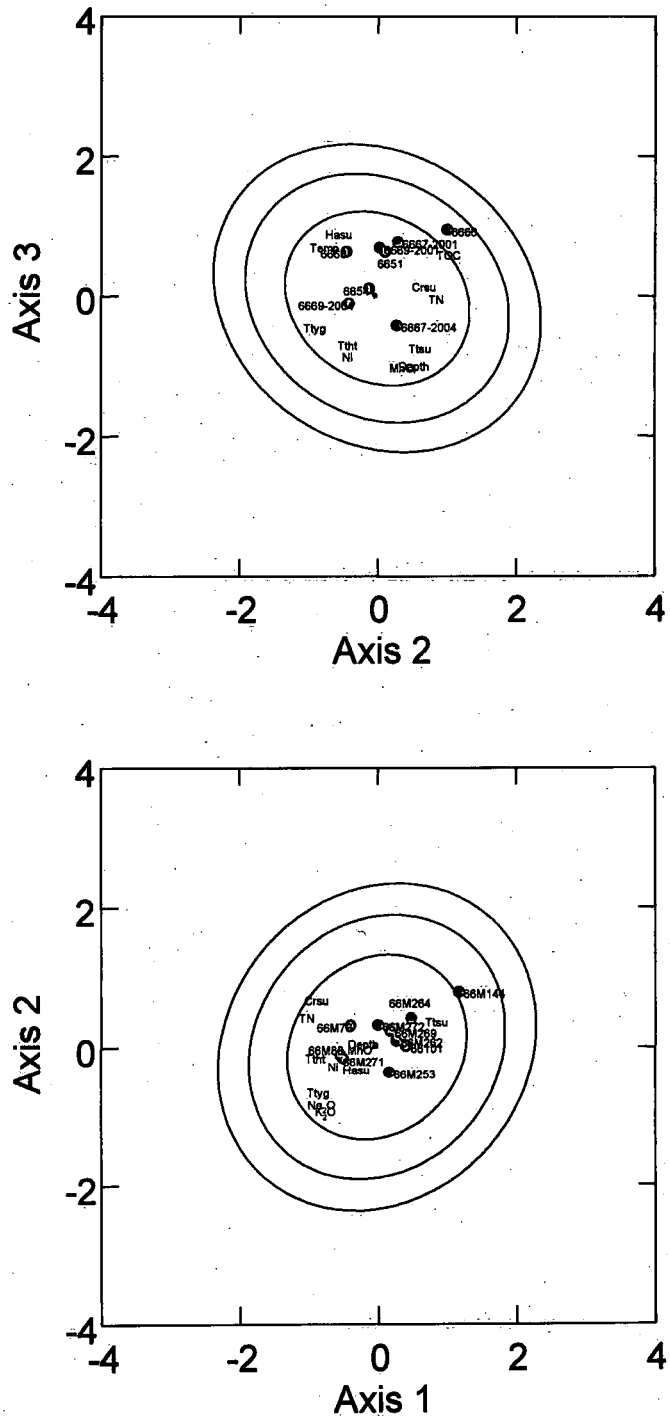


Figure G2. Ordination of subset of test sites using 10 toxicity test endpoints summarized on Axes 2 and 3 (top) and Axes 1 and 2 (bottom), showing 90%, 99%, and 99.9% probability ellipses around reference sites (not shown). [*Chironomus* survival (Crsu) and growth (Crgw), *Hexagenia* survival (Hlsu) and growth (Hlgw), *Hyalella* survival (Hasu) and growth (Hagw), *Tubifex* survival (Ttsu), cocoon production (Ttcc), percent cocoon hatch (Ttht) and young production (Ttyg)]. Stress level = 0.089 [top], 0.087 [bottom].

APPENDIX H. Quality Assurance/Quality Control

Table H1. Coefficients of variation for field-replicated samples.

