Final Project Report for Applying the COA Framework to the St. Clair River Area of Concern

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ACRONYMS AND ABBREVIATIONS

%	Percent
#/m^2	number of individuals per square metre
95%UCL	95 percent upper confidence limit
AOC	Area of Concern
AOI	Area of Interest
AR	Anisotropic ratio
AUF	Area use factor
BEAST	Benthic Assessment of Sediment
BMF	Biomagnification factor
BNE	Base neutral extractable
BUI	Beneficial use impairment
CCME	Canadian Council of Ministers of the Environment
cm	Centimetre(s)
COA Framework	Canada-Ontario Decision-Making Framework for Assessment of Great Lakes Contaminated Sediment
EC10	10% effective concentration
EC20	20% effective concentration
ENVIRON	ENVIRON International Corporation
EPT	Ephemeroptera, Plecotera, Trichoptera
ERA	Ecological risk assessment
FIR	Food ingestion rate
g	Gram(s)
g/g-day	Gram(s) per gram body weight per day
g/mol	Gram(s) per mol
GIS	Geographic Information System
GLWQA	Great Lakes Water Quality Agreement
ha	Hectare(s)
HCB/kg	Hexachlorobenzene per kilogram
HCB/kg BW-day	Hexachlorobenzene per kilogram body weight per day
IDW	Inverse distance weighting
K_{ow}	Octanol-water partition coefficient
Kcal/g	Kilocalorie(s) per gram
Kcal/kg-day	Kilocalorie(s) per kilogram body weight per day

kg	Kilogram(s)
kg/day	Kilogram(s) per day
km	Kilometre(s)
LC50	Lethal concentration to 50% of the population tested
LEL	Lowest effect level
LOAEC	Lowest observed adverse effect concentration
LOAEL	Lowest observed adverse effect level
LOE	Line of evidence
LOI	Loss on ignition
m	metre(s)
m^3	cubic metre(s)
mm	millimetre(s)
mg/kg	milligram(s) per kilogram
mg/kg-day	milligram(s) per kilogram body weight per day
MOE	Ontario Ministry of the Environment
n	sample size
NCE	Neutral chlorinated extractable
NOAA	National Oceanic and Atmospheric Administration
NOAEC	No observed adverse effect concentration
NOAEL	No observed adverse effect level
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyl
RAP	Remedial Action Plan
RMSE	Root-mean-square-error
ROI	Receptor of interest
SCRCA	St. Clair Region Conservation Authority
s.d.	Standard deviation
SEL	Severe effect level
SFCMP	Sportfish Contaminant Monitoring Program
SLEA	Sarnia-Lambton Environment Association
SWAC	Spatially weighted average concentration
SQG	Sediment quality guideline
SQG-high	The least conservative sediment quality guideline
SQG-low	The most conservative sediment quality guideline

TEL	Threshold effect level
TOC	Total organic carbon
TRV	Toxicity reference value
UCL	Upper confidence limit
µg/kg	Microgram(s) per kilogram
µg/kg-day	Microgram per kilogram body weight per day
µg/L	microgram(s) per litre
µm	micrometre(s)
µmol/g	Micromol(es) per gram
USACE	United States Army Corps of Engineers
USEPA	United States Environmental Protection Agency
UTM	Universal Trans Mercator

1 INTRODUCTION

The purpose of this report is to apply the Canada-Ontario Decision-Making Framework for Assessment of Great Lakes Contaminated Sediment (COA Framework) to the St. Clair River. The St. Clair River flows 64 kilometres (km) from Lake Huron south to Lake St. Clair and forms the border between the state of Michigan (U.S.A.) and the province of Ontario (Canada) (Figure 1-1). The COA Framework uses an ecosystem approach to sediment assessment to evaluate potential effects on sediment-dwelling and aquatic organisms, as well as potential for contaminants to biomagnify in the food chain. This report primarily focuses on an 8.3 km reach of the St. Clair River, hereafter referred to as the Area of Interest (AOI) (Figure 1-2). This report will form the technical basis for sediment risk management decisions.

In 1985, the St. Clair River was designated as an Area of Concern (AOC) under the 1972 Great Lakes Water Quality Agreement (GLWQA), based on several beneficial use impairments (BUIs). Stage 1 of the Remedial Action Plan (RAP) identified the following impairments in this AOC: restrictions on fish and wildlife consumption; tainting of fish and wildlife flavour; restrictions on drinking water consumption or taste and odour; beach closings; degradation of aesthetics; bird or animal deformities or reproduction problems; added cost to agriculture or industry; degradation of benthos; restrictions on dredging activities; and loss of fish and wildlife habitat. At that time, St. Clair River sediment was affected by nutrient loading and elevated concentrations of metals (including copper, lead, mercury, and zinc), as well as organic compounds. Organic compounds with elevated sediment concentrations include polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), octachlorostyrene, hexachlorobenzene, and hexachlorobutadiene.

The conditions documented in 1985 reflected a long history of industrial development in Sarnia and along the eastern shore of the river. In the 1940s, numerous petrochemical facilities were constructed in the industrial area in and south of Sarnia, in support of the war effort. For example, Dow Chemical developed a diversified petrochemical complex in 1942 in Sarnia, in order to produce synthetic rubber. In the 1950s and 1960s, local industry instituted effluent controls as a means of reducing chemical discharges to the St. Clair River. In 1968, sediment impairment was documented based on impaired benthic communities to the mouth of the river (MOEE 1979). In 1977, a zone of benthic recovery extended about 23 km upriver from the mouth. At that time, areas of benthic impairment and partial recovery existed along 20 km of Ontario shoreline (MOEE 1979). Further effluent controls were instituted in 1985, following a tetrachloroethylene spill to the river at the Dow Sarnia facility. Additionally, on-site remedial measures were implemented to achieve point source load reductions for manufactured chlorinated solvents and byproducts. At that time, the Cole Drain and the First Street 42-inch Sewer were identified as primary point sources for chlorinated organic compounds; discharges from these sources were curtailed. By 1990, the length of the impacted area within the AOC had been reduced to approximately 9 km in river length. Within that reach, three zones (Zones 1, 2, and 3) were identified for further study (RAP Stage 2) (Figure 1-2). In 1996, chlorinated hydrocarbons were removed from a small area immediately downstream of the Cole Drain.

Between 2002 and 2004, 13,370 m^3 of contaminated sediment within Zone 1 was remediated via hydraulic dredging and removed for disposal.

1.1 COA Framework Overview

As excerpted from Environment Canada and Ontario Ministry of the Environment (MOE) (2007) and noted above, the COA Framework uses an ecosystem approach to sediment assessment and considers potential effects on sediment-dwelling and aquatic organisms, as well as potential for contaminants to biomagnify in the food chain. It is intended to standardize decision-making, while maintaining sufficient flexibility to account for site-specific conditions. Figure 1-3 depicts the seven steps of the COA Framework. As shown, the COA Framework focuses on four lines of evidence (LOEs): 1) potential for biomagnification; 2) sediment chemistry; 3) benthic community structure; and 4) sediment toxicity. The four LOEs address different aspects of ecological risk; the COA Framework does not pertain to decision-making related to human health risk, source control, or any concerns other than ecological risk.

Although the COA Framework defines one of the LOEs as "potential for biomagnification," this report instead uses the term "risk from biomagnification" because biomagnification in and of itself is not indicative of ecological harm. It is only when a chemical is biomagnified or bioaccumulated to a toxic level, to that organism and/or those that consume it, that adverse effects are observed. Furthermore, the term "potential" in this instance is overly inclusive: inorganic mercury contained within a sealed container has the "potential" for biomagnification, even when no complete migration or exposure pathways exist. The alternative term "risk" implies a reasonable probability of occurrence. When referring to work conducted for this report, the term "risk from biomagnification" is used, while the term "potential for biomagnification" is used when referring to work previously completed by others. Also, whereas the COA Framework defines subsurface sediment as being greater than "about 10 [centimetre] cm depth," this report considers sediment from 0 cm to 15 cm as surface sediment in calculations and mapping. A slightly broader definition of surface sediment (i.e., 0 cm to 15 cm) was used in this report based on the following rationale. The recent (2006) sediment chemistry data analyzed sediment core depth intervals of 0 cm to 5 cm and 5 cm to15 cm, but not 0 cm to 10 cm. Thus, to use the 2006 sediment chemistry data, it was necessary to choose between using a smaller depth interval (i.e., 0 cm to 5 cm) or larger depth interval (i.e., 0 cm to 15 cm) than is specified in the COA Framework. The larger depth interval (i.e., 0 cm to 15 cm) was selected because it is the more conservative (i.e., environmentally protective) option, in that concentrations of mercury in sediment generally increase with sediment depth and benthic invertebrates generally burrow deeper than 5 cm below the sediment-water interface.

Methods and analyses presented in this report are consistent with four guidance rules defined in the COA Framework:

- Sediment chemistry data are only to be used alone for remediation decision when costs of further investigations outweigh costs of remediation and there is agreement to act, or when sites are subject to regulatory action

- Remediation decisions will be based primarily on biology
- LOEs such as laboratory toxicity tests and models that contradict the results of properly conducted field surveys are incorrect
- If the impacts of a remedial alternative will cause more environmental harm than good, then it should not be implemented

Under the COA Framework, sediment with chemical concentrations below sediment quality guidelines (SQGs) and that do not contain biomagnifying substances are excluded from further consideration. Sediment that does not meet these criteria but has chemical concentrations consistent with reference conditions is also excluded from further consideration. The COA framework defines reference as "a designated site, or set of conditions, used for comparison when evaluating sediment for contamination or pollution." According to the COA Framework, potential for biomagnification is initially addressed by conservative (worst case) modeling and subsequently by additional food chain data and more realistic assumptions. Sediment toxicity and alterations to resident benthic communities are addressed by laboratory studies and field observations, respectively.

1.2 Status Summary

Environment Canada, MOE, the Sarnia-Lambton Environment Association (SLEA), and the St. Clair Region Conservation Authority (SCRCA) have collected substantial data related to the four LOEs evaluated under the COA Framework. All relevant project data are assembled in a georeferenced project database (Appendix A). Studies considered in this application of the COA Framework are summarized below.

1.2.1 2008 Sampling Overview

Richman (2008a) presented results from sampling in Zone 1 through Zone 3 of the St. Clair River, with focus on sediment concentrations of mercury, methylmercury, hexachlorobenzene, hexachlorobutadiene, and octachlorostyrene. Analyses also included total PCBs, tetrachloroethylene, total organic carbon (TOC), nutrients (phosphorus and nitrogen), iron, manganese, and particle size distribution, depending on site-specific sampling objectives. Stations in Zone 1 included locations identified from mid-1990s MOE sampling, including stations in the vicinity of the Cole Drain, along the LanXESS shoreline, and in the vicinity of the 1st Street Sewer. Stations in Zone 2 included locations along the Suncor shoreline, behind the Dow dock upstream of the Dow-Suncor property line, and behind the Shell dock. Stations in Zone 3 included locations along the Guthrie Park shoreline, as well as locations along the St. Clair shoreline downstream of Corunna. As defined by Richman (2008a), sampling in Zone 2 and Zone 3 was designed to confirm 2006 survey data as well as to expand data collection into previously under-sampled areas. Sampling along the Guthrie Park shoreline was specifically designed to assess the depth distribution of mercury in locations where the shoreline might be disturbed through remediation or "shoreline softening" activities.

Richman (2008a) concluded that for Zone 1, sediment in locations downstream of the Cole Drain but upstream of the area remediated by Dow in 2002 through 2004, was characterized by residual chemicals at concentrations lower than had existed prior to the remediation activities. Specifically, with the exception of elevated octachlorostyrene concentrations at one station, surface sediment chemical concentrations were consistently below the RAP proposed remediation targets.

For Zones 2 and 3, surface sediment mercury concentrations frequently exceeded MOE's severe effect level (SEL) of 2 milligrams per kilogram (mg/kg) (Persaud et al. 1993), and reached 40 mg/kg in the vicinity of the Shell dock and 63 mg/kg in the vicinity of Guthrie Park (Richman 2008a). The elevated mercury concentration in the vicinity of the Shell dock was co-located with elevated concentrations of methylmercury and octachlorostyrene. As noted by Richman (2008a), sampling in the vicinity of Guthrie Park revealed elevated mercury concentration in surface sediment and subsurface sediment (reaching 137 mg/kg). Cores collected at locations in Zone 2 and Zone 3 demonstrated sometimes significant variability in mercury concentrations within discrete depth sections of replicate cores.

1.2.2 Richman and Milani (2008) Overview

Richman and Milani (2008) reviewed existing surface sediment data for mercury, hexachlorobenzene, hexachlorobutadiene, and octachlorostyrene to assess the extent to which sediment chemical concentrations have declined over time in Zone 2 and Zone 3 of the St. Clair River. Using existing data that explored the relationship between sediment methylmercury concentration and the concentration of methylmercury in the tissue of benthic invertebrates, Richman and Milani (2008) also estimated biomagnification potential for the broader areas within Zone 2 and Zone 3 for which 2006 surface sediment methylmercury data existed, but co-located benthic invertebrate tissue data were not collected.

For sediment mercury concentrations, comparison of 2006 surface sediment data with data from earlier sampling intervals (1990 to 2004) suggested that surface sediment mercury concentrations have not decreased consistently over this interval. Richman and Milani (2008) concluded that, whereas a significant decline in mercury discharge following closure of the chlor-alkali facility likely resulted in declines in surface sediment mercury concentrations particularly in sediment adjacent to the facility discharge, residual sediment contamination remains evident in Zone 2 and Zone 3 of the St. Clair River. With respect to methylmercury, Richman and Milani (2008) concluded that measured (2001-2004) and estimated (2006) invertebrate tissue concentrations of methylmercury are greater in Zone 2 and Zone 3 than in upstream reference stations, and a risk of methylmercury biomagnification therefore exists for most stations within Zone 2 and Zone 3. For higher trophic level consumers, extrapolation of these results suggests that the tissue residue guideline (Environment Canada 2002) would be exceeded at the majority of the sites in Zone 2 and Zone 3 for which extrapolation was performed. This conclusion is consistent with fish tissue (walleye [*Sander vitreus*]) data from the St. Clair River, and confirms assumptions regarding elevated potential for biomagnification in this river system (Richman and Milani 2008).

Overall, Richman and Milani (2008) concluded that sediment remains an important source of methylmercury to biota in the St. Clair River, and that although sediment quality has improved over time with respect to concentrations of hexachlorobenzene, hexachlorobutadiene, and octachlorostyrene, the continued bioavailability of methylmercury in river sediment, possibly extending throughout the length of the river, suggests that it is unlikely that remediation of sediment in any one location will significantly influence overall concentrations of mercury in sport fish. Accordingly, Richman and Milani (2008) advise that remediation options for this reach of the river should therefore focus on source control strategies for limiting the continued downstream transport of mercury and methylmercury.

1.2.3 Biberhofer et al. (2007) Overview

Biberhofer et al. (2007) presented results from 2006 sediment sampling in the St. Clair River. Sampling targeted locations that had been sampled in 2001 by MOE. Target analytes included mercury, methylmercury, hexachlorobenzene, hexachlorobutadiene, and octachlorostyrene. Sediment analyses also included nutrients (phosphorus and nitrogen), iron and manganese, and particle size distribution. Biberhofer et al.'s (2007) objectives were to broaden the current understanding of chemical distributions in surface and subsurface sediment of the St. Clair River, as well as to assess temporal changes in surface sediment chemical concentration and chemical distribution since the 2001 sampling event. Vertical chemical distribution was defined by recovery and sectioning of cores into 0 cm to 5 cm and 5 cm to 15 cm increments. Biberhofer et al. (2007) defined the 0 cm to 5 cm increment as surface sediment, and defined the 5 cm to15 cm increment as subsurface sediment.[1]

Biberhofer et al. (2007) concluded that results of the 2006 survey further confirm previous observations of a discontinuous and irregular shoreline distribution of sediment and sediment-associated chemicals in the St. Clair River. Moreover, the location of fine grained sediment was principally restricted to embayments and marine facilities such as docks and jetties. With respect to chemicals of concern, both total mercury and methylmercury persist in St. Clair River sediment at elevated concentrations in both surface and subsurface sediment. For organic chemicals, although the distribution of hexachlorobenzene, hexachlorobutadiene, and octachlorostyrene suggest general trends of decreasing concentration with the direction of flow, surface sediment chemical concentrations (as with mercury data) are not consistently lower than subsurface chemical concentrations. Biberhofer et al. (2007) concluded that, based on the vertical distribution of sediment chemical data in the locations sampled, recent sedimentation is not mitigating potential biological exposure from sediment-associated chemicals of concern.

[1] In contrast, the present analysis defines the 0 cm to 15 cm interval as surface sediment, and depths greater than 15 cm as subsurface sediment. This practice ensures the protectiveness of the assessment, given that depths to 15 cm may be biologically active.

1.2.4 Milani et al. (2007) Overview

Milani et al. (2007) completed the first four steps of the COA Framework. As part of that work, the previously defined Zone 1 is referred to as Zone A, while the previously defined Zones 2 and 3 are referred to as Zone B (Figure 1-2). Specifically, Zone B stretches from the northern terminus of Zone 2 to the southern terminus of Zone 3. Thus, the following description addresses Zones 1 through 3, while this report focuses on Zones 2 and 3. Conclusions from the first four steps of the COA Framework are as follows.

Mercury biomagnification potential. Total mercury and methylmercury concentrations in sediment and invertebrates (chironomids, oligochaete worms at most sites exposed to historical industrial discharges (Zones A and B) were elevated above those at upstream reference sites. Milani et al. (2007) tested the relationship between total mercury and methylmercury levels in sediment and corresponding concentrations in benthic invertebrates, with results suggesting that concentrations of total mercury and methylmercury in sediment were good predictors of the corresponding concentrations in benthic invertebrates.

Under intermediate exposure and uptake assumptions, several sampling stations were predicted to have concentrations of methylmercury in receptors higher than the maximum reference site receptors and to exceed the tissue residue guideline (Environment Canada 2002) for the protection of piscivorous (fish-consuming) wildlife, as follows:

- White sucker (*Catostomus commersonii*) – 0 sites
- Yellow perch (*Perca flavescens*) – 7 sites, 4 of which were in Zone B (i.e., the AOI)
- Walleye[2] – 14 sites, 11 of which were in Zone B (i.e., the AOI)

Sediment chemistry. Most sampling stations within the AOI had sediment mercury concentrations elevated above upstream reference stations. Prior to remediation in 2004, the highest sediment mercury concentrations were found along the industrial sector (Zone A; up to 25-fold higher than the SEL). Elevated concentrations extend to the southern end of Stag Island (Zone B; up to 1.9-fold higher than the SEL).

Benthic invertebrate community. Most sampling stations where benthic communities were assessed (2001 stations) showed strong evidence of different communities compared to Great Lakes reference stations, primarily due to enriched Tubificidae and Chironomidae and high taxon diversity. However, despite the addition of several St. Clair River reference stations to the Great Lakes reference database, habitat characteristics at about half of the test stations were not well matched to any reference group; therefore, results were interpreted with caution. Multivariate comparisons of benthic communities within the river indicated no differences between upstream and test stations. Overall, only one station (6662), which is located within Zone A, was deemed impaired, based on low taxon diversity and high abundance of tubificid

[2] Also referred to as pickerel

worms. No relationship between mercury concentrations and benthic community structure was evident, and impairment was not observed in Zone B (i.e., the AOI).

Sediment toxicity. There was no evidence of severe sediment toxicity at any site; however, *Hexagenia* survival was reduced at two stations (one each in Zones A and B) and *Tubifex* cocoon production was reduced at one station in Zone B. Concentrations of mercury in sediment were not correlated with observed responses. Due to the low magnitude of toxicity and the fact that only one of ten toxicity test endpoints was affected at each location, Milani et al. (2007) did not recommend further action with respect to sediment toxicity.