Parameter	Coefficient of Variation	
	6668	6669
Alkalinity	1.2	0.1
Al_2O_3	18.4	1.9
CaO	5.7	4.5
Clay	-	-
Co	6.3	0
Cr	13.3	12.8
Cu	3.0	5.9
Fe	3.0	3.7
Gravel	74.6	60.8
THg sediment (Caduceon)	12.1	9.3
THg sediment (Flett)	-	14.5
MeHg sediment (Flett)	-	54.1
K_2O	5.2	2.7
LOI	6.0	2.5
Mg	4.6	2.1
Mn	12.0	4.1
Na	3.1	5.6
Ni	6.4	9.1
NO_3/NO_2	2.6	2.0
P_2O_5	6.3	44.4
Pb	12.8	8.5
Sand	5.0	2.3
Silt	9.0	5.2
SiO_2	4.7	1.2
TiO_2	11.5	2.3
TKN water	6.7	32.2
TKN sediment	7.5	14.5
TOC	47.4	11.2
TP water	12.1	5.4
TP sediment	0.8	12.1
V	4.5	5.3
Zn	14.0	10.8

Table H2. Flett laboratory QA/QC results for sediment mercury analyses.

TOTAL HG SEDIMENT

Standards	Hg STD made Dec 2/04	Recovery (%)
	Hg STD 1 (0.02 ng/L)	105.6
	Hg STD 2 (0.1 ng/L)	97.1
	Hg STD 3 (0.25 ng/L)	97.9
	Hg STD 4 (0.5 ng/L)	98.6
	Hg STD 5 (1.0 ng/L)	100.8

Sample Spike Recovery	SAMPLE	Sample Type	Net Total Hg conc. (ng/g wet wt.)	Net Total Hg conc. (ng/g dry wt.)	Hg Recovery (%)
	6669		1232		
	6669	Spike	1515		93.7
	6662		101		
	6662	Spike	421		91.0
	66M269		873.6	1378.0	
	66M269	Spike	4837.4	7630.0	99.1
	66M269	Spike	3949.8	6229.9	86.1
	Relative Percent Difference 66M269		8.9		
	66101		375.4	520.1	
	66101	Spike	5287.2	7326.0	110.0
	66101	Spike	4882.4	6765.1	105.9
	Relative Percent Difference 66101		3.2		
	Mean of Spike Recoveries				**97.6**

QC Samples	Standard	Net Total Hg conc. (ng/g wet wt.)	Net Total Hg conc. (ng/g dry wt.)	Hg Recovery (%)
	Mess - 2 (92 ng/g)		90.6	
	Mess - 2 (92 ng/g)		86.9	96.5
	Mess - 2 (92 ng/g)		81.9	
	Mess - 2 (92 ng/g)		84.6	90.5
	Mess - 2 (92 ng/g)		86.6	94.1
	Mess - 2 (92 ng/g)		86.8	94.4
	Mess - 2 (92 ng/g) Mean		86.7	**93.9**
	OPR (solids)-1 (1 ng/mL)	1.04		104.3
	OPR (solids)-1 (1 ng/mL)	1.02		102.4
	OPR (solids)-1 (1 ng/mL) Mean	1.03		**103.4**

METHYL HG SEDIMENT

Sample Spike Recovery	SAMPLE	Sample Type	Net CH_3Hg as Hg (ng/g) Wet Wt.	Net CH_3Hg as Hg (ng/g) Dry Wt.	CH_3Hg Recovery (%)
	6699		7.59		
	6699	Spike	8.69		103.1
	6698		0.31		
	6698	Spike	1.24		84.8
	6648		0.96		
	6648	Spike	2.29		101.0
	666900	Spike	22.21	22.29	98.0
	666900	Spike	19.68	19.74	89.4
	666900		3.19	3.20	
	66M264	Spike	18.94	19.00	83.4
	66M264	Spike	15.13	15.18	80.0
	66M264		4.00	4.01	
	Mean of Recoveries				**91.4**