In summary, Milani et al. (2007) concluded that 16 of the 26 stations[3] required further assessment of the potential for mercury biomagnification. Eleven of those stations are located in Zone B (i.e., the AOI). One station in Zone A (Station 6662) required further assessment of the reasons for benthos alteration, and the remaining nine sites required no further action.

1.2.5 Houtby and Moran (2006) Overview

Houtby and Moran (2006) presented results of sampling on behalf of SLEA in support of a chemical bioaccumulation monitoring program on the St. Clair River. The first iteration of this monitoring program was conducted in 2001, and because it occurred prior to the remediation of Zone 1, is not discussed further in this report. Exclusion of data generated prior to the remediation of Zone 1 is per the instructions of the Technical Team (pers. comm. September 23, 2008). As presented by Houtby and Moran (2006), the second iteration of sampling was conducted in 2005 and was designed to allow testing of hypotheses that could not be resolved during the 2001 sampling survey. Results from the 2005 survey were also considered as baseline data for long term monitoring objectives to assess natural attenuation and/or the effect of active remedial efforts on chemical bioaccumulation and/or biomagnification potential.

For data presented in Houtby and Moran (2006), sampling occurred at nine locations, including five locations in the AOI, and included surface sediment chemistry, as well as mussel *(Dreissena polymorpha* and *D. bugenis*), and round goby (*Neogobius melanostomus*) tissue data. Station locations are numbered #1 through #9, with Stations #4 through #8 located within the AOI. Chemical analyses in sediment and tissue included metals (but not methylmercury), base neutral extractable (BNEs) contaminants including PAHs, neutral chlorinated extractable (NCEs) contaminants, and PCBs. TOC concentration was also analyzed in sediment samples.

As compared to 2001 data, Houtby and Moran (2006) concluded that sediment chemical concentrations in 2005 were generally consistent between sampling intervals, with several exceptions. For mercury, Houtby and Moran (2006) report that overall concentrations have declined at seven of nine stations over the 2001-2005 period, with that decline also reflected in a decrease in the number of stations with sediment mercury concentration exceeding MOE's

[3] In Zone A, stations 6663, 6664, 6665, 66M76; in Zone B stations 6699, 66M262, 66M272, 6666, 66M271, 66M144, 6667, 66M80, 6668, 66M264, 6669; and downstream station 66101.

SEL of 2 mg/kg (Persaud et al. 1993). In 2001 Stations #4, #5, and #7 were characterized by mercury concentration exceeding the SEL, whereas in 2005 only Stations #4 and #7 were characterized by mercury concentrations exceeding the SEL. For hexachlorobenzene, there was an increase in the number of stations at which this chemical was detected (from two stations to eight stations), whereas for octachlorostyrene and hexachlorobutadiene, these chemicals were consistently detected in both 2001 and 2005 sediment sampling.

For analysis of biotic tissue, Houtby and Moran (2006) reported that results from 2005 sampling were generally consistent with results from 2001 sampling. In terms of biological uptake of chemicals of concern, Houtby and Moran (2006) concluded that biomagnification of mercury may be inferred for gobies at Stations #3, #5, #7, #8, and #9; bioaccumulation of lead may be inferred for gobies at Stations #8 and #9; and bioaccumulation of barium, manganese, strontium, zinc, and PCBs may be inferred for gobies at the majority of sample locations.

1.2.6 Moran et al. (2005) Overview

Moran et al. (2005) presented results of a sediment quality triad study conducted in 2003 on behalf of SLEA. The sediment quality triad study included sediment chemistry analysis, benthic community surveys, and sediment toxicity testing and was designed to test the hypothesis that contaminated sediment was causing deleterious impacts to aquatic biota of the St. Clair River. This study included nine monitoring locations on the Canadian side of St. Clair River, including five locations within the AOI, as well as eight monitoring locations on the U.S. side of the river. As noted above for Houtby and Moran (2006), stations are numbered from low number to high number moving downstream, with Canadian Stations #4 through #8 located within the AOI. As defined by Moran et al. (2005), locations on the Canadian side of the river were selected to include a location representative of influent conditions to the St. Clair River, at a location downstream of the City of Sarnia but upstream of Priority 1 sediment zones; locations upstream, within and downstream of the Priority 1 sediment zones, and a location downstream of the Priority 1 zone (Moran et al. 2005). Moran et al. (2005) defined the Priority 1 zone as areas in the St. Clair River where sediment chemical concentrations exceed respective SELs and/or degraded benthos and/or sediment toxicity have been identified.

For data presented in Moran et al. (2005), sampling included surface water chemistry, surface sediment chemistry, benthic community composition and sediment toxicity testing with the amphipod *Hyalella azteca,* the midge *Chironomus tentans* and fathead minnows (*Pimephales promelas*). Sediment toxicity to amphipods and midges was assessed in the laboratory, whereas sediment toxicity to fathead minnows was assessed through *in situ* deployment of minnows in field chambers. Chemical analyses in surface water included pH, alkalinity and nitrate. Chemical analysis in sediment collected from the Canadian monitoring stations included metals (but not methylmercury), BNEs including PAHs, NCEs, TOC content as defined by mass loss on ignition (LOI), and grain size analysis. Chemical analysis in sediment collected from the U.S. monitoring stations was limited to LOI determination, grain size analysis and a subset of background metals.

Moran et al. (2005) reported that lowest effect levels (LELs) (Persaud et al. 1993) were exceeded for ten compounds at various monitoring locations, including exceedance for one NCE compound, several PAHs and two metals, including mercury. Sediment mercury concentrations exceeded the SEL at one station (#4). Moran et al. (2005) also report that sediment concentrations of hexachlorobenzene and hexachlorobutadiene have increased in multiple sampling locations, with hexachlorobenzene detected above the LEL at Stations #3, #4, and #5. Several PAH compounds were also reported to exceed their respective LELs at Station #3.

Although no toxicity was observed for amphipod growth relative to what was observed in control sediment, reduced amphipod survival was apparent at five stations (#1, #2, #4, #7, and #8), including the upgradient reference station. For midges, reduced growth was apparent at one station (#7), and reduced survival was apparent at one station (#1), defined as the upgradient reference station. For fathead minnows, *in situ* deployments revealed no inhibitory effects on either growth or survival. Taken together, Moran et al. (2005) reported that three stations (#3, #5, and #6) demonstrated no toxicity in terms of reduced growth or survival for any of the species tested. Moran et al. (2005) concluded that analytes correlated with negative toxicity endpoints included lead (associated with a decrease in amphipod and midge survival and midge growth), total PAHs and total NCEs (associated with a decrease in amphipod growth rates), and total mercury (associated with a decrease in fathead minnow survival). For benthic invertebrate sampling, Moran et al. (2005) concluded that none of the monitoring locations are considered degraded, and that no differences in community composition exist between the Canadian versus U.S. upgradient reference communities or the Canadian exposure community versus the combined Canadian and U.S. reference communities.

Overall, Moran et al. (2005) concluded that, based on their methods of analysis, the hypothesis of contaminated sediment causing deleterious effects on St. Clair River biota is accepted for Stations #1 (upstream reference station), #2, #4, #7, #8, and #9 (downstream reference station), but is rejected for Stations #3, #5, and #6.

1.2.7 Kauss et al. (2001) Overview

Several chlorinated organic compounds have also been of concern in St. Clair River sediment in Zone 1 (i.e., upgradient of the AOI). Kauss et al. (2001) used generic tissue targets and site-specific bioaccumulation data to identify sediment targets for hexachlorobenzene, hexachlorobutadiene, octachlorostyrene, as follows:

- *Hexachlorobenzene:* The hexachlorobenzene sediment target (0.22 mg/kg, Kauss et al. 2001) was based on a Health & Welfare Canada tissue guideline for the protection of human health (100 micrograms per kilogram [µg/kg]), which was evidently more sensitive than ecological endpoints.
- *Hexachlorobutadiene:* The hexachlorobutadiene sediment target (3.5 mg/kg, Kauss et al. 2001) was based on an ecological tissue target developed by New York State (1,300 µg/kg).

- *Octachlorostyrene:* The octachlorostyrene sediment target (0.02 mg/kg, Kauss et al. 2001) was highly uncertain, because it was based on a New York State tissue target (20 µg/kg, Newell et al. 1987) that used a 100-fold cumulative uncertainty factor to interpret a single study of subacute liver damage in rats.

Although the Kauss et al. (2001) study focused on a reach of the St. Clair River that is upgradient of the AOI, the analysis is useful for purposes of identifying which chemicals are expected to be of greatest concern in the AOI. A screening evaluation of the data assembled for the AOI indicates that most of the sediment concentrations and all of the tissue concentrations of hexachlorobenzene and hexachlorobutadiene are well below the targets listed above. However, concentrations of octachlorostyrene exceed the target concentrations in many cases, although the targets are highly uncertain. Therefore, this report addresses potential effects of octachlorostyrene, as well as mercury.

This report applies Steps 5 through 7 of the COA Framework to the St. Clair River AOI to complete the site-specific decision matrix following Table 2 of the COA Framework (reproduced as Table 1-1 of this report). The primary objectives of this report are to refine the evaluation of mercury and octachlorostyrene biomagnification, as well as to prioritize further investigation or sediment management within subzones of the AOI.

2 RISK FROM BIOMAGNIFICATION

Risk from biomagnification is one of the four LOEs used to evaluate sediment quality in this report. Concentrations of biomagnifying chemicals in sediment, benthic organisms, and/or predators of those organisms are modeled through to top predators, in order to evaluate ecological risk (Grapentine et al. 2003a,b, as cited in COA Framework). Biomagnification is an important LOE because consumption of fish and other aquatic organisms by piscivorous fish and wildlife species may pose an ecological risk if chemical residues accumulate to toxic levels within the food chain. This section builds on work previously completed by Milani et al. (2007) and Moran et al. (2005), which concluded that there is the potential for adverse effects as a result of mercury biomagnification. Neither Milani et al. (2007) nor Moran et al. (2005) evaluated the likelihood that such adverse effects will occur or the severity of such effects, as would be considered in an ecological risk assessment (ERA). ENVIRON International Corporation (ENVIRON) was not retained to conduct an ERA for the AOI. Rather, ENVIRON conducted a streamlined analysis based on ERA principles and practices, with the goal of refining the current understanding of the risk from biomagnification LOE. This section evaluates the risk from biomagnification by: 1) selecting ecological receptors of interest (ROIs); 2) characterizing chemical concentrations in aquatic organisms; and 3) comparing chemical concentrations to toxicity reference values (TRVs) derived from the literature, as follows.

2.1 Receptors of Interest

As a first step towards interpreting risk from biomagnification, ENVIRON evaluated candidate ROIs based on exposure potential (i.e., consumption of aquatic organisms), expected presence in the AOI given the available habitat, sensitivity to mercury, and availability of information related to life history, exposure parameter values, ecotoxicity, and site-specific monitoring data. Because this exercise represents a refinement of the previous conservative analyses, it targets realistic receptors—species likely to forage in the river—rather than worst-case conditions. Thus, any decisions that flow from the analysis will be based on actual or probable risks, rather than hypothetical risks. At the same time, selecting ROIs that are among the most highly exposed and most sensitive species helps ensure that conclusions are protective of other species that also may forage within the AOI.

Selected ROIs are:

- Fish populations, represented by multiple species sampled in the AOI for tissue residue analysis
- Piscivorous birds, as represented by double-crested cormorants (*Phalacrocorax auritus*)
- Omnivorous birds, as represented by herring gulls (*Larus argentatus*)
- Omnivorous mammals, as represented by raccoons (*Procyon lotor*)

The rationale for selecting each of these species is provided below.

Fish that contain mercury are often evaluated with respect to chemical exposures in fish-eating wildlife, but fish themselves may also be adversely affected. The extent of bioaccumulation differs among fish species, depending on their position in the food web and the amount of time spent in the contaminated area. Thus, while top predator fish species are most likely to accumulate high chemical concentrations, territorial predators such as northern pike (*Esox lucius*) are likely to be more exposed than migratory predators such as walleye, which range widely within the Great Lakes and connecting rivers. Mercury and/or octachlorostyrene have been measured in 15 fish species representing a range of life history characteristics within the AOI; all of these species are included in the evaluation.

The double-crested cormorant is a colonial waterbird in the family Phalacrocoracidea. Adult males are usually larger (1,270 grams [g] to 2,498 g) than adult females (1,112 g to 2,162 g) (Hatch and Weseloh 1999). Double-crested cormorants occur both along inland and coastal areas where they prefer to nest on rocky islands, tall trees, or other tall structures in the nearshore zone. Double-crested cormorants are breeding residents in the Great Lakes region. Migrating individuals usually begin arriving in the Great Lakes region by early to mid-April and depart for wintering grounds along coastal areas on the Pacific Coast, mid Atlantic Coast, and in the Caribbean. Typical foraging ranges are areas close to shore within 1 km to 3 km of nesting colonies during the breeding season (Coleman et al. 2005). Preferred feeding habitats include rocky areas, kelp forests, and seagrass beds where fish schools are abundant. In the Great Lakes, double-crested cormorants forage almost exclusively on fish, although aquatic invertebrates are also occasionally utilized (Neuman et al. 1997). Preferred fish prey lengths are 42 to 413 millimetres (mm) (Hatch and Weseloh 1999).

As described by United States Environmental Protection Agency (USEPA) (1993), the herring gull is a common colonial-nesting sea bird in the family Laridae. Adult female herring gulls are smaller (800 g to 1,000 g) than males (1,000 g to 1,300 g). Herring gulls occur along coastal waterways and inland rivers and lakes in the Great Lakes region. Preferred nesting habitats include protected islands and shorelines of lakes and connecting rivers, although some birds may nest along shoreline marshes or in association with inland structures such as piers and buildings. Adult and older subadult herring gulls are typically resident birds all year in the Great Lakes, but foraging patterns usually shift from offshore areas during the fall and spring to inshore areas associated with lakes and bays during the breeding season. Herring gulls typically forage within 1 km to 5 km of the shore in open water, where they can dive into concentrated schools of fish or other prey items. The foraging range of herring gulls ranges from 5 km to 15 km (Pierotti, personal communication as cited in USEPA [1993]). Preferred fish prey lengths are 100 mm to 300 mm (Pierotti and Annette 1987, 1991). Gulls are omnivorous and consume a range of prey items depending on their availability including fish, molluscs, invertebrates, small mammals, birds, and duck and gull eggs and chicks. Herring gulls nest along the St. Clair River (Brewer et al. 1991). As year round residents, the potential for biomagnification is greater in herring gulls than in other avian piscivores that are only present during the breeding season.

As described by USEPA (1993), the raccoon is a mid-sized mammal in the Procyonidae family that is typically found near aquatic habitats or water sources, which it relies upon for foraging

and drinking water. Adult raccoons typically range from 66 cm to 101 cm in length (nose to tail) and weigh between 3 kilograms (kg) and 9 kg. The raccoon's omnivorous and opportunistic diet includes fruits, nuts, acorns, insects, frogs, crayfish, eggs, and a variety of animal and plant matter. Preferred fish prey lengths range from 76 mm to 229 mm (Giles 1940, Yeager and Rennels 1943, Baker et al. 1945). During the breeding season in late spring and summer, raccoons consume a higher proportion of animal prey than plant matter, but plant matter dominates their diet during the non-breeding season. Adult raccoons in northern climates enter a period of winter dormancy that is usually triggered by snow cover. Home range sizes are highly variable depending on the sex of the animal and season, but typical home ranges in Michigan riparian habitats range from 18.2 hectares (ha) to 814 ha for adult males between May and December and 5.3 ha to 376 ha for adult females during the same period. Compared to other mammals, raccoons consume a larger portion of invertebrates and fish during the breeding season and are more tolerant of human disturbance, development, and agriculture that is prevalent along the shores of the St. Clair River.

In evaluating candidate wildlife ROIs, ENVIRON considered those evaluated by Milani et al. (2007), great blue herons (*Ardea herodias*) and mink (*Mustela vison*). We selected different ROIs because Milani et al's analysis is a conservative screen for biomagnification potential, while the current analysis is intended to characterize realistic risk from biomagnification. Cormorants and herring gulls were selected instead of great blue herons, because inspection of aerial photographs and a review of background reports revealed that the majority of the Canadian shoreline of the St. Clair River is significantly impacted by development and shoreline structures that virtually eliminate foraging habitat for great blue herons (Figure 2-1). During a site reconnaissance conducted on September 23, 2008, many gulls and cormorants were observed, while no great blue herons were observed. Furthermore, given the double-crested cormorant's smaller body weight and foraging range as compared to the great blue heron, it represents the more conservative (i.e., health protective) ROI.

Examples of physical shoreline structure that alter or reduce habitat value for wading birds include groins (i.e., artificial structures built perpendicular to shoreline to reduce water flow and stabilize eroding areas), sea walls or bulkheads (i.e., metal or concrete structures built vertically against the shoreline to retain soil and prevent land from sliding towards a channel), revetments (i.e., covers or structures built against shorelines to protect the slope from eroding from wave action or water action), outfall structures (i.e., a concrete or hardscaped surface to direct waste or stormwater into a body of water), and rubble (i.e., rock or other concrete material placed along shoreline). Like the very limited foraging habitat currently available in the AOI, there are few if any potential breeding sites in the AOI for great blue herons, which nest in large trees in areas without significant disturbance. Future plans for restoring great blue heron breeding habitat within the AOI are unknown. However, given the colonial breeding behaviour of herons and their intolerance for human disturbance (Butler 1992), restoration actions targeted at improving breeding habitat for great blue herons would not likely be cost-effective within the AOI.

ENVIRON selected raccoons instead of mink because key habitat features for mink denning and foraging, such as irregular shorelines with ample brush and tree cover, are also absent

from the AOI (Figure 2-1). However, as detailed in the following subsection, the evaluation of raccoons conservatively assumes that raccoons and mink are equally sensitive to mercury, in that the mercury TRV applied to raccoons is derived from a study of mink.

2.2 Toxicity Reference Values

The second step in refining the evaluation of risk from biomagnification was to derive TRVs for the ROIs exposed to mercury and octachlorostyrene. TRVs are threshold tissue concentrations (expressed in mg/kg) or doses (expressed in milligrams of chemical per kilogram body weight per day or mg/kg-day) that represent a level at which adverse effects are not anticipated in ROIs exposed over the long term. Tissue concentrations are generally used to express thresholds that are protective of fish, while doses are most often used to express thresholds that are protective of wildlife. However, TRVs protective of birds also may be based on egg concentrations.

2.2.1 Methodology for Deriving Toxicity Reference Values

TRVs were derived based on the general methodology of Sample et al. (1996), by applying uncertainty factors to laboratory study results, as detailed below:

Eqn. 1

$$TRV = \frac{\text{Test Species Dose}}{\text{Uncertainty Factor}}$$

The test species dose is a daily dose of a chemical associated with a particular endpoint and effect. It may also be represented as a tissue concentration, as in the case of fish TRVs and avian TRVs based on egg concentrations. Test species doses or concentrations were identified from the scientific literature, with preference given to peer-reviewed primary sources. The following criteria were applied in selecting applicable studies used to derive TRVs for this study:

- Relatedness of test species used in the study as compared to the ROI – Studies on species that are similar with respect to taxonomic order and/or feeding guild were preferred over studies on species that are less closely related. In addition, studies on wild species were preferred over studies on domesticated species.
- Effects evaluated – Studies focused on most sensitive effects were preferred over studies on less sensitive effects; consequently, sublethal studies were preferred over lethal studies and studies on sensitive life stages were preferred over studies on adult non-breeding organisms.
- Type of endpoint – Studies with multiple dose groups that allow identification of a dose response curve, or both a no observed adverse effect level (NOAEL) and a lowest observed adverse effect level (LOAEL), were preferred over studies that yield only frank effect levels (e.g., lethal dose to 50 percent [%] of the test organisms) or only a NOAEL or only a LOAEL.

- Duration of the dosing period – Lifetime or chronic duration studies were preferred over subchronic, acute, and single dose studies.
- Dose administration method – Studies utilizing dietary dosing were preferred over other oral dosing methods, which were preferred over injection, dermal, or inhalation dose administration.
- Chemical form tested – Studies on methylmercury were preferred over those conducted on elemental or salt forms of mercury.
- Documentation of study methods and quality control – Studies that clearly document the study design and methods that demonstrate adequate quality control were preferred over those that provide limited discussion on these topics.

As noted above, to the extent that response data were available for multiple dose groups, the use of a dose response curve and the effect concentration in 10% or 20% of the test organisms (EC10, EC20) was preferred over either the NOAEL or the LOAEL as the basis for the TRV. NOAELs and LOAELs are strongly influenced by the toxicity test study design, and the true threshold of an effect is likely to fall between the two values. Furthermore, the slope and shape of the dose response curve can inform the severity of the predicted effect, whereas exceedances of the NOAEL and/or LOAEL cannot. However, ecotoxicity data limitations often preclude consideration of dose response curves, necessitating the use of NOAELs and LOAELs in TRV derivation.

NOAELs are commonly used in TRV derivation in screening level analyses, but are overly conservative for more realistic estimates of risk. Consequently, in the absence of dose response data suitable for derivation of the EC10 or EC20, the geometric mean of the NOAEL and LOAEL was used as the basis for the TRV.

As previously noted, TRVs that are protective of fish are typically based on tissue concentrations in fish[4] (in mg/kg), since this metric integrates all sources of exposure for the test organisms. For wildlife, TRVs are generally[5] reported on—or converted to—a mg/kg-day basis. These units of dose allow comparisons among organisms of different body sizes (Sample et al. 1996). In cases where the underlying study states the effect level or no effect level as a dietary concentration (i.e., in units of mg /kg food), the geometric mean of the effect level and no effect level was converted to a test species dose:

Eqn. 2

[4] Fish TRVs are based on tissue concentrations in the fish that are the ROIs themselves, rather than the prey of piscivorous fish.
[5] Avian TRVs for mercury can also be expressed as egg concentrations that are without deleterious reproductive effects.

$$\text{Dose} = \frac{C \times FIR}{BW}$$

Where:

Dose	=	test species dose (mg/kg-day)
C	=	chemical concentration in food (mg/kg)
FIR	=	food ingestion rate (kilogram per day or kg/day)
BW	=	body weight (kg)

Uncertainty factors may be identified based on three characteristics of the experimental conditions associated with the test species dose: 1) the duration of exposure; 2) the endpoint measured; and 3) differences in sensitivity among test and receptor species (Calabrese and Baldwin 1993, Ford et al. 1992, Opresko et al. 1994, Sample et al. 1996, USEPA 1996a, Watkin and Stelljes 1993, Wentsel et al. 1994).

The sections below describe the studies reviewed for TRV development. Although toxicological studies suitable for development of mercury TRVs are readily available, comparable information for octachlorostyrene is quite limited. ENVIRON elected to use hexachlorobenzene as a surrogate for octachlorostyrene because its chemical structure is similar, it is better studied, and comparative studies indicate hexachlorobenzene is more toxic than octachlorostyrene. For example, Smith et al. (1994) fed rats a diet containing 100 mg/kg octachlorostyrene with iron overload for 18 months, resulting in only minor liver effects. By comparison, hexachlorobenzene dosing with a similar regime caused liver cancer and other severe effects (Smith et al. 1994).

2.2.2 Toxicity Reference Values for Fish

Fish TRVs are generally calculated as tissue concentrations in fish ROIs that are protective of the fish themselves. That is, the tissue-based TRV represents a concentration in the receptor—not the prey—that is not expected to adversely affect that fish. Fish TRVs are sometimes referred to as maximum acceptable tissue concentrations.

2.2.2.1 Mercury TRV for Fish

Scientific studies were identified linking whole body mercury concentrations with chronic effects on fish, including reductions in reproductive success, growth, and survival. All primary sources were obtained and reviewed to ensure the accuracy and relevance of the reported toxicity data. Study results applicable to methylmercury concentrations in adult whole body fish are presented in Table 2-1.

Beckvar et al. (2005) reviewed many of these studies and identified a concentration of 0.2 mg/kg as the TRV for mercury in tissue of juvenile and adult fish. This concentration is equal to the NOAEL identified from Matta et al. (2001), who evaluated effects on three generations of mercury-exposed mummichog (*Fundulus heteroclitus*). Male mortality was the most sensitive

endpoint in this study (LOAEL = 0.47 mg/kg), with effects on the sex ratio of offspring (female-biased; LOAEL = 1.1 mg/kg) and second-generation fertilization success (LOAEL = 12 mg/kg) observed at higher exposures.

The TRV of 0.2 mg/kg also lies between the mercury concentrations in control fish (typically approaching 0.1 mg/kg) and the unbounded LOAELs reported for several other fish species (Table 2-1). For example, Friedmann et al. (1996a) identified a LOAEL associated with adverse effects on gonadal development in walleye containing 0.25 mg/kg mercury (the lowest concentration tested). Although this is only an indirect measure of potential reproductive effects, Hammerschmidt et al. (2002) demonstrated that in fathead minnows containing a similar tissue residue (0.39 mg/kg), impaired gonadal development was associated with impaired reproduction. As an alternative to the TRV identified by Beckvar et al. (2005), one could consider the mercury concentration of 0.06 mg/kg measured in control fish by Friedmann et al. (1996a) to be a NOAEL, and select a TRV between 0.06 mg/kg and 0.25 mg/kg (e.g., the geometric mean). However, this approach results in a TRV that is similar to mercury concentrations in control fish from various other studies and thus is not plausible as a toxicity threshold.

Sensitivity to mercury varies significantly across fish species. For example, McKim et al. (1976) observed no reproductive toxicity in brook trout (*Salvelinus fontinalis*) at concentrations as much as an order of magnitude higher than those identified as toxic by Matta et al. (2001) and Friedmann et al. (1996a). However, mercury toxicity to fish has not been sufficiently studied to clearly define the most sensitive species and response endpoints. Behavioural effects detrimental to spawning, foraging, and escaping predators have been observed at relatively low exposures, consistent with mercury's action as a neurotoxicant (Sandheinrich and Miller 2006, Webber and Haines 2003). Although Matta et al. (2001) observed selective toxicity to males in methylmercury-exposed mummichog, Mulvey et al. (1995) observed sex ratios skewed in favour of males in mosquitofish (*Gambusia affinis*) exposed to waterborne inorganic mercury in experimental mesocosms. This effect was not observed in subsequent multi-year tests with mercury-contaminated sediment in the same mesocosms; rather, mosquitofish populations were skewed toward females in both control and test exposures (consistent with female-biased sex ratios normally observed for this species in the field) (Tatara et al. 1999, 2002). Methylmercury suppresses sex hormones in fathead minnows, with associated effects on behaviour and reproductive success (Drevnick and Sandheinrich 2003, Sandheinrich and Miller 2006).

Studies of mercury-related effects on wild fish are often difficult to interpret due to the co-occurrence of multiple chemicals and other stressors. Several researchers have attempted to circumvent these issues by focusing on remote lakes affected primarily by atmospheric deposition of mercury. For example, Friedmann et al. (1996b) examined gonadal development and function in northern pike collected from Lake Champlain, with mercury concentrations in muscle ranging from 0.12 mg/kg to 0.62 mg/kg; no effects were observed. Drevnick et al. (2008) found a negative relationship between mercury in liver tissue and fish condition (weight relative to length) in northern pike collected from several lakes on Isle Royale, Michigan. The fish contained muscle mercury concentrations ranging from 0.07 mg/kg to 0.62 mg/kg, and the threshold for effects on fish condition in these populations appears to be approximately 0.3

mg/kg mercury in muscle (extracted from graphical results). Similarly, Suns and Hitchin (1990) observed a negative relationship between mercury tissue residues and fish condition in yellow perch collected from several Ontario lakes; however, lake pH covaried with mercury tissue concentrations and appeared to explain most of the variability in fish condition. Latif et al. (2001) investigated hatching success of eggs from mercury-contaminated walleye (averaging 2.7 mg/kg in muscle) collected from Clay Lake, Ontario, near a former chlor-alkali plant. While the most highly contaminated eggs exhibited lower hatching success, the relationship between mercury and hatching success was highly variable and not statistically significant.

While both field and laboratory data defining mercury concentration-response relationships for fish are limited, the effects on northern pike observed by Drevnick et al. (2008) are consistent with the whole-body TRV of 0.2 mg/kg identified above. This TRV is protective and appropriate for use in this assessment.

2.2.2.2 Octachlorosytrene TRV for Fish

No studies examining effects of octachlorostyrene on fish were identified from the scientific literature. Although hexachlorobenzene can be used as a surrogate to evaluate octachlorostyrene effects on wildlife, this approach is not as useful for predicting effects on fish. Hexachlorobenzene effects on fish have never been observed despite extensive testing, because the concentration of hexachlorobenzene in water that causes toxicity in fish is higher than the solubility limit (as reviewed by Barber et al. 1997). While this comparison suggests that octachlorostyrene also may not be toxic to fish, it is possible that exposures via food or sediment ingestion pathways could result in higher exposures than those occurring in water-only toxicity test exposures. Therefore, an alternative approach is used to identify a TRV for octachlorostyrene effects on fish.

Di Toro et al. (2000) investigated the relationship between chemical properties and toxicity for 156 chemicals and 33 species, including fish, amphibians, and invertebrates, and interpreted the results using USEPA's derivation methods for ambient water quality criteria. The resulting target lipid model can be used to identify chemical concentrations in tissue that are protective of 95% of species on a chronic exposure basis, as follows:

$$FCV_{tissue} = FAV_{tissue} \times CF \times 1/ACR \qquad \text{Eqn. 3}$$

Where

FCV_{tissue} = final chronic value on a tissue basis (micromole per [µmol/g] lipid)

FAV_{tissue} = final acute value on a tissue basis, equal to 35.3 µmol/g lipid

CF = chemical class correction factor for halogenated chemicals, equal to 0.570

ACR = acute-chronic ratio, equal to 5.09

Based on a molecular weight of 379.71 grams per mol (g/mol) for octachlorostyrene, the chronic tissue TRV is identified as 1,500 µmol/g lipid. Based on wet weight lipid concentrations in fillet and whole fish samples from the AOI that range from 0.1% to 12%, the TRV ranges from 1,500 to 180,000 µg/kg wet weight (1.5 to 180 mg/kg wet weight). This TRV range is several orders of magnitude higher than the octachlorostyrene concentrations observed in fish from the AOI, indicating that octachlorostyrene-related effects on fish are very unlikely.

2.2.3 Toxicity Reference Values for Birds

Avian TRVs for mercury and octachlorostyrene are selected and described in this subsection. The effects of methylmercury on birds have been widely studied in both field and laboratory settings, while no avian toxicological studies are available for octachlorostyrene. Therefore, this report uses hexachlorobenzene as a surrogate, based on consistent reports that it is more toxic than octachlorostyrene (Smith et al. 1994). Avian TRVs for mercury and hexachlorobenzene are both expressed as doses, in units of mg/kg-day, which are expected to be without deleterious effects even when experienced throughout a bird's lifetime. In addition, egg-based mercury TRVs are identified for double-crested cormorants and herring gulls. Such egg-based TRVs can be compared directly to concentrations of mercury measured in field-collected eggs.

2.2.3.1 Mercury TRV for Birds

The toxicity of methylmercury to mallards (*Anas platyrhynchos*) under controlled laboratory conditions is well understood. In a multi-generation study testing a single exposure level, mallards exposed to 0.078 mg/kg-day were not affected in the first generation, but duckling production decreased in the second and third generations (Heinz 1979). Overall, mercury exposure caused an 18% decrease in production of surviving ducklings. Dr. Heinz characterized this dose as being very close to the true threshold of a subtle (rather than severe) effect (pers. comm., Phyllis Fuchsman, ENVIRON, December 2, 2008). The mercury concentration measured in eggs of mercury-exposed mallards was 0.8 mg/kg. Both Environment Canada (2002) and USEPA (1995) selected this study as the basis for assessing risks to birds, based on a review of mercury toxicity data for a variety of avian species. USEPA (1995) used an uncertainty factor of 2 to estimate a NOAEL from the measured LOAEL, because the LOAEL appeared to be very near the threshold for effects of mercury on mallards. This choice of uncertainty factor more fully considers the available dose-response information than would application of Environment Canada's default LOAEL-to-NOAEL uncertainty factor of 5.6. Indeed, the percent effect noted in this study lies between an EC10 and an EC20, the preferred endpoints for TRV derivation listed in Section 2.2.1; thus, the application of any uncertainty factor is conservative. USEPA's approach yields a NOAEL and LOAEL for mallards of 0.039 mg/kg-day and 0.078 mg/kg-day, respectively; the geometric mean of these values is 0.055 mg/kg-day. Applying the same approach to the egg concentration from Heinz (1979) yields an egg-based TRV of 0.6 mg/kg.

In order to determine the appropriateness of applying the mallard TRV to cormorants and herring gulls, the broader avian ecotoxicological literature was considered. Effects of methylmercury have been evaluated in both field and laboratory settings for a wide variety of

avian species, including loons (*Gavia sp.*), egrets and herons (Ardeidae), quail (*Coturnix sp),* mallards, tree swallows (*Tachycineta bicolour*), hawks (Accipitridae), zebra finches (*Taeniopygia guttata*), and others. Mercury exposure-response relationships in wild birds are particularly well developed for common loons, which are susceptible to effects of atmospheric mercury deposition on northern lakes. Evers et al. (2008) present an analysis of nearly 5,500 loon mercury measurements collected over 18 years from 700 lakes in 13 U.S. states and 4 Canadian provinces. These data indicate adverse effects of mercury on loon reproductive success, with threshold concentrations identified as 0.16 mg/kg in prey and 1.3 mg/kg in eggs. Burgess and Meyer (2008) reported similar results from a 7-year study of loons on 120 lakes in Wisconsin and the Canadian Maritimes, indicating a reproductive EC50 of 0.21 mg/kg in prey. Based on the food ingestion rate (FIR) and body weight of loons identified by CCME (1999), the threshold of 0.16 mg/kg in prey corresponds to a mercury dose of 0.029 mg/kg-day.

Information on mercury toxicity to double-crested cormorants is available from two field studies (Wolfe and Norman 1998, Henny et al. 2002). Breeding populations of cormorants at Clear Lake, California were qualitatively judged to be stable or increasing, despite consuming a diet containing 0.35 mg/kg mercury (Wolfe and Norman 1998), equivalent to a daily intake of approximately 0.06 mg/kg-day. In contrast, consumption of a diet containing 1.44 mg/kg mercury from the Carson River, Nevada resulted in significant histological damage in young cormorants, as well as low production of young per nest compared to Great Lakes colonies (Henny et al. 2002). This exposure was equivalent to a daily intake of about 0.2 mg/kg-day.

Vermeer et al. (1973) evaluated the reproductive success of a herring gull colony at Clay Lake, Ontario, an area contaminated with mercury from a chlor-alkali plant. The first egg of each clutch was analyzed for mercury, and hatching success was evaluated for the remaining eggs in 18 nests. Overall productivity of the colony was also compared to that observed elsewhere. No reproductive impairment was observed, despite mercury concentrations ranging from 2.3 mg/kg to 15.8 mg/kg in eggs (average = 8.4 mg/kg). Chemical concentrations in eggs are expected to vary with laying order, often with the highest concentration in the first laid eggs (e.g., Heinz and Hoffman 2004, Van den Steen et al. 2009). Therefore, mercury concentrations in the analyzed eggs were likely higher than in the eggs monitored for hatching success. While mercury concentrations in the Clay Lake herring gulls' diets were not determined, it is clear that exposures were higher than in the St. Clair River AOI. Clay Lake yellow perch contained 2.7 mg/kg mercury (Vermeer et al. 1973), one to two orders of magnitude higher than concentrations in yellow perch from the AOI (Table 2-13).

Additionally, Gilman et al. (1977) evaluated herring gull reproductive success in four Great Lakes colonies. While herring gull reproduction was impaired at the Lake Ontario colony, chlorinated organic compounds rather than mercury appeared to be the primary cause. Reproduction at the three remaining colonies was considered successful. Average mercury concentrations in herring gull eggs from the successful colonies ranged from 0.22 mg/kg to 0.39 mg/kg. This study suggests that herring gulls are not significantly more sensitive to mercury than are mallards, given that the average concentration of mercury in herring gull eggs in the Gillman et al. (1977) study is within the same order of magnitude of the egg-based TRV (0.6 mg/kg) and Gillman et al. (1977) did not observe adverse effects in gulls. Although the sample

size is too low to allow the Gillman et al. (1977) study to serve as a species-specific basis for an egg-based TRV, it does suggest that risks to herring gulls are not likely underestimated based on the selected TRV.

While the field studies identified for double-crested cormorants and herring gulls do not clearly support the identification of species-specific TRVs, they indicate that the TRV derived for mallards from Heinz (1979) are protective. Additional information on interspecies differences in mercury sensitivity is available from Heinz et al. (2008), who measured mortality in methylmercury-injected eggs of several bird species. In contrast to the results of Vermeer (1973), herring gulls were found to be considerably more sensitive than mallards. Double-crested cormorants were less sensitive than mallards, consistent with the field studies cited above. Mercury exposure via injection was found to artificially increase toxicity compared to maternal transfer, and thus Dr. Heinz recommended against using the 2008 study as a basis for quantitative interspecies extrapolation factors (pers. comm., Phyllis Fuchsman, ENVIRON, December 2, 2008). Instead, he advised using the mallard study (Heinz 1979) as a basis for an avian TRV for methylmercury, while qualitatively considering potential differences in sensitivity among species. That recommendation is applied in this report, such that the mallard-based TRV of 0.055 mg/kg-day is applied to both herring gulls and double-crested cormorants, with the acknowledgement that it likely overestimates the sensitivity of cormorants and is a less certain estimate of the sensitivity of gulls.

To study the effects of selenium on mercury, Conover and Vest (2009) sampled California gull (*Larus californicus*) eggs and determined selenium and mercury concentrations in blood plasma, and liver tissue from three different colonies at the Great Salt Lake in Utah, USA in 2006 and 2007. The authors sampled a single, randomly selected egg from 24 different nests at 3 colonies representing a total of 72 eggs. Mean selenium concentrations in eggs were 3.0 ± 0.10 mg/kg (sample size [n] = 35) in 2006 and 2.8 ± 0.10 mg/kg (n = 12) in 2007, which the authors indicated are elevated levels compared to typical background conditions for birds (1.5 mg/kg to 2.5 mg/kg) and may have provided some protection from mercury toxicity. In 2007, the average mercury concentration in eggs was 0.26 ± 0.05 mg/kg. Concentrations of selenium and mercury in eggs were not correlated ($r^2 = 0.03$). The authors inspected the contents of all 72 eggs and reported all but 1 egg contained viable, late stage embryos with no deformities. In addition, the authors also indicated inspection of 100 newly hatched chicks showed no evidence of teratogenesis. Given the lack of correlation between selenium and mercury concentrations in the California gull eggs tested, the potential for a protective effect from selenium remains uncertain. Nonetheless, this study does suggest that mercury concentrations in eggs averaging 0.26 mg/kg represent an unbounded NOAEL for reproductive effects in gulls. Consistent with Heinz's (1979) egg-based TRV of 0.6 mg/kg, the threshold for adverse effects in gulls is presumably greater than the unbounded NOAEL of 0.26 mg/kg.