	Standard	Net CH_3Hg as Hg (ng/g) Wet Wt.	Net CH_3Hg as Hg (ng/g) Dry Wt.	Net CH3Hg as Hg (ng/L)	CH_3Hg Recovery (%)
QC Samples	IAEA 405 (5.49± 0.53 ng/g)	4.21	4.30		78.3
	IAEA 405 (5.49± 0.53 ng/g)	5.29	5.40		98.3
	Mean of IAEA 405	4.75	4.85		**88.3**
	DORM II (4470 +- 320ng/g)				
	Alpha (200 ng/L)			186.0	93.0
	IAEA 405 (5.49± 0.53 ng/g)	4.68	4.78		87.1
	IAEA 405 (5.49± 0.53 ng/g)	4.37	4.46		81.3
	Mean of IAEA 405	4.53	4.62		**84.2**
	Alpha (200 ng/L)			154.9	77.5

Table H3. Flett laboratory QA/QC results for biota total mercury analysis.

TOTAL HG BIOTA

Standards	Hg STD made Dec 2/04	Recovery (%)
	Hg STD 1 (0.02 ng/L)	103.9
	Hg STD 2 (0.1 ng/L)	96.0
	Hg STD 3 (0.25 ng/L)	99.4
	Hg STD 4 (0.5 ng/L)	101.4
	Hg STD 5 (1.0 ng/L)	99.2
	Hg STD Mean	100.0
	Hg STD made Dec 2/04	Recovery (%)
	Hg STD 1 (0.02 ng/L)	96.6
	Hg STD 2 (0.1 ng/L)	98.6
	Hg STD 3 (0.25 ng/L)	98.9
	Hg STD 4 (0.5 ng/L)	104.7
	Hg STD 5 (1.0 ng/L)	101.2
	Hg STD Mean	100.0
	Hg STD made Dec 2/04	Recovery (%)
	Hg STD 1 (0.02 ng/L)	108.9
	Hg STD 2 (0.1 ng/L)	96.6
	Hg STD 3 (0.25 ng/L)	98.8
	Hg STD 4 (0.5 ng/L)	96.6
	Hg STD 5 (1.0 ng/L)	99.1
	Hg STD Mean	100.0
	Hg STD made Jan 3/05	Recovery (%)
	Hg STD 1 (0.02 ng/L)	101.0
	Hg STD 2 (0.1 ng/L)	98.2
	Hg STD 3 (0.25 ng/L)	98.9
	Hg STD 4 (0.5 ng/L)	100.2
	Hg STD 5 (1.0 ng/L)	101.7
	Hg STD Mean	100.0

QC Samples	Standard	Net Total Hg conc. (ng/g) (Dry Wt)	Hg Recovery (%)
	DORM- 2 (4640 ng/g)	4578	99.0
	DORM- 2 (4640 ng/g)	4529	98.0
	DORM- 2 (4640 ng/g)	4577	99.0
	DORM- 2 (4640 ng/g)	4528	98.0
	DORM- 2 (4640 ng/g)	4564	98.0
	DORM- 2 (4640 ng/g)	4465	96.0
	DORM- 2 (4640 ng/g)	4487.3	96.7
	DORM- 2 (4640 ng/g)	4467.2	96.3
	OPR (solids)-1 (1 ng/mL)	0.96	95.9
	OPR (solids)-1 (1 ng/mL)	0.93	93.4
	DORM- 2 (4640 ng/g)	4507.5	97.1
	DORM- 2 (4640 ng/g)	4570.4	98.5
	OPR (solids)-2 (1 ng/mL)	0.97	97.3
	OPR (solids)-2 (1 ng/mL)	0.96	96.5
	DORM- 2 (4640 ng/g)	4527.1	97.6
	DORM- 2 (4640 ng/g)	4511.0	97.2
	OPR (solids)-1 (1 ng/mL)	0.98	98.2
	OPR (solids)-1 (1 ng/mL)	0.97	97.1
	DORM- 2 (4640 ng/g)	4540.8	97.9
	DORM- 2 (4640 ng/g)	4544.5	97.9
	OPR (solids)-2 (1 ng/mL)	0.99	98.7
	OPR (solids)-2 (1 ng/mL)	0.99	99.5
	Mean		97.4
QC Samples	Standard	Net Total Hg conc. (ng/g) (Wet Wt)	Hg Recovery (%)
	DFO 296 (449 ng/g)	470	105.0
	DFO 296 (449 ng/g)	469	104.0
	DFO 296 (449 ng/g)	470	105.0
	DFO 296 (449 ng/g)	469	104.0
	DFO 296 (449 ng/g)	463	103.0
	DFO 296 (449 ng/g)	472	105.0
	DFO 297 (205 ng/g)	225	110.0
	DFO 297 (205 ng/g)	215	105.0
	DFO 297 (205 ng/g)	225	110.0
	DFO 297 (205 ng/g)	214	105.0
	DFO 297 (205 ng/g)	224	109.0
	DFO 297 (205 ng/g)	212	103.0
	Mean		105.7

Sample Spike Recovery	SAMPLE	SAMPLE TYPE	Net Total Hg conc. (ng/g) (Dry Wt)	Hg Recovery (%)
	6648 - oligochaete		131	
	6648 - oligochaete	Spike	20962	100.5
	6697 - chironomid		204	
	6697 - chironomid	Spike	15891	99.8
	Mean			100.2

Table H4. Flett laboratory QA/QC results for biota methyl mercury analysis.

METHYL HG BIOTA

QC Samples	Standard	Net CH_3Hg	Hg Recovery (%)
	DORM- 2 (4.47 ug/g)	4179	
	DORM- 2 (4.47 ug/g)	3977	91.2
	DORM- 2 (4.47 ug/g)	3988	
	DORM- 2 (4.47 ug/g)	3910	88.3
	DORM- 2 (4.47 ug/g)	4113	
	DORM- 2 (4.47 ug/g)	4233	93.4
	DORM- 2 (4.47 ug/g)	4309	
	DORM- 2 (4.47 ug/g)	4559	99.2
	DORM- 2 (4.47 ug/g)	3898	
	DORM- 2 (4.47 ug/g)	4291	91.6
	DORM- 2 (4.47 ug/g)	3785	
	DORM- 2 (4.47 ug/g)	4071	87.9
	DORM- 2 (4.47 ug/g)	4078	91.2
	DORM- 2 (4.47 ug/g)	3786	84.7
	DORM- 2 (4.47 ug/g)	3952	88.4
	DORM- 2 (4.47 ug/g)	3562	79.7
	DORM- 2 (4.47 ug/g)	3450	77.2
	Alpha (200 ng/L)	158.7	79.4
	Alpha (200 ng/L)	181.0	90.6
	Alpha (200 ng/L)	197.2	98.6
	Mean		**88.7**

Sample Spike Recovery	SAMPLE	SAMPLE TYPE	Net CH_3Hg conc. (ng/g) (Dry Wt)	CH_3Hg Recovery (%)
	6668 - oligochaete		7	
	6668 - oligochaete	Spike	739	88.4
	6667 - chironomid		42	
	6667 - chironomid	Spike	761	99.4
	6662 - chironomid		9	
	6662 - chironomid	Spike	801	107.4
	6651 - Oligochaete		1	
	6651 - Oligochaete	Spike	781	103.1
	6667 - chironomid		55	
	6667 - chironomid	Spike	793	102.1
	6669 - Oligochaete	Spike	224	107.8
	6669 - Oligochaete	Spike	217	94.9
	6669 - Oligochaete		20	
	6667 - oligochaete	Spike	346	97.3
	6667 - oligochaete	Spike	328	97.0
	6667 - oligochaete		38	
	66M272 - oligochaete	Spike	497	95.0
	66M272 - oligochaete	Spike	602	87.8
	66M272 - oligochaete		11	
	Mean			**98.2**

Table H5. Laboratory QA/QC data from Caduceon Environmental Laboratory (2001 data).