2.2.3.2 Octachlorosytrene TRV for Birds

No avian toxicological studies on octachlorostyrene are available. Therefore, this report uses hexachlorobenzene as a surrogate for octachlorostyrene as discussed above.. Dose-response information on the effects of hexachlorobenzene in birds (Japanese quail [*Coturnix coturnix*],

American kestrel [*Falco sparverius*], and domestic chicken [*Gallus* sp.]) is presented in Table 2-2. Bird species that have been tested for effects of hexachlorobenzene under controlled laboratory or field conditions include those listed above, as well as mallard and ring-necked pheasant (*Phasianus colchicus*). Seven studies were identified and reviewed that contained quantitative dose-response information. The reviewed studies indicate that hexachlorobenzene is not acutely toxic. Hill et al. (1975) report lethal dietary concentrations to 50% of population tested (LC5Os) of 617 mg/kg for ring-necked pheasant and >5000 mg/kg for mallard. Acute and subchronic no observed adverse effect concentration (NOAEC) dietary values range from 5 mg/kg (for 90 days) for Japanese quail (Vos et al. 1971) to 707 mg/kg (five days) for mallards (Hill et al. 1975). A lifecycle NOAEC of 100 mg/kg was reported for chickens (Avrahami and Steele 1972). Among the studies of hexachlorobenzene toxicity to birds, the Vos et al. (1971) study is a chronic duration study that measured effects to reproductive endpoints. Vos et al. (1971) conducted a 90-day study of Japanese quail fed 0, 1, 5, 20, and 80 mg/kg (in turkey starter mash). Feeding was unrestricted. FIRs and estimated doses were not reported. Measurements included terminal body weight, mortality, reproduction (hatchability of eggs), and numerous minor biochemical and physiological parameters that are not considered ecologically significant. All birds appeared healthy except at the 80 mg/kg dietary treatment, in which the birds showed clinical signs of toxicity and exhibited high mortality (33%). The NOAEC values for various measured effects ranged from 5 mg/kg to 80 mg/kg. By comparison, Schwetz et al. (1974) report a 90-day lowest observed adverse effect concentration (LOAEC) for decreased egg-hatching at 20 mg/kg, for the same species.

Test-species NOAEL and LOAEL doses were derived from the Vos et al. (1971) experimental study based on body weight and duration data presented in the study. Because Japanese quail were exposed to the hexachlorobenzene for greater than 10 weeks, these test-species doses were considered chronic exposures, per Sample et al. (1996). An estimated FIR for Japanese quail is 0.02 kg food wet weight/day, based on a body weight of 0.15 kg (Vos et al., 1971). Using these generic exposure values, the estimated test-species NOAEL and LOAEL values for hexachlorobenzene are 0.67 milligrams of hexachlorobenzene per kilogram of body weight per day (mg/kg-day) and 2.67 mg/kg-day, respectively. The geometric mean of these two values, 1.34 mg/kg-day, is employed as the avian TRV for octachlorostyrene.

2.2.4 Toxicity Reference Values for Mammals

Mammalian TRVs for mercury and octachlorostyrene are selected and described in this subsection and summarized in Tables 2-3 and 2-4. Mammalian TRVs are also expressed as doses, in units of mg/kg-day, which are expected to be without deleterious effects even when experienced throughout a mammal's lifetime. As detailed below, the effects of methylmercury on mammals have been widely studied, while pertinent toxicological studies are lacking for octachlorostyrene. Therefore, hexachlorobenzene is again used as a surrogate for octachlorostyrene, given its higher toxicity.

2.2.4.1 Mercury TRV for Mammals

Studies of the chronic toxicity of organic mercury to mammals have included tests with rats (*Rattus sp.)*, mice (*Mus sp*.), dogs (*Canis lupus familiaris*), cats (*Felis catus*)*,* seals (*Halichoerus grypus)*, and mink (ATSDR 1999, Eisler 2006, Sample et al. 1996, USEPA 1995). Among these species, mink are considered the most relevant for identifying TRVs applicable to raccoons, because: 1) mink are a wildlife species and are in the same taxonomic order as raccoons; 2) there is an abundance of ecotoxicological data on mink; and 3) mink are considered a sensitive sentinel species with respect to chemicals with the potential to biomagnify such as mercury (Basu et al. 2007).

Table 2-3 summarizes the available toxicity data for mink exposed to methylmercury. The results of Dansereau et al. (1999) provide the most appropriate basis for a TRV, based on study design, documentation, duration (two generations), and inclusion of sensitive reproductive endpoints. Because mercury was administered in this study via consumption of contaminated fish, there is some potential for confounding effects of other chemicals, although the authors report that no other measured chemicals were present at elevated concentrations. However, the study results are generally consistent with those from studies in which methylmercury was added to feed, suggested that any effects related to other chemicals were minimal. The results of Dansereau et al. (1999) provide a NOAEL of 0.023 mg/kg-day and a LOAEL of 0.12 mg/kg-day. The geometric mean of these values, 0.052 mg/kg-day, is identified as the mammalian TRV for calculation of a target fish tissue concentration to protect raccoons.

2.2.4.2 Octachlorosytrene TRV for Mammals

Due to a paucity of pertinent toxicological data on the effects of octachlorostyrene on mammals, hexachlorobenzene was again used as a surrogate. In contrast to octachlorostyrene, there is a relatively large amount of literature available regarding the acute, subchronic, and chronic effects of hexachlorobenzene in mammals, although none very recent and relatively little focused on mink, which is among the most sensitive species tested for the effects of halogenated aromatic hydrocarbons (Bleavins et al. 1984). The most relevant studies identified in a review of the scientific literature are presented in Table 2-4. The majority of the reviewed literature indicates that hexachlorobenzene is not acutely toxic to mammals at environmental concentrations, but causes chronic effects at concentrations that may be present in the environment. Many of the test-species doses shown in Table 2-4 are based on data for domesticated animals and common laboratory test species that are not ROIs, such as mice, rats, swine [*Sus domestica*], sheep [*Ovis aries*], rabbits [*Leporidae*], dogs and ferrets [*Mustela putorius furo*]. Given the relatively limited research on mink, and in contrast with the mammalian ecotoxicity literature on mercury, it is appropriate to summarize the available literature on the range of species tested. However, in light of their demonstrated sensitivity to halogenated aromatic hydrocarbons (Bleavins et al. 1984), mink represent a conservative surrogate that is protective of risks to raccoons and other mammals.

A mink study conducted by Bleavins et al. (1984) was used as the basis for deriving a test-species NOAEL and LOAEL. Bleavins et al. (1984) exposed adult male and female mink to

hexachlorobenzene in feed at concentrations of 1, 5, 25, 125, and 625 mg/kg feed, and then bred them. All adults in the two highest exposure groups (125 and 625 mg/kg feed) died during the exposure period. NOAECs and LOAECs generated by this study vary across endpoints, as follows.

Bleavins et al. (1984) observed increased kit mortality after 6 weeks in the 1, 5, and 25 mg/kg feed treatment groups (44.1%, 77.4%, and 86.7%, respectively) relative to controls (8.2% mortality), although statistical significance was not tested for this endpoint. Since reproductive effects were measured, the chronic LOAEC for kit mortality is 1 mg/kg feed. Bleavins et al. (1984) also reported effects of hexachlorobenzene on litter size, number of live births, and kit body weight; however, these endpoints were less sensitive than kit mortality.

In order to convert Bleavins et al.'s (1984) findings from a dietary concentration to a dose, the FIR for the test animals must first be estimated, as it was not reported in the study. An FIR for farm-raised adult mink was estimated at 0.22 grams per gram body weight per day (g/g-day) (USEPA, 1993).

Based on the above results, the Bleavins et al. (1984) reproductive LOAEC of 1 mg/kg feed is conservatively selected as the most appropriate endpoint. Integrating the estimated FIR of 0.22 g/g-day with Bleavins et al.'s (1984) results for dietary concentration (1 mg/kg feed LOAEC) yields a dose-based LOAEL of 0.22 mg/kg-day for reproductive effects. The LOAEL is "unbounded" (i.e., a NOAEL for reproductive effects was not presented). Because the effect on mink reproduction was relatively severe (44% kit mortality), a default uncertainty factor of 5.6 was used to estimate a NOAEL of 0.039 mg/kg-day. The geometric mean of the LOAEL and the estimated NOAEL yields a mammalian TRV of 0.093 mg/kg-day for hexachlorobenzene, which serves as a surrogate for octachlorostyrene in this report.

2.3 Target Tissue Concentrations

In the third step in the evaluation of risk from biomagnification, ENVIRON calculated aquatic organism tissue concentrations of mercury and octachlorostyrene that are protective of the ROIs. The target tissue concentrations were then compared to measured tissue concentrations to yield refined estimates of risk from biomagnification in the AOI.

2.3.1 Target Tissue Concentrations Protective of Fish

For protection of fish, the fish-tissue based TRV for mercury of 0.20 mg/kg served as the acceptable risk-based concentration. For octachlorostyrene, the TRV for protection of fish is identified as 1,500 µmol/g lipid. Based on the range of lipid concentrations reported in fish tissue samples from the AOI, this value corresponds to a TRV range of 1.5 mg/kg to 180 mg/kg.

2.3.2 Methods of Calculating Target Tissue Concentrations Protective of Wildlife

For protection of wildlife, ENVIRON used the dose-based TRVs selected in Section 2.2 to calculate acceptable risk-based concentrations of mercury and octachlorostyrene in fish and

other aquatic prey, as shown in Equation 4. This equation was derived by solving the hazard quotient equation for the prey concentration term, while holding the target hazard index constant at 1, as detailed in Appendix B.

Eqn. 4

$$C_{aqprey} = \frac{TRV \times BW}{AUF \times FIR \times P_{aqprey}}$$

Where:

C_{aqprey}	=	target aquatic prey tissue concentration (mg/kg)
TRV	=	toxicity reference value (mg/kg-day)
BW	=	body weight (kg)
AUF	=	area use factor (unitless)
FIR	=	food ingestion rate (kg/day)
$P_{aq\ prey}$	=	proportion of diet composed of aquatic prey

While the basis for the TRVs for birds and mammals is discussed in Sections 2.2.3 and 2.2.4 above, inputs for the other variables included in Equation 4 are primarily drawn from USEPA (1993), as detailed below.

Area use factors (AUFs) may be used to account for the fraction of diet derived from the AOI, considering the foraging range of the ROI and the size of the AOI. In particular, if the foraging range of a wildlife ROI is greater than the 8.3 km length of the AOI, that ROI would only derive part of its diet from the AOI. Even ROIs with foraging ranges that are less than 8.3 km in length may consume some aquatic prey from outside the AOI. However, for this assessment, it was conservatively assumed that all wildlife ROIs derive all of their aquatic prey from within the AOI, and all AUFs were set equal to 1. In actuality, double-crested cormorants nesting in the northern part of the AOI likely derive some of their prey from Lake Huron. Similarly, the home ranges or foraging ranges of herring gulls and raccoons are quite variable, such that some individuals likely derive all of their aquatic prey from within the AOI and some likely also forage outside of the AOI. Given this variability, the protectiveness of this assessment is ensured by employing an AUF of 1.0 for all wildlife ROIs.

FIR for double-crested cormorants and herring gulls are based on empirical values reported in the literature. In the absence of a suitable empirically-derived FIR for raccoons, the FIR is calculated based on their metabolic rate and the metabolic energy provided by the raccoon's prey, as described in USEPA (1993):

Eqn. 5

$$FIR = NIR_{total} \times BW \times 0.001$$

Where:

NIR_{total}	=	total normalized ingestion rate gram per kilogram bodyweight per day (g/kg-day)

Eqn. 6

$$NIR_{total} = \frac{NFMR}{\sum(P_k \times ME_k)}$$

Where:

NFMR = normalized free-living metabolic rate of predator (kilocalorie per kilogram body weight per day [kcal/kg-day])

P_k = proportion of diet of kth prey item (unitless)

ME_k = metabolic energy of kth prey item (kilocalorie per gram [kcal/g] wet weight)

Eqn. 7

$$ME = GE \times AE$$

Where:

GE = gross energy (kcal/g wet weight)

AE = assimilation efficiency (unitless).

2.3.2.1 Parameter Values for Double-Crested Cormorants

Food ingestion rate – An FIR for double-crested cormorants of 0.320 kg/day is adopted based on empirical values reported in Hatch and Weseloh (1999) for this species across its range.

Dietary composition – Dietary preferences are derived from conservative synthesis of information reported for the Great Lakes by Bur et al. (1997), Neuman et al. (1997), and Hatch and Weseloh (1999) from multiple studies. Exposure assumptions are based on the double-crested cormorant's dietary preferences in the summer (i.e., breeding season) for populations in western Lake Erie. Double-crested cormorants primarily consume fish, although aquatic invertebrates occasionally represent a very small portion of the diet. In this analysis, the double-crested cormorant's diet is assumed to be comprised of 100% fish based on the dietary composition described for this species by Bur et al. (1997). Preferred fish prey lengths are 42 to 413 mm (Hatch and Weseloh 1999); this report uses fish sample results within this size range to evaluate risks to cormorants.

Body weight – The body weight of 1.96 kg equals the mean of adult male and female double-crested cormorant body weights during the breeding season in New York (Cummings 1987).

Area use factor – Double-crested cormorants typically forage within 2.9 km of a breeding colony or individual nesting sites, where water depths are less than 7.5 m (Coleman et al. 2005). In Ontario, cormorants prefer to nest in open areas, particularly islands or peninsulas, along coastal areas or inland lakes (Weseloh 2007). Because the foraging range of breeding cormorants is smaller than the length of the AOI, any cormorants nesting within the AOI would likely derive all of their prey from the AOI. Therefore, an AUF of 1 is appropriate for this

species. However, this assumption may overestimate exposure for some double-crested cormorants, particularly those that forage in the northern portion of the AOI, which may also derive some prey from Lake Huron.

2.3.2.2 Parameter Values for Herring Gulls

Food ingestion rate – An FIR for herring gulls of 0.34 kg/day is adopted from the CCME Environmental Quality Guidelines (CCME 1999).

Dietary composition – Dietary preferences of herring gulls are based on Fox et al.'s (1990) data for summer (i.e., breeding season) populations on Lake Huron. Herring gulls typically consume fish, insects, garbage, gull chicks, adult birds, earthworms, and crayfish (Fox et al. 1990 as reported in USEPA 1993). Because dietary composition percentages presented in Fox et al. (1990) and summarized in USEPA (1993) do not sum to 100%, ENVIRON normalized the reported values to 100% for proper inclusion in the target concentration equation. Thus, the herring gull's diet is assumed to be comprised of 69% fish, 2% avian matter (i.e., gull chicks and adult birds), 16% invertebrates (i.e., crayfish, earthworms, and insects), and 13% garbage. Aquatic prey comprises 85% of the herring gull's diet. The preferred fish prey size range of herring gulls is 100 mm to 300 mm.

Body weight – The body weight of 1.135 kg equals the mean of adult male and female herring gulls body weights as described by CCME (1999).

Area use factor – Herring gulls forage in both aquatic and terrestrial environments (mostly coastal areas and landfills). USEPA (1993) reports that the foraging range of adult herring gulls ranges from 5 km to 15 km. Thus, individual herring gulls with smaller foraging ranges likely derive all of their aquatic prey from the AOI, while those with larger foraging ranges also likely forage outside of the AOI. An AUF of 1.0 is applied for herring gulls, recognizing that it may overestimate exposures for some herring gulls.

2.3.2.3 Parameter Values for Raccoons

Food ingestion rate –The FIR for raccoons was derived based on the composition of the diet, the gross energy in each food group, the efficiency with which raccoons assimilate the gross energy in each food group, and the normalized free-living metabolic rate of raccoons, as detailed in Equations 5 through 7, and as shown in Table 2-5. The basis for each of these parameters is described below.

Dietary composition – Dietary preferences for the raccoon are derived from a synthesis of information reported by USEPA (1993) from multiple studies and focuses on studies conducted in the spring (i.e., breeding season) in Michigan (Alexander 1977 and Stuewer 1943 as cited in USEPA 1993). This approach is conservative because raccoons consume a higher proportion of animal matter during the spring and summer, and animal matter typically contains higher mercury concentrations than plants. Based on USEPA's (1993) synthesis of the literature on the raccoon's diet, it is assumed to be comprised of 14% fish, 19% bird and mammal matter, 17% amphibians and reptiles, 16% aquatic invertebrates, 10% terrestrial invertebrates, and

24% terrestrial plants. Thus, aquatic prey comprises 30% of the raccoon's diet. The preferred fish prey size range of raccoons is from 76 mm to 229 mm.

Gross energy of food groups – Gross energy calculations are based on information provided in USEPA (1993). A gross energy of 1.6 kcal/g wet weight is used for fish, based on the mean of values reported for fish in multiple studies reviewed by USEPA (1993). A gross energy of 1.8 kcal/g wet weight is used to represent birds and mammals, based on the mean values for birds and mammals (USEPA 1993). A gross energy of 1.3 kcal/g wet weight is used for amphibians and reptiles based on the mean for both groups (USEPA 1993). A gross energy of 0.95 kcal/g wet weight is used for aquatic invertebrates, based on the mean values reported in multiple studies reviewed by USEPA (1993). A gross energy of 1.3 kcal/g wet weight is used for terrestrial invertebrates (USEPA 1993). A gross energy of 1.3 kcal/g wet weight is used to represent terrestrial plants, based on the mean of wet weight adjusted gross efficiencies for all terrestrial plants (USEPA 1993).

Assimilation efficiency for food groups –An assimilation efficiency of 91% is used for mammals consuming fish based on the value reported by USEPA (1993). The value of 84% is used for both the assimilation efficiency of mammals consuming mammals and small birds, and reptiles and amphibians as reported by USEPA (1993) because separate values for amphibians and reptiles are not available. A value of 87% is used for invertebrates, based on USEPA's (1993) value selected from multiple studies for small mammals consuming insects. This value is used as the assimilation efficiency for both aquatic and terrestrial invertebrates. An assimilation efficiency of 78% is used for mammals consuming terrestrial plants (i.e., seeds, nuts, and forbs) based on an average of selected plants as reported by USEPA (1993).

Normalized free-living metabolic rate – The selected value of 185 kcal/kg-day represents the mean of estimated values for free-living adult male and female raccoons, as reported by USEPA (1993).

Body weight – The body weight of 5.8 kg equals the mean of adult male and female raccoon body weights reported in multiple studies cited by USEPA (1993).

Area use factor – Home ranges of raccoons are quite variable, depending on season and sex of the animal. Given that home ranges can be as small as five ha, some raccoons are likely to derive all of their aquatic prey from the AOI. Therefore, an AUF of 1 is appropriately conservative.

2.3.3 Calculated Target Tissue Concentrations Protective of Wildlife

The calculated target tissue concentrations of methylmercury and octachlorostyrene for aquatic prey protective of each wildlife ROI including double-crested cormorants, herring gulls, and raccoons are shown in Table 2-6. Individual input parameters are summarized in Section 2.3.2.

2.4 Evaluation of Risk from Biomagnification

The foregoing subsections detail the process used to develop target tissue concentrations protective of fish and wildlife ROIs due to exposure to methylmercury and octachlorostyrene, both of which may bioaccumulate and possibly biomagnify in the food chain. This subsection uses those target tissue concentrations to evaluate the risk from biomagnification to the ROIs, concluding that biomagnification risks are driven by potential adverse effects to sportfish.

2.4.1 Treatment of Tissue Data

The analysis of risk from biomagnification compares measurements of mercury and octachlorostyrene in representative tissue samples (i.e., invertebrates and whole body fish of the size targeted by the ROIs) to target tissue concentrations derived in Sections 2.1 through 2.3 above. Only the most recent fish sampling results (e.g., collected in 2000 or after) were used in this analysis, in order to focus findings on current conditions.

2.4.1.1 Total Mercury and Methylmercury Analytical Results

All fish tissue samples were analyzed for total mercury, rather than methylmercury. The biological methylation of mercury and its biomagnification suggest that virtually all mercury in freshwater fish is present as methylmercury (Bloom 1992). All mercury present in fish tissue samples was assumed to be present as methylmercury.

Data are available for concentrations of methylmercury in invertebrate tissue for chironomids and oligochaetes. These data indicate that the proportion of total mercury in invertebrate tissue that is methylated ranges from 5% to 44% in chironomids (mean = 18%, standard deviation or s.d. = 11%) and from less than 1% to 12% in oligichaetes (mean = 5%, s.d. = 3%). In these cases, methylmercury tissue results are used instead of total mercury tissue results in the comparison of measured tissue concentrations to target tissue concentrations.