			Laboratory Duplicate (Site 1325)			Certified Reference Materials											
						WH89-1			STSD-3			SO-2			STSD-1		
Analyte	Units	Det Limit	Concn 1	Concn 2	CV	measured	reference	recovery	measured	reference	recovery	measured	reference	recovery	measured	reference	recovery
K	pct	0.05	0.25	0.23	0.059												
Li	µg/g	1	20	19	0.050				19	23	0.826						
Mg	pct	0.01	0.94	0.88	0.047												
Mn	µg/g	1	641	614	0.030				2340	2630	0.890				3480	3740	0.930
Mo	µg/g	1	1	<1					6	7	0.857				2	2	1.000
Na	pct	0.01	0.04	0.04	0.000												
Nb	µg/g	5	<5	<5													
Ni	µg/g	1	42	39	0.045				28	25	1.120				23	18	1.278
Pb	µg/g	1	33	34	0.021				42	39	1.077				37	34	1.088
Sb	µg/g	5	<5	<5													
Sn	µg/g	20	<20	<20													
Sr	µg/g	1	43	41	0.029												
Ti	µg/g	1	1107	950	0.108												
V	µg/g	25	45	41	0.071				50	61	0.820				35	47	0.745
W	µg/g	20	<20	<20													
Y	µg/g	1	20	19	0.033												
Zn	µg/g	1	137	133	0.021				175	192	0.911				145	165	0.879
Al2O3	pct	0.01	12.89	12.9	0.001	12.2	12.1	1.008				14.51	15.1	0.961			
BaO	pct	0.001	0.071	0.071	0.005	0.288	0.29	0.993				0.101	0.111	0.910			
CaO	pct	0.01	2.77	2.82	0.013	5.91	5.9	1.002				2.72	2.77	0.982			
Cr2O3	pct	0.01	0.01	0.01	0.079	0.04	0.04	1.000				<0.01	<0.01				
Fe2O3	pct	0.01	5.76	5.72	0.005	6.97	6.9	1.010				7.76	7.89	0.984			
K2O	pct	0.01	2.90	3	0.024	2.25	2.21	1.018				3.06	2.94	1.041			
MgO	pct	0.01	2.23	2.24	0.002	3.5	3.5	1.000				0.87	0.89	0.978			
MnO	pct	0.01	0.10	0.1	0.006	0.09	0.09	1.000				0.09	0.07	1.286			
Na2O	pct	0.01	1.75	1.61	0.059	1.25	1.34	0.933				2.41	2.48	0.972			
P2O5	pct	0.03	0.42	0.39	0.052	0.2	0.19	1.053				0.66	0.69	0.957			
SiO2	pct	0.01	55.43	55.38	0.001	60.96	60.5	1.008				54	53.42	1.011			
TiO2	pct	0.01	0.73	0.73	0.003	0.9	0.9	1.000				1.31	1.43	0.916			
LIO	pct	0.05	13.34	13.47	0.007	4.75	5	0.950									
				mean CV	0.031		mean recovery	0.998		mean recovery	0.929		mean recovery	1.000		mean recovery	0.987

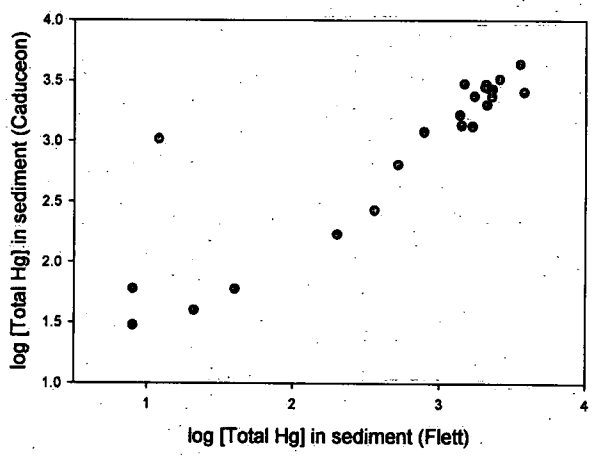
Table H6. Laboratory QA/QC data from Caduceon Environmental Laboratory (2004 data).