2.4.1.2 Fillet to Whole Body Fish Tissue Conversions

Available fish tissue samples include both whole body and fillet results. The assessment of risks to fish and wildlife is most accurate if based on whole body concentrations, given that whole body concentrations most accurately represent ecological exposures. Fillet sample results for mercury were converted to equivalent whole body concentrations of mercury as follows. No comparable methodology was identified for octachlorostyrene. Therefore, fillet results for octachlorostyrene were used as reported.

The relationship between fillet and whole body concentrations of mercury has been well characterized and is relatively consistent across species (Bevelhimer et al. 1997, Goldstein et al. 1996, Peterson et al. 2005). Because mercury concentrates in fish muscle (i.e., fillet), concentrations in fillet samples are generally higher than in whole body samples. For this project, fillet concentrations of mercury were converted to whole body concentrations using an equation derived from 210 paired analyses representing 13 species (Peterson et al. 2005):

Eqn. 9

$$\log[\text{whole-body Hg}] = -0.2712 + 0.9005\log[\text{fillet Hg}] \ (R^2=0.96).$$

2.4.1.3 Grouping of Prey Samples by Receptor

When considering fish as receptors, all analytical results for all fish samples were evaluated, with groupings by young-of-year vs. adult sportfish, sampling location and species. Grouping by location considers both general sampling locations (i.e., Blocks 1, 2, and 3, which correspond to upstream of the AOI, within the AOI, and downstream of the AOI, respectively) and specific sampling locations within the AOI. The distribution of samples considered for fish as receptors is summarized in Table 2-7.

In the case of the wildlife ROIs, we grouped analytical results for fish and invertebrates according to the ROIs' feeding preferences. Thus, because double-crested cormorants target fish ranging from 4 cm to 41 cm in length, all results for fish within that range were grouped together. Prey samples are also grouped by general location (i.e., Blocks 1, 2, and 3). Prey samples were not grouped by specific location within the AOI because the local population of cormorants is assumed to forage throughout the AOI and fish are similarly mobile. The distribution of samples considered for double-crested cormorants is summarized in Table 2-8.

Because herring gulls target fish ranging in size from 10 cm to 30 cm (69% of diet) and invertebrates (16% of diet), we grouped together fish results for that size range plus invertebrate results. Prey samples were also grouped by general location (i.e., Blocks 1, 2, and 3). Again, prey samples were not grouped by specific location within the AOI because the local population of herring gulls is assumed to forage throughout the AOI and fish are mobile. Table 2-9 summarizes the distribution of samples considered for herring gulls.

Because raccoons target fish ranging in size from 8 cm to 23 cm (14% of diet) and invertebrates (16% of diet), we grouped together fish results for that size range plus invertebrate results. Again, prey samples were grouped by general location (i.e., Blocks 1, 2, and 3), but not by specific location within the AOI. The distribution of samples considered for raccoons is summarized in Table 2-10.

2.4.1.4 Categories of Risk

Categories of risk from biomagnification are defined in different manners for fish and wildlife ROIs. In assessing risks to fish as ROIs, trends in mercury and octachlorostyrene concentrations are evaluated by fish species, age group, size class, and sampling location. These comparisons allow calculation of the percent of samples that exceeds the target concentrations protective of fish**.** The magnitude of risk posed to each species of fish is characterized based on the percentage of pertinent tissue samples that exceeds the target tissue concentration that is protective of fish. This approach is appropriate for fish, in that it captures potential population-level risks to fish based on the proportion of individual fish affected.

In this report, negligible risks are defined for fish species with 20% or fewer of the pertinent tissue samples exceeding the target tissue concentration. Under these circumstances, it is expected that the local population of that species will not be adversely affected, even if a relatively small proportion of individuals is affected. Intermediate risks are defined for fish species with 21% to 50% of the pertinent tissue samples exceeding the target tissue concentration. In this case, population-level effects are considered possible, given that exposures in up to half the local population exceed the target threshold. Finally, high risks are defined for fish species with 51% or more of the pertinent tissue samples exceeding the target tissue concentrations. In this case, population-level effects are considered likely, given that exposures in the majority of individuals in the local population exceed the target threshold. Upgradient and downgradient conditions are also considered in this analysis due to the mobility of fish, as well as the potential for downstream transport of chemicals originating in the AOI. Potential risk to fish both upgradient (sampling Block 1) and downgradient (Block 3) of the AOI are specifically addressed by evaluating age-specific results for young-of-year and adult sportfish. Given the limited mobility of young-of-year fish, this approach facilitates an evaluation of AOI-specific risks that is not confounded by mobility patterns typical of adult sportfish.

Categories of risk from biomagnification in wildlife ROIs are defined as follows. Mean and 95% upper confidence limit (95%UCL) prey concentrations for each wildlife ROI are calculated and compared to the target concentration protective of that wildlife ROI. Because double-crested cormorants only consume fish, the mean employed here is arithmetic. Because herring gulls and raccoons consume both fish and invertebrates the mean and 95%UCLs are weighted, according to the proportions of fish and invertebrates in their diets.

The mean and 95%UCL concentrations represent exposures to individual wildlife ROIs as they average their intake by consuming a variety of prey from throughout the AOI. The 95%UCL concentration is a conservative estimate of the mean dietary concentrations (USEPA 2002). For purposes of this analysis, if both mean and 95%UCL concentrations are below the target concentration, risks to individual organisms are considered negligible. If the mean concentration is below the target concentration, but the 95%UCL concentration is above the target concentration, risks are generally defined as intermediate, in that the most highly exposed individual organisms may be adversely affected. If both the mean and 95%UCL concentrations exceed the target concentration, risks are generally defined as high, as both average and highly exposed organisms may be adversely affected. While ENVIRON developed the guidelines described above for differentiating severity of risk to wildlife, they are generally consistent with USEPA's classification of human risks between central tendency (based on average exposure assumptions) and high end (based on conservative exposure assumptions) (USEPA 1989). These guidelines are also consistent with the definitions of the metrics employed (i.e., average, 95%UCL).

2.4.2 Nature and Extent of Risk from Biomagnification

This subsection characterizes the nature and extent of risk from biomagnification posed to fish, double-crested cormorants, herring gulls, and raccoons.

2.4.2.1 Nature and Extent of Risk from Biomagnification to Fish

Potential risks to fish from biomagnification of mercury are presented in Tables 2-11 through 2-13, based on various alternatives for grouping the fish tissue results. As illustrated in Table 2-11, when all fish tissue data from Block 2 are grouped together, 20% of samples exceed the TRV that is protective of fish (0.20 mg/kg), suggesting negligible risk. However, when the fish tissue samples are segregated with respect to young-of-year and adult sportfish data, none of the young-of-year samples exceed the TRV and 31% of the adult sportfish samples exceed the TRV, suggesting intermediate risk. Findings for Block 3 (the lower St. Clair River) parallel those for Block 2, while negligible risks are found for young-of-year, adult sportfish and all fish in Block 1 (the upper St. Clair River). Table 2-11 also clearly demonstrates that elevated concentrations of mercury within the AOI (Block 2) compared to upgradient (Block 1) or downgradient (Block 3) concentrations for young-of-year fish can be attributed to AOI-specific exposure because young-of-year fish are not very mobile and unlikely to spend significant time outside the AOI. However, the same trend is less pronounced for adult sportfish, indicating adult sportfish mobility may confound interpretation of location-specific exposure.

Table 2-12 adds some spatial resolution to the evaluation of risks to young-of-year samples. However, because only one station each in Blocks 1, 2, and 3 was sampled for adult sportfish, this analysis does not change the conclusions from Table 2-11. Table 2-13 adds further resolution with respect to fish species. Upstream of the AOI, in Block 1, freshwater drum *(Aplodinotus grunniens*) and smallmouth bass (*Micropterus dolomieui*) are predicted to be at high risk (i.e., more than 50% of samples exceed the TRV that is protective of fish). Intermediate risks are predicted for walleye collected in Block 1. Risks to these species in Block 1 may reflect the broad foraging ranges of these species, in that the fish collected in Block 1 may have also foraged in Block 2 and/or 3. These risks may also reflect local or regional sources of mercury. Negligible risks are predicted for all other fish species collected in Block 1.

As also shown in Table 2-13, for Block 2 (i.e., the AOI), northern pike and redhorse sucker (*Moxostoma* spp.) are predicted to be at high risk, while carp (*Cyprinus carpio*), freshwater drum, white sucker, and yellow perch are predicted to be at intermediate risk. Negligible risks are predicted for all other species caught in Block 2.

For Block 3 (i.e., downstream of the AOI), intermediate risks are predicted for brown bullhead (*Ameiurus nebulosus*), carp, freshwater drum, largemouth bass (*Micropterus salmoides*), rock bass (*Ambloplites rupestris*), and walleye. Risks to these species in Block 3 may be attributable to the fish foraging in Block 2, local or regional sources of mercury, downstream transport of mercury from Block 2 to Block 3, high methylation of mercury in Zone 3 due to TOC in sediment, or a combination of these factors.

The above analysis hinges on a literature-derived TRV for all fish (i.e., 0.20 mg/kg). Therefore, in an effort to better understand whether the sportfish community is actually impaired in the St. Clair River, ENVIRON evaluated reproductive and fitness data collected along with the tissue chemistry data as part of the Sportfish Contaminant Monitoring Program (SFCMP). Male mortality, skewed sex ratios, and decreased fitness have been identified as endpoints for mercury toxicity in fish species (see Section 2.2.2.1). Specifically, as detailed below, ENVIRON

compared SFCMP data on sex ratios and fitness from Lake Huron, Lake St. Clair, Lake Erie, the Detroit River, and the St. Clair River. These endpoints (i.e., sex ratios and fitness) were also tested for significant correlations with mercury concentrations in fish tissue.

For the 11 species predicted to be at high or intermediate risk in any block of the St. Clair River (i.e., carp, white sucker, redhorse sucker, brown bullhead, yellow perch, freshwater drum, smallmouth bass, largemouth bass, rock bass, walleye, and northern pike), sex ratios in adult fish were calculated by species for each water body (Lake Huron, St. Clair River, Lake St. Clair, Detroit River, and Lake Erie). Data from the three St. Clair River blocks were combined because the populations inhabiting the three blocks of the river are not likely discrete and because the sample sizes of the individual blocks were insufficient to support individual statistical analyses. Sex ratios were calculated as the ratio of males to all fish, such that values below 0.5 indicate female bias (i.e., more females than males). Confidence intervals for the average sex ratio were also generated, as presented in Figure 2-2. In general, large confidence intervals reflect small sample sizes (e.g., 6 northern pike samples in the Detroit River). Sample sizes in the St. Clair River range from 11 to 56, depending on the species of fish.

As shown in Figure 2-2, sex ratios for freshwater drum in all waterbodies tend to be female-biased, with the greatest bias evident in Lake St. Clair and no clear difference between freshwater drum in the St. Clair River and Lake Huron, the Detroit River, and Lake Erie. Although the sample size of smallmouth bass for the St. Clair River is relatively small (n=11),, the sex ratio appears to be female-biased relative to the other waterbodies. For northern pike and redhorse sucker, there are no clear differences in sex ratios across waterbodies, although relatively low sample sizes in some waterbodies may obscure any differences that may exist. For the fish species found to be at intermediate risk (i.e., walleye, carp, white sucker, yellow perch, brown bullhead, largemouth bass, and rock bass), there were generally no clear differences in sex ratios across water bodies. Yellow perch is a notable exception, in that sex ratios for this species are significantly female-biased in the St. Clair River and Lake St. Clair. Sample sizes for yellow perch range from 56 to 1,082 in the various waterbodies (i.e., Lake Huron, Lake St. Clair, Lake Erie, Detroit River, St. Clair River); these relatively high sample sizes suggest that the apparent differences among waterbodies are not due to chance.

Figure 2-3 illustrates the relationships between sex ratios and mercury tissue concentrations for the four fish species found to be at high risk and the seven species found to be at intermediate risk in the St. Clair River. Individual fish samples were binned into mercury concentration classes by rounding the concentration to the nearest 0.2 mg/kg. Binning individual samples by concentration allowed sufficient sample sizes to calculate a mean sex ratio for each species and for each bin. Thus, the sample sizes (n) shown in Figure 2-3 reflect numbers of bins, while numbers of individual fish samples per bin are shown in parentheses above each bin symbol. Large numbers fish samples comprise most bins (i.e., up to 1,725), increasing confidence in each bin's calculated sex ratio.

Although different waterbodies may be characterized by differences in environmental variables that influence mercury cycling and/or mercury trophic transfer rates, the extent to which mercury is stored in biological tissue and the organism's toxicological response is more strongly dictated

by a species' physiology than by ambient environmental conditions. Thus, for fish species examined in this analysis, binning by tissue concentration within species is a suitable strategy to increase the sample size for robust statistical analysis.

A significant female-bias is correlated with the concentration of mercury in tissue of freshwater drum, smallmouth bass, northern pike and yellow perch, but not redhorse sucker walleye, carp, white sucker, brown bullhead, largemouth bass, or rock bass. The correlations in four species suggest a dose-response relationship for mercury for some species, especially those at high risk. However, there may be other factors (i.e. confounding factors) that partially or fully account for the female-bias and it is important to note that correlation does not necessarily imply a causal relationship. For example, mercury may co-occur with ubiquitous endocrine-disrupting chemicals, such as PCBs (NRC 2001). Because both mercury and PCBs are closely associated with fine-grained organically-enriched sediment, PCBs in fish tissue are a possible confounding factor in this analysis. Although no significant interaction between sex ratio and concentration of PCBs in fish tissue is apparent, sample sizes are very small (n = 3 to 8, depending on species). Therefore, a PCB effect may not be detectable even if one exists. Similar findings are expected for other endocrine disrupting chemicals.

Timing of sampling may represent another potential confounding factor, in that males and females may congregate in a non-random manner during spawning. Therefore, if fish are sampled during spawning, there may not be an equal probability of collecting males vs. females. In general, we found no significant interaction between sex ratio and timing of sampling for the majority of the species examined, suggesting that timing of sampling did not affect the overall findings. White sucker and rock bass were exceptions, in that timing could be a factor in the observed sex ratios for these species. For white sucker, the sex ratio was 0.2 in November and December, as compared to 0.38 to 0.55 for the remainder of the year. For rock bass, the sex ratio was 0.74 in December, as compared to 0.35 to 0.55 for the remainder of the year. When rock bass collected in December and white sucker collected in November and December are excluded from the analysis, the correlation coefficients and p-values are nearly identical to those based on the uncensored data set. Thus, seasonal effects did not affect the analysis of the relationship between sex ratio and mercury concentration.

Sexual dimorphism in certain fish species may represent a confounding factor in the analysis of relationships between concentrations of mercury in tissue and sex ratios. Of the fish species at high risk and intermediate risk, northern pike, freshwater drum, yellow perch, and walleye are sexually dimorphic, with females growing larger and living longer than males (Clarke and Steinbach 1959, Rypel 2007, Henderson et al 2003). Male northern pike greater than 80 cm are reportedly less common than large females in the wild (Clarke and Steinbach 1959). Indeed, the dataset employed in this analysis included no male northern pike specimens greater than 95 cm, no male freshwater drum specimens greater than 50 cm, no male walleye greater than 67 cm, and no male yellow perch greater than 33 cm in length. Independent of the biologically expected sexual dimorphism in these species, mercury concentrations in fish typically exhibit a strong correlation with fish size. Over the life span of a fish, continued bioaccumulation of mercury and continued growth of the fish occur concurrently. Thus, the observed relationship between concentrations of mercury in fish tissue and female-biased sex ratio may be at least

partially a consequence of expected sex-specific size differences, in light of a sampling program that targets larger fish.

To test whether sexual dimorphism influences the observed relationship between sex ratio and tissues concentration, we explored relationships between size, concentrations of mercury in fish tissue, and sex ratios. Northern pike, freshwater drum, walleye, and yellow perch were first binned by size class in 5-cm increments. Correlation coefficients were generated for concentrations of mercury in fish tissue and sex ratio for each size class. Testing for correlation within narrow size ranges is expected to control for the effects of sexual dimorphism. For small northern pike (< 70 cm in length), we observed no correlation between concentrations of mercury in fish and sex ratio. However, because concentrations in small fish were lower than those in large fish (as expected), mercury concentrations in small fish may have been well below toxic levels. For northern pike of 70 cm, 75 cm, and 80 cm in length, there was a significant correlation between tissue concentration and sex ratio. For northern pike larger than 80 cm in length, there were too few males to allow an assessment of the correlation. For freshwater drum less than 30 cm in length, tissue concentrations were low and there was no significant correlation with sex ratio. For freshwater drum of 35 cm and 40 cm in length, sex ratio and tissue concentration were significantly correlated. For freshwater drum larger than 40 cm, the sex ratio was exclusively female and tissue concentrations were high, preventing an assessment of the correlation with sex ratio. For walleye, sex ratio and tissues mercury concentrations are correlated for fish of 50, 55, 60 and 65 cm length. However, the direction of the correlation is inconsistent. For fish of 50 and 55 cm in length, the proportion of males increases with increasing mercury concentration. For fish 60 and 65 cm in length, the proportion of females increases with increasing mercury concentration. This inconsistency could be due to random variation in the data and not indicative of a functional relationship. For yellow perch, there was no relationship between length, mercury concentration, and sex ratio. Thus, for the two species at high risk (northern pike and freshwater drum), there is a significant correlation between sex ratio and tissue concentration in intermediate-sized fish. For large fish, sexual dimorphism is a potential confounding factor.

The relationship between length, tissue concentration, and sex ratio was also explored using ANOVA. In both species at high risk (northern pike and freshwater drum), if tissue concentration was modeled first and length was modeled second, tissue concentration was a significant factor. However, if length was modeled first, tissue concentration was not a significant factor. For yellow perch and walleye, no significant relationships to tissue concentrations were found when length was included in the ANOVA. Given these inconclusive results of the ANOVA and the significant correlation between length and tissue concentration, the ANOVA does not provide strong evidence either for or against a relationship between tissue concentration and sex ratio. Therefore, the likelihood of a biological relationship between tissue concentration and sex ratio should not be dismissed, despite the apparent confounding effects of sexual dimorphism in two species. It is also worth noting that sexual dimorphism in smallmouth bass is not evident in the data set, yet they also exhibit a significant relationship between tissue concentration and sex ratio (Figure 2-3), offering further evidence of mercury-associated toxicity in fish.

In summary, sex ratios appear skewed for smallmouth bass and yellow perch in the St. Clair River, relative to other water bodies in the region. Skewed sex ratios are correlated with mercury tissue concentrations in freshwater drum, smallmouth bass, northern pike, and yellow perch. Given the potential for confounding factors, particularly with respect to co-contaminants and sexual dimorphism, available data should be considered suggestive rather than conclusive with regard to a causal relationship between tissue mercury concentration and sex ratios. With this caveat, the sex ratio analysis provides site-specific biological information that is consistent with predictions from the literature-based evaluation of tissue chemistry data, but does not provide definitive evidence of a mercury effect on fish populations.

Potential effects of mercury on impaired fitness were evaluated by first calculating fitness factors:

Eqn. 10

$$\text{Fitness factor} = (100{,}000*[\text{weight (g)}]/1{,}000) / ([\text{length (cm)}]^3)$$

As shown in Figure 2-4, fitness factors for all species by water body consistently exceed 0.6 and often exceed 1.0. Drevek et al. (2008) reported that a fitness factor of 0.5 or less was rarely observed in fish with low mercury liver concentrations, while high mercury liver concentrations were consistently associated with fitness factors below 0.6. Based on a benchmark of 0.5 to 0.6, there is no evidence of impaired fitness in fish collected from the St. Clair River or other regional water bodies. As shown in Figure 2-5, the relationship between fitness and mercury tissue concentrations are significant for freshwater drum, northern pike, walleye, carp, largemouth bass, and rock bass. In the case of freshwater drum, carp, and largemouth bass, the Pearson's r is positive (0.12, 0.17, 0.16 respectively), which is counter to an adverse effect due to mercury. The negative Pearson's r for northern pike (-0.13), walleye (-0.08), white sucker (-0.04) and rock bass (-0.19) are very low, indicating that mercury explains very little (8% to 19%) of the variability in fitness. In any event, as previously discussed, fitness factors for northern pike in the St. Clair River are consistently above 0.5 to 0.6. In conclusion, the site-specific biological information on fitness does not provide evidence of adverse effects on fitness due to mercury.