			6669-1		Duplicate	Lab	QA/QC
			Sample ID:		Relative Percent Difference	Blank (water)	%Recovery
Parameter	Units	M.D.L.	Reference Method	Date Analyzed			
Total Organic Carbon	% by wt	0.1	LECO	29/Nov/04	6.4	N/A	102
Total Kjeldahl Nitrogen	µg/g	10	EPA 351.2	29/Nov/04	4.4	< 0.05	101
Phosphorus-Total	µg/g	3	EPA 365.4	29/Nov/04	5.2	< 0.01	99
Aluminum	µg/g	300	EPA 6010	30/Nov/04	4.6	< 0.01	89
Antimony	µg/g	0.1	SM 3114	30/Nov/04	8.8	< 0.001	99
Arsenic	µg/g	1	SM 3114	30/Nov/04	7.3	< 0.001	97
Barium	µg/g	1	EPA 6010	30/Nov/04	23	< 0.001	96
Beryllium	µg/g	0.2	EPA 6010	30/Nov/04	38.5	< 0.002	104
Bismuth	µg/g	5	EPA 6010	30/Nov/04	N/A	< 0.02	N/A
Cadmium	µg/g	0.5	EPA 6010	30/Nov/04	19	< 0.005	97
Calcium	µg/g	100	EPA 6010	30/Nov/04	1.5	< 0.02	85
Chromium	µg/g	1	EPA 6010	30/Nov/04	1.7	< 0.002	98
Cobalt	µg/g	1	EPA 6010	30/Nov/04	3	< 0.005	92
Copper	µg/g	1	EPA 6010	30/Nov/04	15	< 0.002	93
Iron	µg/g	300	EPA 6010	30/Nov/04	3.9	< 0.005	90
Lead	µg/g	5	EPA 6010	30/Nov/04	19	< 0.02	98
Magnesium	µg/g	100	EPA 6010	30/Nov/04	1.4	< 0.01	95
Manganese	µg/g	1	EPA 6010	30/Nov/04	4.5	< 0.001	96
Mercury	µg/g	0.005	SM 3112	29/Nov/04	4.2	< 0.00006	91
Molybdenum	µg/g	1	EPA 6010	30/Nov/04	22.5	< 0.01	120
Nickel	µg/g	1	EPA 6010	30/Nov/04	10.4	< 0.01	95
Potassium	µg/g	300	EPA 6010	30/Nov/04	2.9	< 0.1	94
Selenium	µg/g	0.1	SM 3114	30/Nov/04	2.1	< 0.001	98
Silver	µg/g	0.1	EPA 6010	30/Nov/04	N/A	< 0.005	104
Sodium	µg/g	200	EPA 6010	30/Nov/04	4.0	< 0.2	65
Strontium	µg/g	1	EPA 6010	30/Nov/04	3.5	< 0.001	76
Thallium	µg/g	0.02	EPA 6020	30/Nov/04	0.0	< 0.0002	97
Tin	µg/g	10	EPA 6010	30/Nov/04	0.0	< 0.05	N/A
Titanium	µg/g	1	EPA 6010	30/Nov/04	8.9	< 0.005	88
Tungsten	µg/g	20	EPA 6010	30/Nov/04	14.1	< 0.005	N/A
Vanadium	µg/g	1	EPA 6010	30/Nov/04	2.2	< 0.005	91
Yttrium	µg/g	0.5	EPA 6010	30/Nov/04	2.3	< 0.005	94
Zinc	µg/g	1	EPA 6010	30/Nov/04	1.7	< 0.005	103
Aluminum (Al2O3)	%	0.01	IN-HOUSE	1/Dec/04	1.5	< 0.05	98
Barium (BaO)	%	0.001	IN-HOUSE	1/Dec/04	0.0	< 0.05	100
Calcium (CaO)	%	0.01	IN-HOUSE	1/Dec/04	3.0	< 0.05	98
Chromium (Cr2O3)	%	0.01	IN-HOUSE	1/Dec/04	54.6	< 0.05	102
Iron (Fe2O3)	%	0.05	IN-HOUSE	1/Dec/04	3.8	< 0.05	98
Magnesium (MgO)	%	0.01	IN-HOUSE	1/Dec/04	6.3	< 0.05	96
Manganese (MnO)	%	0.01	IN-HOUSE	1/Dec/04	22.2	< 0.05	99
Phosphorus (P2O5)	%	0.03	IN-HOUSE	1/Dec/04	0.0	< 0.05	90
Potasium (K20)	%	0.01	IN-HOUSE	1/Dec/04	0.0	< 0.05	97
Silica (SiO2)	%	0.01	IN-HOUSE	1/Dec/04	1.8	< 0.05	101
Sodium (NaO)	%	0.01	IN-HOUSE	1/Dec/04	1.1	< 0.05	95
Titanium (TiO2)	%	0.01	IN-HOUSE	1/Dec/04	3.8	< 0.05	93
Whole Rock Total	%		IN-HOUSE	1/Dec/04	N/A	N/A	N/A
Loss on Ignition	%	0.05	IN-HOUSE	1/Dec/04	6.2	N/A	96
				mean	8.0		95.6