2.4.2.2 Nature and Extent of Risk from Biomagnification to Wildlife

With respect to biomagnification risk to wildlife, mean and 95%UCL concentrations of methylmercury and octachlorostyrene in prey tissue are below the target concentrations protective of double-crested cormorants, herring gulls, and raccoons (Tables 2-14 through 2-16). Figures 2-6 and 2-7 compare prey tissue concentrations for each wildlife ROI to their target concentrations for methylmercury and octachlorostyrene, respectively.

As described in Section 2.2.3.1, the dose-based TRVs used to evaluate risks to double-crested cormorants and raccoons are most likely over-protective, whereas conflicting evidence exists as to the relative sensitivity of herring gulls. Therefore, in an effort to ensure the protectiveness of this assessment, we compared mercury concentrations in herring gull eggs to egg-based TRVs. Initially, the scientific literature was reviewed in an effort to identify diet-to-egg biomagnification

factors (BMFs) for herring gulls. However, few studies were identified that reported mercury concentrations in both herring gull eggs and prey, and those studies provided widely divergent estimates of biomagnification (Otorowski 2005, Vermeer et al. 1973). Another important data gap is the absence of any data on mercury concentrations in herring gull eggs collected from the St. Clair River.

It is possible, however, to draw inferences from the Canadian Wildlife Service's herring gull monitoring data for the Detroit River, based on the relative levels of mercury in fish from the Detroit and St. Clair Rivers[6]. Average mercury concentrations in herring gull eggs from the Detroit River are approximately 0.15 mg/kg (Koster et al. 1996, Weseloh et al. 2008). The sportfish monitoring data for the Detroit River and the St. Clair River AOI have five fish species in common, of which two species have higher average mercury concentration in the Detroit River (rock bass and walleye) and three have higher average mercury concentrations in the AOI (carp, freshwater drum, and northern pike). The largest concentration difference is observed for northern pike, with average mercury concentrations in the AOI (0.41 mg/kg, n=9), which is two-fold higher than in the Detroit River (0.20, n=6). If herring gull eggs in the AOI are assumed to contain twice as much mercury as those sampled on the Detroit River, the resulting egg concentrations would be 0.3 mg/kg. This concentration is lower than the mercury concentrations associated with adverse effects on mallards, loons, and herring gulls (Section 2.2.3.1). Thus, adverse effects on herring gulls appear unlikely, consistent with the dose-based analysis for this species.

In summary, risks from biomagnification to wildlife have been assessed for wildlife species expected to occur in the AOI, based on methylmercury and octachlorostyrene concentrations measured in prey tissue. Adverse effects on double-crested cormorants, herring gulls, and raccoons due to methylmercury or octachlorostyrene biomagnification in the AOI are unlikely.

[6] Two pooled herring gull egg samples were collected from the St. Clair River, in 1987 and 1991. Neither sample was analyzed for mercury. The samples are preserved in the Canadian Wildlife Service's archive.

3 SEDIMENT CHEMISTRY

The sediment chemistry LOE involves the comparison of sediment chemistry data to SQGs and reference conditions. The objective of this LOE is to determine whether: 1) chemicals are present in sediment at concentrations greater than conservative screening levels or lower bound SQG (SQG-low); and/or 2) chemicals present in sediment could biomagnify and affect the health of biological communities at higher trophic levels. Under the COA Framework, the Canadian Threshold Effect Levels (TELs) or the Ontario LELs serve as the SQG-low, subject to regional considerations and best professional judgement. Following a summary of the available sediment chemistry data, the SQGs are described and analytical results for samples collected from the AOI are compared to those SQGs. Although the summary of available chemistry data opens with an overview of the full range of chemicals detected in sediment, subsequent discussions in this section focus on two biomagnifying and/or bioaccumulative chemicals, mercury and octachlorostyrene.

This LOE focuses on samples collected in 2005 or later. Sediment chemistry data collected in 2005-2008 were evaluated using the Geographic Information System (GIS) technique of anisotropic interpolation (e.g., elliptical inverse distance weighting) in a flow-oriented (s,n) coordinate system, adapted from that described by Merwade (2006). The methods employed are detailed in Appendix C. In summary, an anisotropic interpolation can account for the greater variability of physical and habitat characteristics transverse to river flow, as opposed to along the longitudinal axis of the river. ENVIRON conducted the anisotropic interpolation by assigning each sampling station an “s” value derived from its location along the length of the river in metres, and an “n” value derived from its distance from the river centerline. Next, a blank grid was created as an overlay in x,y coordinate space. After the interpolation was performed, the resulting grid was brought back into Cartesian (x,y) coordinate space (i.e., Universal Trans Mercator or UTM) for display or further analysis. The resulting grids were used to assign chemical concentration data values to those locations that lacked empirical data. The values for the chemistry parameters were interpolated to yield a grid value for each of the parameters.

Anisotropic interpolation was used because it reduces the uncertainty associated with variability in sediment characteristics transverse to river flow. Using Geostatistical Analyst in ArcGIS, inverse distance weighting (IDW) was employed in s, n, coordinate space to interpolate both sediment chemical concentrations and physical parameters. An anisotropic ratio (AR) of four was employed in all interpolations; this was chosen based on river characteristics, sediment data, and best professional judgement. The AR determines the search neighbourhood used in the interpolation. By using an AR of four, the search neighbourhood is four times greater in the direction of river flow compared to transverse to river flow. This effectively minimized the root mean square error (RMSE) of the interpolations. In addition, a power of two was used for all interpolations, meaning that sample results closest to each unsampled location were given higher weight than sample results farther away. A maximum of 15 sample results were used to determine the value at each unsampled location.

3.1 Summary of Sediment Chemistry Data (2005-2008)

As noted above, this evaluation of surface sediment chemistry data focuses on samples collected in 2005 or later. Surface sediment chemistry results are presented in Richman (2008a), Biberhofer et al. (2007), and Houtby and Moran (2006) and summarized in Sections 1.2.1, 1.2.3 and 1.2.5, respectively. The underlying data and GIS layers are also provided in the project database (Appendix A).

Briefly, Richman (2008a) presents results from sampling of mercury, methylmercury, hexachlorobenzene, hexachlorobutadiene, and octachlorostyrene, as well as total PCBs and tetrachloroethylene, TOC, nutrients (phosphorus and nitrogen), iron, manganese, and particle size distribution. For results presented in Richman (2008a), sampling objectives varied by river Zone, such that not all chemicals were analyzed at all sampling stations.

Biberhofer et al. (2007) present results from 2006 sediment sampling focused on mercury, methylmercury, hexachlorobenzene, hexachlorobutadiene, and octachlorostyrene. Sediment analyses also included nutrients (phosphorus and nitrogen), iron and manganese, and particle size distribution.

Houtby and Moran (2006) provide sediment chemistry data for five stations within the AOI, which were sampled in 2005. Sediment samples were analyzed for metals, BNEs including PAHs, NCEs, PCBs, and TOC.

Results of all three studies confirm previous observations of a discontinuous and irregular shoreline distribution of sediment-associated contaminants in the St. Clair River. With respect to chemicals of concern, these studies conclude that mercury and methylmercury are present in St. Clair River surface sediments at elevated concentrations. The maximum mercury and methylmercury concentrations in AOI surface sediment are 41 mg/kg and 0.12 mg/kg, respectively. For organic chemicals, the distribution of hexachlorobenzene, hexachlorobutadiene, and octachlorostyrene suggest general trends of decreasing concentration along an upriver to downriver gradient. Further discussion of relevant SQGs is presented in Section 3.2, and discussion of risks predicted by sediment chemical concentrations is presented in Section 3.3.

3.2 Sediment Quality Guidelines

The sediment chemistry LOE requires comparison of analytical results for bulk sediment chemistry to SQGs. Consistent with the COA Framework, concentrations of mercury in sediment are compared to the LEL (as the SQG-low) and the SEL (as the upper bound SQG or SQG-high) (Persaud et al. 1993). Persaud et al. (1993) define the LEL as the concentration below which toxicity to benthic invertebrates is unlikely. The LEL for mercury is 0.2 mg/kg. Persaud et al. (1993) define the SEL as the concentration above which toxicity to benthic invertebrates is likely. The SEL for mercury is 2 mg/kg. These screening values were developed using a co-occurrence approach, where data from biological monitoring at a large number of sites (e.g., information on the presence and absence of benthic organisms) were

compared to the site chemistry data. It is widely accepted that empirical SQG, such as these, do not necessarily represent cause-effect, concentration-response relationships between chemical concentrations and biological effects (Wenning et al. 2005). Indeed, under the COA Framework, biological and toxicity studies are weighed more heavily than comparisons of sediment concentrations to SQGs.

No published SQGs are available for octachlorostyrene. However, the equilibrium partitioning approach (Di Toro et al. 1991) provides a basis to identify a sediment quality benchmark protective of benthic organisms, based on aquatic toxicity data. Lee et al. (2008) examined the chronic toxicity of octachlorostyrene to midges based on 20-day survival, pupation and emergence, adult sex ratio, and reproductive success. They used acetone as a carrier solvent to achieve exposure concentrations exceeding the solubility limit of approximately 2 micrograms per liger (µg/L), although measured concentrations were nevertheless much lower than nominal concentrations. The test endpoints were significantly affected following exposure to the highest octachlorostyrene concentration (5,000 µg/L nominal, 20 µg/L average measured) but not to lower octachlorostyrene concentrations (500 µg/L and 50 µg/L nominal). Because octachlorostyrene concentrations were measured only at the highest test level, identification of a NOAEC from this test requires extrapolation. If the exposure concentrations are assumed to be proportional to the nominal concentrations, then the NOAEC can be estimated as 2 µg/L (i.e., 10-fold lower than the measured LOAEC).

The equilibrium partitioning approach identifies SQGs by determining the whole-sediment concentration that would result in a specified water quality benchmark concentration in sediment porewater. Chemical partitioning between sediment organic carbon and porewater is estimated from the sediment-specific organic carbon content and the octanol-water partition coefficient (K_{ow}; approximately equal to the organic carbon-water partition coefficient) (Di Toro et al. 1991). Based on a log K_{ow} of 7.46 and a water quality benchmark of 2 µg/L, the SQG for octachlorostyrene is estimated as approximately 43 mg per gram organic carbon, or 430 mg/kg for sediment containing 1% TOC. Adjusting for an average of 1.5% TOC in surface sediment in the AOI, the carbon-normalized octachlorostyrene benchmark is 650 mg/kg.

3.3 Nature and Extent of Risk Predicted by Sediment Chemistry

Summary statistics for surface and subsurface sediment chemistry results for all detected analytes are presented in Tables 3-1 and 3-2, respectively. These tables list the analytes, units, range of detected concentrations, and mean and 95%UCL concentrations. The results represent a range of analytes including nutrients and metals, organics, PCBs, and physical parameters. Although mercury is only one of a subset of metals analyzed, elevated concentrations in subsurface sediment compared to surface sediment are noteworthy, in that the 95%UCL concentrations in surface and subsurface sediment are 5.5 mg/kg and 24 mg/kg, respectively. Organic analytes including hexachlorobenzene, hexachlorobutadiene, octachlorostyrene, and PCBs, are also elevated in subsurface sediment compared to surface sediment. Physical parameters are generally comparable in surface and subsurface sediment, with the exception of silt and clay and TOC, which are higher in subsurface sediment.

The analytes presented in Tables 3-1 and 3-2 present sediment chemistry results for all detected analytes. Subsequent work by Kauss et al. (2001) determined that hexachlorobenzene and hexachlorobutadiene concentrations in the upper St. Clair River are below the sediment remediation targets that Kauss et al. (2001) developed for these two compounds, leaving octachlorostyrene and mercury as the primary chemicals of concern. Further work by Milani et al. (2007) also indicated potential risk from biomagnification for mercury using the COA Framework. Therefore, all subsequent discussion of sediment chemistry in this report focuses solely on mercury and octachlorostyrene. Summary statistics for total mercury and octachlorostyrene in surface sediment, including the range of detected concentrations, mean, 95%UCL, LEL, SEL, and percent of samples exceeding the LEL and SEL are show in Table 3-3. Total mercury concentrations at all sampling stations exceed the LEL, while 61% of sampling stations exceed the SEL (Table 3-3).

Figures 3-1, 3-2, and 3-3 depict total mercury, methylmercury, and organic carbon-normalized octachlorostyrene concentrations in surface sediment based on sampling conducted in 2005-2008. These figures black out a portion of the AOI where extensive erosion by river currents—that is, scouring—has prevented accumulation of sediment and collection of any sediment samples (hereafter referred to as the scoured area). The anisotropic interpolation presented in Figure 3-1 does not show discernable gradients in mercury concentrations in surface sediment. The highest concentrations of mercury occur in two areas, one of which is immediately south of the scoured area shown in black and one of which is just south of the mouth of Talfourd Creek.

Spatial trends for methylmercury in surface sediment also do not show a clear gradient or pattern (Figure 3-2). The highest concentrations of methylmercury occur in two locations, one of which is north of the scoured area shown in black and one of which is immediately south of the scoured area. Most other areas of the AOI have relatively low concentrations of methylmercury compared to the total range measured within the AOI. However, there are reaches within the AOI that show moderate concentrations of methylmercury in surface sediment but relatively low concentrations of total mercury, such as the reach north of the scoured area and the reach that parallels the southern end of Stag Island. Patterns of total mercury around Stag Island show the opposite trends, with higher concentrations of total mercury northeast of Stag Island, as compared to the southeast side of the island.

As illustrated in Figure 3-3, spatial trends in octachlorostyrene concentrations are similar to spatial patterns of total mercury concentrations, in that the highest concentrations occur in three discrete areas, including an isolated location in the upper AOI, immediately south of the scoured area, and downstream of the mouth of Talfourd Creek. However, all extrapolated concentrations of octachlorostyrene in surface sediment in the AOI are well below the SQG of 650 mg/kg, indicating a low risk of toxicity to benthic organisms due to octachlorostyrene (Table 3-3).

Figures 3-4 and 3-5 illustrate the spatial distribution of TOC and grain size using anisotropic interpolation, while Figure 3-6 illustrates the bathymetry of the AOI based on high-resolution multibeam sonar. The physical parameters of TOC, grain size, and bathymetry aid in identifying locations where conditions may enhance mercury deposition, especially where enriched organic

matter is present. The highest TOC occurs along the southeastern side of Stag Island where methylmercury concentrations are also elevated, south of the scoured area, and surrounding the mouth of Talfourd Creek. The highest percent of fines occurs in the upper AOI north of the scoured area, immediately south of the scoured area, and along the southeastern side of Stag Island.

In conclusion, although all areas of the AOI have total mercury concentrations exceeding the SQG-low (i.e., the LEL of 0.2 mg/kg) and many areas of the AOI have total mercury concentrations exceeding the SQG-high (i.e., the SEL of 2 mg/kg), these screening values do not necessarily represent cause-effect, concentration-response relationships between chemical concentrations and biological effects (Wenning et al. 2005). The discrete areas of the most elevated total mercury concentrations in the AOI, as well as the methylmercury distribution are more informative than the SQG comparisons, for purposes of integrating multiple LOEs and characterizing overall risks in support of remediation decisions. Because concentrations of octachlorostyrene are below the equilibrium partitioning-based SQG throughout the AOI, octachlorostyrene is not likely to adversely affect benthic invertebrates in the AOI.

4 BENTHOS ALTERATION

The objective of the benthos alteration LOE is to determine whether the benthic community structure in the AOI differs significantly from reference sites. Benthic community structure is often described in terms of the diversity, abundance, and dominance of different invertebrate species living in or on the sediment. Assessment of the benthic community may involve multimetric and/or multivariate analysis for full characterization. As detailed below, Milani et al. (2007) and Moran et al. (2005) evaluated the benthic community in the AOI. This section summarizes those findings, with particular attention to defining the magnitude and spatial extent of any impairment observed. Milani et al.'s (2007) and SLEA's findings are tabulated in Appendix A.

4.1 Environment Canada Benthic Invertebrate Community Assessment

Milani et al. (2007) collected sediment and benthos samples at 16 sampling stations in the St. Clair River in 2001. The benthic invertebrate community was evaluated using the Benthic Assessment of SedimenT (BEAST) methodology. The benthic community structure line of evidence is one of the elements in the BEAST approach, which examines changes in taxonomic composition and abundance of the benthic invertebrate community using multivariate analysis. Benthic community results for Zone 2 (corresponding to the AOI) are described below. Employing the BEAST methodology, benthic community taxonomy was assessed at the family level, because this level is typically adequate for determination of stress.

The characterization of benthic community structure to the genus and species level is included in Appendix E of Milani et al. (2007). In Milani et al. (2007), discussion of species- or genus-level taxonomy is largely restricted to comparison of results from a 1994 benthic community survey conducted by Farara and Burt (1997). As described by Milani et al. (2007), densities of the most common taxa—tubificids and chironomids—were lower in the 1994 survey than in the current study. In terms of dominant species, the 1994 survey identified 14 tubificid species, with the most common including *Limnodrilus hoffmeisteri* and *L. udekemianus,* as well as immature tubificids without chaetal hair (as reported in Milani et al. 2007). These results are compared with the data from the current study, in which 16 species were identified, with the most common species including the pollution-indicative species (Alden 2002) *Aulodrilus pigueti*, *L. hoffmeisteri*, and *L. udekemianus,* as well as *Quistradrilus multisetosus* and immature tubificids. For immature tubificids, Milani et al. (2007) report general trends in presence of chaetal hairs, with hairs more likely to be present in immature tubificids collected from downstream stations versus upstream stations. Induced changes in chaetal hair morphology (including appearance and disappearance) in common tubificid species have been linked with exposure to pollution (Milbrink 1983), as well changes in water pH, hardness, or salinity (Chapman and Brinkhurst 1987). For chironomids, the 1994 survey identified 33 genera, with the most common identified as the pollution tolerant genera *Polypedilum* and *Phaenopsectra* (as reported by Milani et al. 2007). Results from the current study identified 38 genera with the most common including *Polypedilum, Tribelos*, *Procladius* and *Chironomus.* The genus *Chironomus* was present at 15

of the 16 locations sampled in the current study, whereas it was only occasionally observed in the 1994 sampling survey.

Milani et al. (2007) note that differences in species composition and organism density between these two sampling events are likely influenced by differences in sampling season (i.e., early summer in 1994 versus early fall in the current study), as well as sample sorting procedures (i.e., sieving through a 600-micrometre (µm) mesh in the 1994 study versus sieving through a 250-µm mesh in the current study). The difference in sampling season is also reflected in difference in the density of chironomid pupae between these two sampling events. For early summer sampling in 1994, for example, chironomid pupae were identified in 92% of the samples (as described in Milani et al. 2007), whereas no chironomid pupae were identified at any sampling locations in the more recently collected (early fall) data set.

Overall, based on the conclusions of Reynoldson et al. (2000) and Reynoldson et al. (2001) that benthic community bioassessment at the level of family is adequately sensitive for the determination of stress, and observations of Feio et al. (2006) that the ability to predict reference group membership is frequently not significantly enhanced at lower taxonomic levels (genus or species) than at the level of family or order, the outcome of species-level BEAST assessment for the St. Clair River would not likely generate results different from results for the family-level assessment applied to this location. Moreover, because upgradient and downgradient stations are dominated by pollution tolerant families (i.e., Tubificidae and Chironomidae), and species or genera distribution within these families is inconsistently predicted by sediment pollution (e.g., Bahrndorff et al. 2005; Carew et al. 2007), there is little clear evidence that results of the upgradient versus downgradient comparison would change based on a lower taxonomic level bioassessment.