N/A = Not Available/Applicable

Inter-Laboratory Comparison of Analyses of Total Hg in Sediment from the St. Clair River

Analyses for concentrations of total mercury (THg) in sediment were performed by two laboratories: Flett research Ltd., which was selected to measure THg and methyl mercury in sediment and biological samples, and Caduceon Environmental Laboratory, which conducted THg analyses on all sites. Each lab received a sediment subsample from the same homogenized sample collected at each site. Those submitted to Flett were sent frozen, and those submitted to Caduceon were first freeze-dried. The figure below shows how the site measurements compare graphically.



Overall agreement between labs for the determinations of THg in sediment is indicated by the slope of a regression involving the two variables. As recommended by McArdle (1988) and Draper and Smith (1998), the regression was estimated by the geometric mean (GM, aka reduced major axis) method instead of the ordinary least squares (OLS) method. The OLS method assumes negligible error in the X variable, and can result in biased slope estimates when applied to data in which both X and Y variables are subject to errors of the same magnitude, a situation which clearly applies here. Rather than minimizing the sum of the squares of the deviations of observed Y values from the regression line, as in the OLS method, the GM method minimizes the sum of the areas of the triangles formed by the data point, the point on the line corresponding to the X value, and the point on the line corresponding to the Y value. Geometric Mean slope, b_{GM}, was estimated by

$b_{GM} = s_y / s_x$ (Legendre and Legendre 1998)

where s_y = standard deviation of Y - values, and s_x = standard deviation of X - values. The b_{GM} estimate is also the geometric mean of the OLS slope of Y on X and the reciprocal of the slope of X on Y. (Note that when the purpose of the analysis is not to estimate functional parameters such as the slope, but only to predict values of Y for given X's, OLS regression is suitable (Legendre and Legendre 1998). For this reason, the GM method was not used for the invertebrate Hg – sediment Hg regressions.)

Geometric mean regression slope for $\log[THg]_{Caduc}$ vs $\log[THg]_{Flett}$:

Standard deviation of $\log[THg]_{Caduc} = 0.689418 = s_y$
Standard deviation of $\log[THg]_{Flett} = 0.903535 = s_x$

$b_{GM} = s_y / s_x = 0.689418 / 0.903535 = \mathbf{0.763}$

OLS regression of Y vs X: $\log[THg]_{Caduc} = 1.1024 + 0.6728 \log[THg]_{Flett}$
OLS regression of X vs Y: $\log[THg]_{Flett} = -0.6673 + 1.1556 \log[THg]_{Caduc}$

For the regression, $P<0.001$ and $r^2 = 77.8\%$.
As a check, using the alternate slope estimation method: $b_{GM} = (0.689418 \times [1 / 1.1556])^{1/2} = \mathbf{0.763}$

The overall agreement in measurements of THg in sediment is reasonable because the slope estimate is fairly close to 1. This suggests that either (a) the analyses of the labs are accurate or (b) analyses are biased in identical ways. The unexplained 22.2% of the variation of the regression should be attributed to laboratory measurement error.

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