As part of the BEAST methodology, benthic community composition is compared to a large data set of Great Lakes reference sites. Selection of reference sites is intended to establish baseline conditions for selected endpoints, and to determine what constitutes a 'normal' range of biological variability. Test sites are matched to predefined groups of reference sites based on habitat characteristics related to geographic location, water depth, sediment characteristics, and hydrodynamics. In general, a test site is considered a good match to a reference group if its probability of belonging to the group is at least 60%. Site characteristics for the Great Lakes reference locations were not well matched with the St. Clair River AOC, because the reference locations were dominated by lake sites. Therefore, the BEAST methodology was revised to include additional reference sites from the St. Clair River.

As shown in Table 4-1, for the five St. Clair River stations in Zone 2 (i.e., the AOI) only one demonstrated a probability of at least 60% of belonging to a reference group (Milani et al. 2007). For these five stations, the probability of belonging to Reference Group 3 ranged from 47% to 60%, whereas the probability of belonging to Reference Group 1 ranged from 30% to 41%. Overall, these stations therefore demonstrated a higher probability of belonging to Reference Group 3, although Milani et al. (2007) suggest that such probabilities are suboptimal for accurate comparison. For context, Reference Group 3 is based on 51 sites, including Georgian Bay (n = 20), the North Channel of Lake Huron (n = 10), the St Clair River (n = 9), Lake Ontario

(n = 7), Lake Erie (n = 3), and Lake Huron (n = 2). Reference Group 1 is based on 35 sites, including Lake Erie (n = 22), Lake Michigan (n = 5), Georgian Bay (n = 4), Lake Ontario (n = 3), and the St Clair River (n = 1). The applicability of the BEAST methodology at any test site requires that field conditions at that site are within the range of field conditions defined for particular reference groupings. As shown in Table 4-2, sampling stations in the St. Clair River were characterized by increased abundance of pollution-tolerant Chironomidae and Tubificidae relative to Reference Group 3. However, Milani et al. (2007) suggest that caution should be employed in interpreting these results. Although Milani et al. (2007) determined that one location in Zone 1 exhibited benthic community impairment, no locations in Zone 2 (i.e., the AOI) were deemed impaired.

Given the limitations of comparisons to reference groups, Milani et al. (2007) compared benthic community structure in upstream and downstream stations. Upstream and downstream were defined relative to the location of the industrial area in Zone 1, upstream of the AOI. This comparison found no significant differences in community structure between upstream and downstream sites ($p \leq 0.05$). Comparisons assessing family diversity, abundances of tubificids, and abundance of chironomids also found no significant differences between upstream and downstream sites.

4.2 SLEA Benthic Community Assessment

Moran et al. (2005) collected data in 2003 in support of a benthic community assessment for the AOI. Sediment samples for enumeration of benthic invertebrates were collected in triplicate by a mini Ponar grab sampler. Moran et al. (2005) collected samples on the U.S. side of the St. Clair River, to allow segregation of stations within Zones 1 through 3 on the Canadian shore from stations considered as in-river “reference” locations. The category of reference stations also included two stations on the Canadian side of the river, with one station upgradient of Zone 1 (and therefore co-located with reference stations presented by Milani et al. 2007) and one station downgradient of Zone 3, in the vicinity of Lake St. Clair. Benthic community results are summarized in Table 4-3.

Moran et al. (2005) performed a variety of statistical analyses to evaluate benthic community composition, with sometimes conflicting results. The assessment considered five metrics (taxa richness, abundance, diversity, number of chironomids, and number of Ephemeroptera, Plecotera, Trichoptera [EPT] taxa), as well as the “raw” benthic community composition data. Multivariate hypothesis testing identified no significant differences between test and reference stations. However, univariate tests found reduced taxa richness and abundance at the test stations. Principal components analysis of the “raw” data identified location U.S. #7 as the least similar to the other stations, while location #1 (the upstream reference site) was the next most dissimilar. Also, the U.S. reference locations were somewhat different than the Canadian sites. Moran et al. (2005) did not clearly determine which of the conflicting analyses should receive greater weight in determining whether benthic community impairment was observed.

Many of the differences observed by Moran et al. (2005) may be explained by substrate characteristics, a key determinant of benthic community composition. Location U.S. #7 had a higher percentage of fine sediment than any other sampling site. However, many of the other

U.S. reference stations exhibited much higher percentages of gravel substrate compared to the Canadian sites, which were primarily sandy. The upstream reference site (#1) was characterized by coarser sediment and deeper water than the other Canadian sites. Thus, as with Milani et al. (2007), interpretation of the Moran et al. (2005) benthic community results is challenging due to the difficulty of appropriately defining reference conditions. However, it is reasonable to conclude that no severe impairment is evident.

4.3 Spatial Distribution and Representativeness of Benthic Community Results

Because Moran et al.'s (2005) data were collected during the same time interval as data presented in Milani et al. (2007), and are presented using the same metric (i.e., family abundance as defined by number of individuals per square metre [#/m^2]), the two sources of benthic community data are integrated in the project database. Figure 4-1 maps all benthic community data collected since 2000, by discrete sampling station. Results for individual stations are presented as pie charts, with the size of each pie indicating organism abundance. For the stations shown in Figure 4-1, organism density ranges from 831/m^2 to 96,200/m^2. Within each pie chart abundance is considered for three categories of organisms: 1) caddisflies, mayflies, and stoneflies, representative of pollution intolerant orders (i.e., EPT Species); 2) Chironomidae (midges) and Tubificidae (oligochaete worms), representative of pollution tolerant families; and 3) Other Species. For stations along the St. Clair River where the benthic community is dominated (> 50%) by the Other Species category, the organism found at greatest relative abundance is the zebra mussel (*Dreissena polymorpha*). Zebra mussels may form dense colonies that affect sediment habitat quality, with resultant effects on benthic community composition (MacIsaac 1996).

Spatial coverage of benthic community structure remains relatively sparse as compared with sediment chemistry data. Neither Milani et al. (2007) nor Moran et al. (2005), however, observed significant relative degradation of community structure along an upgradient to downgradient transect of the St. Clair River. The absence of community degradation relative to reference stations largely reflects the dominance of pollution tolerant organisms at all stations (reference and AOI stations). Of the 32 stations for which data are presented in Figure 4-1, pollution tolerant families comprise greater than 70% of the community at 23 stations (i.e., 72% of the stations), and greater than 50% of the community at 27 stations (i.e., 84% of the stations). On average for all stations, pollution tolerant families comprise 73% of all families present, with an overall range of between 7% and 99%.

For stations presented in Milani et al. (2007) for which benthic community composition was assessed in the AOI, total mercury concentrations in sediment ranged from 0.78 mg/kg to 2.57 mg/kg, and methylmercury concentrations ranged from 0.005 mg/kg to 0.014 mg/kg. For stations presented by Moran et al. (2005) for which benthic community composition was assessed, total mercury concentrations ranged from 0.63 mg/kg to 5.52 mg/kg. Methylmercury concentrations were not presented in Moran et al. (2005). The concentrations of total mercury and methylmercury presented in 2005-2008 data (Figure 3-1 and Figure 3-2) are generally similar to the concentrations presented in Milani et al. (2007) and Moran et al. (2005). Although

some surface sediment concentrations of total mercury and methylmercury are elevated for recent sampling intervals relative to sampling conducted coincident with assessment of benthic community structure, 85% of the current surface sediment samples from within the AOI have both mercury and methylmercury concentrations within the range determined coincident with assessment of benthic community structure.

Although the spatial distribution of benthic community structure data is less than for sediment chemistry data, ancillary variables such as TOC and sediment grain size can be used to assess the extent to which the benthic conditions at the sampled locations are representative of the range of conditions that occur within the AOI. This assessment is semi-quantitative because Milani et al.'s 2007 sample locations for community structure were not co-located with either TOC concentration or sediment grain size data collected in 2006-2008.

For TOC, surface sediment data collected in 2001 coincident with Milani et al's (2007) data for benthic community structure ranged from 0.3% to 3.2%, with a mean percent TOC of 1.5%. Surface sediment data collected coincident with sample collection by Moran et al. (2005) for assessment of benthic community structure ranged from 0.8% to 2.5%, with a mean percent TOC equal to 1.5%. Considered together, these TOC concentrations span a typical range for riverine sediment (e.g., Feng et al. 1998, Jia and Peng 2003) and do not define a system enriched in organic matter. For the Milani et al. (2007) data in which benthic community structure and TOC data are co-located, 5 of the 16 stations are characterized by greater than 90% pollutant-tolerant species, and community structure and TOC concentration are not correlated. Likewise, for the Moran et al. (2005) data in which benthic community structure and TOC data are co-located, 5 of the 17 stations are characterized by greater than 90% pollutant-tolerant species, and community structure and TOC concentration are not correlated.

It should be noted that for data presented in Moran et al. (2005), it is not always clear whether organic matter content is presented in terms of percent TOC or as the percent of sample mass that is lost following high temperature combustion of the sample (i.e., LOI). The magnitude of organic matter content presented by Moran et al. (2005) (i.e., ranging from 0.8% to 2.5%) is consistent with the magnitude of organic carbon contents presented in Milani et al. (2007) as TOC values, although the data in Moran et al. (2005) are defined interchangeably as TOC and LOI. As presented in Milani et al. (2007), the percent LOI ranges from 5.2% to 12.9%, and significantly exceeds the percent TOC for the same stations (ranging from 0.3% to 3.2% as discussed above). Based on the organic matter contents presented as TOC in Milani et al. (2007) and their similarity to the data presented in Moran et al. (2005), data from Moran et al. (2005) are considered as TOC values in this report.

For the percent of fine grained particles in sediment (defined as the silt-size fraction plus the clay-size fraction), surface sediment data collected coincident with (but not co-located with) sample collection by Milani et al. (2007) ranged from 1.7% to 42.9% with a mean percent fines of 18.4%. Surface sediment data collected coincident with sample collection by Moran et al. (2005) ranged from 7.2% to 22.3%, with a mean percent fines equal to 11.1%. These grain size distributions span a typically broad range for river sediment, including both depositional areas enriched in finer-grained sediment and erosional areas enriched in coarser-grained sediment.

In summary, assessing benthic invertebrate community quality in the AOI is challenging, due to the difficulty of defining reference conditions for this unique area. However, there is no clear evidence of severe impairment. Even if the benthic community were deemed to be somewhat impaired, toxicity test results for the AOI indicate that toxicity due to sediment chemical concentrations is not a likely cause of impairment, as described in Section 5.

5 SEDIMENT TOXICITY

The objective of the sediment toxicity LOE is to determine whether survival, growth and/or reproduction of sediment-associated invertebrates and minnows are impaired in the St. Clair River AOI. For all organisms tested, impairment is defined relative to the testing outcome for either reference sediment (for laboratory testing) or reference stations within the river (for *in situ* testing). If impairment is observed as the result of toxicity testing, this LOE also considers whether the observed adverse effects are caused by or otherwise correlated with chemical concentrations in the sediment. Finally, this LOE characterizes the severity and spatial distribution of any observed toxicity. As detailed below, Milani et al. (2007) and Moran et al. (2005) completed a number of toxicity tests using AOI sediment. Their findings are summarized in this section and presented in Table 5-1 and Table 5-2, respectively.

5.1 Toxicity Test Methods

Milani et al. (2007) evaluated whether the survival, growth, and reproduction of four species of invertebrates were reduced following exposure to St. Clair River sediment relative to exposure to reference sediment using multivariate analysis (BEAST methodology). Sediment was collected in 2001 and 2004 from a total of 26 locations, including 13 locations in the current AOI. Invertebrates tested in this assessment were midge (*Chironomus riparius*), amphipod (*Hyalella azteca*), mayfly (*Hexagenia* spp.), and oligochaete (*Tubifex tubifex*). Test durations and endpoints included 10-day survival and growth (midge), 21-day survival and growth (mayfly), 28-day survival and growth (amphipod), and 28-day adult survival and reproduction (oligochaete).

Moran et al. (2005) collected data in 2003 to test for sediment toxicity in St. Clair River sediment. A total of nine stations were evaluated for toxicity, including five locations within the current AOI. Laboratory toxicity testing included 10-day survival and growth of midge (*Chironomus tentans*) and 14-day survival and growth of amphipod (*Hyalella azteca*). *In situ* toxicity testing focused on fathead minnow, with survival and growth assessed following a 21-day exposure period.

5.2 Toxicity Test Results

Figures 5-1 through 5-3 illustrate the spatial distribution of toxicity test results for oligochaetes, amphipods and chironomids, and mayflies, respectively. Results are also summarized in Table 5-1. The following subsections summarize toxicity test results for each study and evaluate consistency among studies.

5.2.1 Environment Canada Toxicity Test Results

Milani et al.'s (2007) multivariate assessment of endpoints (i.e., survival, growth and reproduction) indicates that there is no strong evidence of toxicity in St. Clair River sediment. There was decreased mayfly survival at one AOI station (Station 6666) upstream of Talfourd

Creek) and decreased oligochaete reproduction at one AOI station (Station 66M144) downstream of Talfourd Creek. Due to the low magnitude of toxicity and the fact that only one of ten toxicity test endpoints was affected at each location, Milani et al. (2007) did not recommend further action with respect to sediment toxicity.

For stations in the AOI, correlations were not observed between toxicological responses and concentrations of either mercury or methylmercury in sediment. That is, neither mercury nor methylmercury is elevated at these two stations (6666 and 66M144) relative to concentrations measured at stations in which toxicity testing demonstrated no adverse toxicological effects. For Station 6666, concentrations of mercury and methylmercury in sediment were 1.41 mg/kg and 0.0085 mg/kg, respectively, while for Station 66M144, concentrations of total mercury and methylmercury in sediment were 2.0 mg/kg and 0.009 mg/kg, respectively. Several AOI stations, including Stations 6699, 66M272, 66M253, and 66M269 are characterized by concentrations of mercury and/or methylmercury that are elevated relative to concentrations at Stations 6666 and 66M144, with no observed toxicity on any test organisms. Moreover, the mercury concentrations presented by Milani et al. (2007) are within the range of concentrations that have not proven to be toxic in testing of either *H. azteca* or other amphipod species such as *Leptocheirus plumulosus* (Sferra et al. 1999). The lack of mercury-related toxicity in St. Clair River sediment is also consistent with toxicity test results for mercury-contaminated sediment in Peninsula Harbour, Lake Superior (Milani and Grapentine 2005).

5.2.2 SLEA Toxicity Test Results

Moran et al. (2005) observed reduced amphipod survival at stations both upstream of and within the AOI. Midge survival was reduced at locations upstream, within, and downstream of the AOI; for those stations with reduced growth and/or survival, there was a weak association between sediment chemistry and invertebrate growth and/or survival rates. In particular, within the AOI, reduced amphipod survival was observed at Stations #4, #7, and #8, while reduced midge survival was observed at Station #7. Correlations between sediment chemistry and reduced survival and/or growth rates were apparent for lead (for amphipod and midge survival and midge growth) and PAHs (amphipod growth), but these correlations appeared to be controlled by results for a single sample in each case. For the station driving this apparent correlation between reduced growth and lead exposure (Station #7), the sediment lead concentration was 47 mg/kg, elevated relative to the LEL (31 mg/kg), but significantly below the SEL (250 mg/kg). No correlation with toxicity test results was observed for mercury or octachlorostyrene. As is evident from Figures 5-1 through 5-3, there is little systematic pattern in sediment toxicity across the study area.

Several aspects of data presentation in Moran et al. (2005) suggest that caution is warranted when interpreting results, particularly with respect to the effect of sediment chemical concentrations on invertebrate toxicity. For logistic regression of the effect of PAH concentration on amphipod growth, Moran et al. (2005) noted that the data set includes a significant number of non-detectable measurements for individual PAHs. Because regression analysis included summation of all PAHs, and because non-detects were recorded at half the detection limit, the data reduction techniques employed for the logistic regression model may

have influenced the correlation between chemical concentration and biological effect. Moran et al. (2005) noted a positive correlation between sediment mercury concentration and midge survival. As presented, the high percent survival of midges at stations with elevated mercury concentration is considered evidence that these variables are positively correlated, rather than as evidence (more likely correct) that midge survival is not impacted by the mercury concentrations measured in this data set. Also, the finding of significant toxicity at the upstream reference station, despite very low chemical concentrations, indicates that Moran et al. (2005)'s toxicity test results do not reflect an effect that is particular to the AOI.

For the *in situ* toxicity tests conducted with fathead minnows, no significant adverse effects were observed in AOI stations with respect to either survival or growth (length or weight) of test organisms (Table 5-2). Although Moran et al. (2005) stated that logistical regression analysis suggests that sediment mercury concentrations (as well as calcium concentrations) are predictive of fathead minnow survival across all stations considered in their assessment, this relationship is not apparent at AOI stations. Based on the data presented, and across all replicates for all AOI stations, fathead minnow survival ranged from 50% to 100%, with the lowest percent survival of 50% in one replicate of Station #6. However, sediment mercury concentrations were lower at Station #6 (0.88 mg/kg) than at all other stations in the AOI. The highest sediment mercury concentration in the AOI stations was at Station #4 (2.68 mg/kg), at which fathead minnow survival ranged from 80% to 100% in three replicate assays, with a mean percent survival of 87%. This high percent survival suggests that these concentrations of mercury in sediment are not likely responsible for either chronic or acute toxicity in fathead minnows in the St. Clair River.

5.2.3 Comparison of Environment Canada and SLEA Toxicity Test Results

Whereas the results of Milani et al. (2007) indicate a general lack of sediment toxicity in the AOI, the results of Moran et al. (2005) suggest that sediment toxicity within the AOI may be widespread and severe. This inconsistency is observed despite the fact that Milani et al. (2007) conducted a broader battery of toxicity tests, including a longer exposure of the same amphipod species tested by Moran et al. (2005) and a closely related midge species tested for the same exposure duration in both studies. Further, each of the Moran et al. (2005) sampling locations was in close proximity to a station tested for toxicity by Milani et al. (2007). Specifically, whereas amphipod survival at SLEA locations CAN #4_C, CAN #7_C, and CAN #8_C ranged from 16% to 24%, survival of the same species at virtually co-located Environment Canada locations 6665, 66M80, and 6668 ranged from 95% to 99%. Likewise, midge survival at location CAN #7_C was 66%and growth was impaired, whereas midge survival at Environment Canada location 66M80 was 93% with no growth impairment. Moran et al. (2005) also found sediment from upstream reference location CAN #1_C to be toxic to both amphipods and midges; again, this result was not replicated in Milani et al.'s (2007) observations for a co-located station (6660). Differences are not evident in sediment chemistry or physical characteristics between the two studies to explain the different biological responses.

Two explanations can be advanced for these contradictory results: 1) unmeasured, transitory stressors caused sediment toxicity in 2003 (SLEA tests) that did not occur in 2001 and 2004

(Environment Canada tests); or 2) the SLEA results represent the heterogeneous distribution of sediment chemical concentrations. An example of an episodic stressor associated with sediment toxicity at other sites, but typically unmeasured, is storm runoff of agricultural or urban pyrethroid pesticides (e.g., Amweg et al. 2006). However, it appears that the sediment toxicity observed by Moran et al. (2005) was not the result of persistent sediment contamination.

5.3 Representativeness of Toxicity Test Locations

The spatial coverage of toxicity test data is sparser than the spatial coverage for sediment chemistry within the AOI. Therefore, the objective of this subsection is to evaluate how representative the toxicity test data are relative to conditions throughout the AOI, in order to ensure that toxicity in AOI is adequately characterized. The robustness of toxicity test data for interpolation may be improved by confirming that conditions within the AOI are broadly similar across all stations with respect to the likely effect of background chemistry on toxicity test organisms. Three sediment variables useful for such confirmation are sediment TOC concentration, grain size distribution, and mercury concentration.

For TOC data presented by Milani et al. (2007), surface sediment concentrations range from 0.3% to 3.2%, with a mean percent TOC of 1.5%. Surface sediment TOC concentrations presented by Moran et al. (2005) for stations in which toxicity testing was conducted ranged from 0.8% to 2.2% with a mean percent TOC equal to 1.6%. TOC concentrations within this range have not been correlated with toxicity to amphipods (Ingersoll et al. 1998), midges (Landrum and Poore 1998), or mayflies (USEPA 1996b, ASTM 1999). Therefore, it is unlikely that interpolation of toxicity test results across the range of TOC concentrations measured in the AOI would generate systematic errors resulting from the negative impact of elevated sediment TOC concentration on benthic organism toxicity. Moreover, although sediment redistribution is likely to have occurred within the St. Clair River between the time interval in which toxicity test sampling was conducted (2001-2004) and the more recent interval defined for presentation and analysis of surface sediment (2005-2008) (Biberhofer et al. 2007, Richman 2008a, Houtby and Moran 2006) sediment TOC concentrations in 2005-2008 data (Figure 3-4) are similar to TOC concentrations discussed in Moran et al. (2005) and Milani et al. (2007). This similarity in range suggests that: 1) TOC concentrations at the toxicity test stations were generally consistent with those measured throughout the AOI; and 2) TOC concentrations in St. Clair River surface sediment are unlikely to negatively impact the benthic community.

For grain size analysis presented by Milani et al. (2007), the grain size distribution in surface sediment ranged from 1.6% fines to 49% fines, with a mean percent fines of 13.9% (where “fines” are defined as silt and clay). For data presented by Moran et al. (2005), the grain size distribution of surface sediment ranged from 7.2% fines to 22.3% fines with mean percent fines of 11.1%. In general, sediment characterized by this broad range of the fraction of fines is not correlated with toxicity due to grain size in either amphipods (Ingersoll et al. 1998) or midges (USEPA 1996b). Specifically, Ingersoll and Nelson (1990) observe, for example, that for *H. azteca*, chronic exposure tests with sediment defined by > 90% fines to 100% sand demonstrated no adverse effects on either survival or growth. Although the grain size distribution of sediment may influence the results of toxicity testing with mayflies (ASTM 1999),

neither the station with the coarsest grained sediment in the AOI (Station 66M271) nor the station with the finest grain sediment in the AOI (Station 66M253) is characterized by reduced mayfly growth or survival. Therefore, it is unlikely that interpolation of toxicity test results across the grain size distribution present in the AOI would result in systematic errors in data interpretation resulting from negative effects of grain size distribution on toxicity to benthic organisms. Moreover, although sediment redistribution likely occurred within the St. Clair River between the time when toxicity test sampling was conducted (2001-2004) and the more recent interval defined for presentation and analysis of surface sediment data (2005-2008), the percent fines in 2005-2008 data ranging from 1.21% to 91.3% with a mean percent fines of 24.2% (Figure 3-5) is similar to the mean values presented in Moran et al. (2005) and Milani et al. (2007). The overall absence of grain size related effects on test organisms, as observed for the range of grain size distributions documented in 2001-2004 as well as 2005-2008, suggests that the grain size distribution in AOI surface sediment is unlikely to directly and negatively impact the benthic community.

For mercury analysis presented by Milani et al. (2007), total mercury concentrations in surface sediment ranged from 0.8 mg/kg to 3.8 mg/kg, with a mean total mercury concentration of 2.1 mg/kg. For data presented by Moran et al. (2005), total mercury concentrations ranged from 0.6 mg/kg to 5.5 mg/kg, with a mean total mercury concentration of 2.1 mg. For methylmercury, concentrations presented by Milani et al. (2007) ranged from 0.005 mg/kg to 0.02 mg/kg, with a mean methylmercury concentration of 0.01 mg/kg. Methylmercury concentrations were not presented in Moran et al. (2005).

Concentrations of total mercury (mean = 4.3 mg/kg, range = 0.58 mg/kg to 41mg/kg and methylmercury (mean = 0.01 mg/kg, range = 0.002 mg/kg to 0.12 mg/kg) presented in 2005-2008 data (Biberhofer et al. 2007 and Richman 2008a (Figures 3-1 and 3-2) are generally similar to the concentration ranges presented in Milani et al. (2007) and Moran et al. (2005). Although some surface sediment concentrations of total mercury and methylmercury are elevated for recent sampling relative to sampling conducted coincident with toxicity testing, 85% of the current surface sediment samples from within the AOI have mercury concentrations within the range assessed during toxicity testing. For methylmercury, 93% of the current surface sediment samples from within the AOI have concentrations within the range assessed during toxicity testing. Overall, this general similarity in mercury and methylmercury concentrations between sampling intervals, coupled with the overall absence of mercury-attributed effects on toxicity test organisms, suggests that the more recently observed concentrations of mercury and methylmercury in AOI surface sediment are unlikely to directly and negatively impact the benthic community.

The finding of no or limited toxicity at the concentrations tested in the AOI is consistent with findings by EC for Peninsula Harbour (Lake Superior) (Milani and Grapentine 2005). Milani and Grapentine (2005) found no evidence of toxicity to benthic organisms due to mercury in Peninsula Harbour, where total mercury concentrations reached 19.5 mg/kg and methylmercury concentrations reached 0.02 mg/kg. Toxicity test endpoints reported by Milani and Grapentine (2005) included survival and growth of amphipods and mayflies following chronic exposures,

survival and growth of midges following subchronic exposures, and survival and reproduction of tubificid worms following chronic exposures.

5.4 Summary

Milani et al.'s (2007) assessment of invertebrate survival, growth, and reproduction demonstrates no strong evidence of toxicity in St. Clair River sediment and no apparent correlation between toxicological responses and concentrations of either mercury or methylmercury in river sediment. Moran et al. (2005) observed reduced amphipod and midge survival, but no effect on fathead minnow growth or survival within several stations in the AOI, and only weak association between sediment chemistry and invertebrate growth and/or survival rates. Neither the range in sediment TOC concentrations nor the grain size distribution measured across all toxicity test stations or more recently collected data are atypical for standard toxicity tests. The ranges of sediment TOC concentrations, grain size distribution, and mercury concentrations in the toxicity test samples are generally consistent with the ranges throughout the AOI. Thus, it is unlikely that interpolation of toxicity test results across the AOI would result in systematic errors in data interpretation due to the direct effect of these variables on test organisms.

6 INTEGRATION OF LINES OF EVIDENCE

The objectives of this section are to: 1) integrate the four LOEs in accordance with the COA Framework; 2) characterize risks associated with subsurface sediment; 3) characterize key sources of uncertainty; 4) propose actions for addressing the most important sources of uncertainty; and 5) summarize overall conclusions of this report. Possible outcomes of this analysis are:

1. Contaminated sediment within an area poses an environmental risk and requires sediment management; OR

2. Contaminated sediment may pose an environmental risk, but further assessment may be required to determine the reasons for the impact before a definitive decision can be made, and to determine what further assessment should be done; OR

3. Contaminated sediment poses negligible environment risk and no further work is required.

Which one of these three outcomes applies to a given sampling station or reach of the St. Clair River depends upon the combination of results for the four LOEs—in particular, findings of impairment or lack thereof for each LOE—in accordance with Table 2 of the COA Framework (reproduced as Table 1-1 in this report).

The key findings of the four LOEs are as follows:

- **Risk from biomagnification**. Certain species of sportfish are predicted to be at risk in the AOI from mercury, based on comparison of measured tissue concentrations to a literature-derived TRV, as well as some evidence of skewed sex ratios that are correlated with concentrations of mercury in fish tissue. It should be noted that there are confounding factors such as sexual dimorphism and potential co-occurrence of chemicals other than mercury and octachlorostyrene that may affect sex ratios. Thus, the sex ratio analyses are considered suggestive, rather than definitive. In addition, fitness factors show no evidence of population level effects on fish. Fish are not expected to be at risk from octachlorostyrene. Wildlife, as represented by double-crested cormorants, herring gulls, and raccoons, are not predicted to be adversely affected by current concentrations of mercury or octachlorostyrene in their prey.
- **Sediment chemistry**. Although concentrations of mercury in sediment consistently exceed the SQG-low and often exceed the SQG-high, neither SQG is predictive of biological effects. However, anisotropic interpolation of total mercury and methylmercury in sediment aids in defining focused areas of the AOI with the most significantly elevated concentrations. Concentrations of octachlorostyrene are consistently below the SQG, suggesting that further evaluation of this chemical is not warranted.
- **Benthos alteration**. Assessment of benthic community structure is complicated by the difficulty of defining suitable reference conditions. However, impairment of benthic

community structure is not evident in studies conducted by Milani et al. (2007) and Moran et al. (2005) within the AOI.

- **Sediment toxicity**. Milani et al.'s (2007) assessment of invertebrate survival, growth and reproduction demonstrates no strong evidence of toxicity in St. Clair River sediment and no apparent correlation between toxicological responses and concentrations of either mercury or methylmercury in river sediment. Moran et al. (2005) observed reduced amphipod and midge survival, but no effect on fathead minnow growth or survival within several stations in the AOI and only weak association between sediment chemistry and invertebrate growth and/or survival rates. Comparison of the Milani et al. (2007) and Moran et al. (2005) results suggests that the effects observed by Moran et al. (2005) were not caused either by mercury or octachlorostyrene. Overall, the toxicity data does not suggest that mercury or other persistent sediment chemicals are causing toxicity to benthic organisms.

This section presents four key topics. First, the four LOEs are integrated in order to map prioritized zones for sediment management. Second, risks associated with contaminated subsurface sediment are evaluated in order to define additional portions of the AOI that warrant sediment management based on potential for resuspension, ice scour, and/or methylation. Third, sources of uncertainty with the greatest influence on overall findings are described. Fourth, recommendations for additional analysis are described. Fifth, this section closes with a summary of the overall report.

6.1 Integration of Lines of Evidence

Based on the COA Framework Decision Matrix (Table 1-1), when the biomagnification LOE indicates impairment and the benthos alteration and sediment toxicity LOEs indicate no impairment—as is the case for the St. Clair River AOI—further assessment of the risk from biomagnification is required, regardless of the outcome of the sediment chemistry LOE (i.e., Scenarios 5 and 9). Thus, integration of the four LOEs is primarily driven by the risk from biomagnification LOE.

As noted in the introduction to this section, risk from biomagnification is driven by fish. Prioritization of different zones of the AOI that drive risks to fish is complicated by the mobility of both fish and their prey, in that fish foraging within the AOI derive varying amounts of mercury from their prey, depending upon where the fish and their prey feed. In this analysis, areas of maximum exposure to fish are defined based on the invertebrate tissue concentrations. Existing invertebrate tissue data for methylmercury offer several advantages for this task: 1) spatial coverage within the AOI is robust; 2) use of empirical data obviates modeling from sediment into invertebrates, as well as estimation of the fraction of mercury that is methylated; 3) invertebrates are relatively sessile, such that invertebrate data can be linked to specific areas of the AOI in a manner that is not possible for fish; and 4) sufficient data exist to generate relatively stable site-specific BMFs that relate concentrations of mercury in fish tissue to concentrations of methylmercury in oligochaetes.

Before detailing the methods and assumptions used to prioritize zones of risk in the AOI, an overview of the five-step process is provided, as follows:

1. Site-specific invertebrate-to-fish BMFs were generated by pairing location-specific tissue results for select fish species and invertebrate taxa and examining the variability within the site-specific data set and comparing results to BMFs reported in the literature. Low end and high end BMFs were selected to reflect the range of results.

2. The target fish tissue concentration that is protective of fish themselves (0.20 mg/kg) (Section 2.2.2) was divided by low end and high end BMFs in order to calculate a range of target concentrations of methylmercury in invertebrates that are protective of fish.

3. The spatially weighted average concentration (SWAC) of methylmercury in invertebrates in the AOI was calculated and compared to the range of target values.

4. Localized areas with the most elevated concentrations of methylmercury in invertebrates were sequentially removed from the dataset, simulating fully effective remediation of hot spots. The SWAC of methylmercury in AOI invertebrates was recalculated until the target invertebrate concentrations based on low end and high end BMFs were attained.

5. Prioritized zones of sediment management were defined based on the range of target invertebrate tissue concentration calculated from the low end and high end BMFs.

The objective of the first step is to derive site-specific invertebrate-to-fish BMFs. To do so, analytical results for fish and invertebrates were first grouped by general sampling area (i.e., Sarnia, Stag Island, and Port Lambton) and by species (i.e., redhorse sucker, northern pike, oligochaete, and chironomid). Redhorse sucker and northern pike were targeted for evaluation because they are the two fish species predicted to be at high risk in the AOI and sample sizes were sufficient to support the analysis. It is expected that, if sediment is managed in a manner that mitigates risk to the fish species at highest risk, risks to fish species at intermediate or low risk will also be mitigated. Thus, this methodology is expected to be protective of all fish species in the AOI. As previously noted, fish samples were analyzed for total mercury and not methylmercury. Oligochaetes and chironomids were targeted for evaluation because fish are unlikely to consume substantial quantities of mussels due to their protective shell and because sample sizes were sufficient to support the analysis. Analytical results by location and species were paired to estimate BMFs, as shown in Table 6-1.

The BMFs based on oligochaetes were selected over those based on chironomids because: 1) oligochaete based BMFs are generally higher than chironomid based BMFs and therefore yield a more conservative (i.e., protective) result; 2) infaunal taxa like oligochaetes are more closely associated with sediment than are epifaunal taxa like chironomids; 3) spatial coverage of oligochaete results is sufficiently robust to support subsequent steps of the analysis; and 4) methylmercury concentrations in chironomids and oligochaetes are highly correlated (Pearson's correlation coefficient = 0.94, $p < 0.001$). BMFs from the Sarnia sampling station were excluded from consideration because that location is upstream of the AOI and the concentration of methylmercury in oligochaetes there is approximately an order of magnitude lower than those

observed within the AOI. Thus, BMFs for Sarnia do not appear representative of BMFs for the AOI. The minimum (13) and maximum (16) of the remaining four BMFs were selected as low end and high end BMFs for use in this analysis. These site-specific values are within the range of literature-derived BMFs presented by Milani et al. (2007), but are preferable for this analysis because they are site-specific. The close agreement of the low end and high end BMFs also suggests relatively low uncertainty and variability in this parameter.

The objective of the second step is to calculate target concentrations of methylmercury in invertebrates that will be protective of fish. We divided the target concentration of total mercury in fish that is protective of fish—0.20 mg/kg—by the low end and high end BMFs in order to yield a range of target concentrations of methylmercury in oligochaetes that are protective of the fish at highest risk in the AOI. As shown in Table 6-2, the resultant target concentrations of methylmercury in oligochaetes are 0.0125 mg/kg to 0.0154 mg/kg, depending on which BMF is applied.

The objective of the third step is to calculate the SWAC of methylmercury in oligochaetes under current (i.e., no action) conditions. To do so, anisotropic interpolation of oligochaete concentrations in the AOI was first plotted, as shown in Figure 6-1. The resulting interpolated surface was used to calculate the SWAC, using the following equation

Eqn. 11

$$SWAC = \frac{\sum Ci \times Ai}{\sum Ai}$$

Where:
SWAC = spatially weighted average concentration (mg/kg)
Ci = concentration of MeHg in each pixel i (mg/kg)
Ai = area of pixel i (m^2)

The SWAC of methylmercury in oligochaete tissue within the AOI under current conditions is 0.020 mg/kg. Because the current SWAC exceeds the target concentration range of 0.0125 mg/kg to 0.0154 mg/kg, sediment management is required in order to reduce concentrations in prey sufficiently to protect fish.

The objective of the fourth step is to prioritize zones of sediment management that are expected to mitigate risks to fish. To do so, the SWAC was recalculated by iteratively replacing the highest oligochaete tissue concentrations with zero until the SWAC was less than the range of target concentrations of methylmercury in oligochaetes. For example, all raster cells[7] with concentrations greater than 0.04 mg/kg were initially replaced with zero to simulate excavation of two discrete hot spots; the resultant SWAC of methylmercury in oligochaetes was found to equal 0.018 mg/kg. Because that value is greater than the upper bound target concentration of

[7] Representing interpolated oligochaete methylmercury tissue concentrations

0.0154 mg/kg, the process continued with the selection of all raster cells with concentrations greater than 0.03 mg/kg; these concentrations were again replaced with zero and the SWAC was recalculated. The resultant SWAC of the second iteration was found to equal 0.0166 mg/kg. Because this value also exceeds the upper bound target concentration of 0.0154 mg/kg, the process continued. In the third iteration, all raster cells with concentrations greater than 0.028 mg/kg were selected and replaced with zero. The resultant SWAC of the third iteration was 0.0160 mg/kg. Because 0.0160 mg/kg approaches the target concentration of 0.0154 mg/kg, the fourth iteration selected all raster cells with concentrations greater than 0.027 mg/kg. Replacing these cells with zero yielded a SWAC of 0.014 mg/kg, which achieves the upper bound target concentration of 0.0154 mg/kg. The process continued to determine the concentration of methylmercury in oligochaete tissue necessary to be removed in order to achieve the lower bound target concentration of 0.0125 mg/kg. Based on this iterative process, ENVIRON determined that oligochaete tissue concentrations greater than 0.025 mg/kg to 0.027 mg/kg need to be removed to achieve SWACs less than the range of target tissue concentrations (Table 6-2).

The objective of the fifth step is to map the resultant prioritized zones of sediment management. Figures 6-2 and 6-3 map the areas requiring sediment management to achieve the oligochaete tissue concentrations protective of fish for each BMF. These figures black out a portion of the AOI where extensive scouring has prevented collection of any sediment samples (scoured area). Sediment management is not contemplated in areas such as the scoured area, where sediment is essentially absent. Figure 6-4 integrates the areas mapped in Figures 6-2 and 6-3, in order to prioritize zones for sediment management based on risks to fish. The surface areas of zones warranting sediment management to mitigate risks to fish range from 47,100 m^2 to 69,700 m^2, as shown in Table 6-2.

6.2 Subsurface Sediment Risk Analysis

Step 7 of the COA Framework involves assessing subsurface sediment. The associated decision point (No. 6) concludes that potential risk exists if chemical concentrations in deeper sediment (defined in the COA Framework as greater than “about 10 cm depth”) exceed the SQG-low and/or one or more chemicals are present that can biomagnify and if sediment may be uncovered under plausible circumstances. Given the presence of elevated concentrations of mercury in subsurface sediment in the AOI (Table 3-2), further assessment is required to determine the likelihood of the sediment being uncovered.

6.2.1 Distribution of Mercury in Subsurface Sediment

Figure 6-5 maps the anisotropic interpolation of maximum concentrations of total mercury detected at any depth greater than 15 cm. Within the AOI, subsurface concentrations of mercury range from 0.07 mg/kg to 190 mg/kg, with a mean concentration of 18 mg/kg. Subsurface sediment samples collected from the AOI have not been analyzed for methylmercury. By definition, subsurface sediment is not currently located within biologically active zones and, therefore, does not currently pose a risk. However, if overlying sediment is

disturbed resulting in re-exposure of buried sediment, currently buried sediment could pose a risk in the future. Therefore, assessment of future risks posed by subsurface sediment hinges on the stability of surface sediment, combined with the spatial distribution of mercury in underlying sediment and the potential for that mercury to be methylated. Figure 6-6 summarizes which portions of the AOI may have elevated future risks from subsurface sediment based on the following factors that affect sediment stability and/or methylation potential: physical structures, vessel traffic, potential for ice scour, and site-specific geochemistry. Another possible means of redistribution of mercury in the system, which is not addressed in Figure 6-6, is associated with any use of St. Clair River water as industrial process water or cooling water. In particular, such activities could affect the current and future distribution of mercury in the system if there are intakes that draw water from the river and it is subsequently discharged back to the river without treatment. However, sufficient information is not currently available to support evaluation of this particular activity. Following an explanation of why disturbance and resuspension of mercury-contaminated sediment is of concern, this section details the basis for the zones depicted in Figure 6-6.

6.2.2 Disturbance and Resuspension Overview

Disturbance and resuspension of subsurface sediment relates to increased potential for exposure of fish and wildlife to methylmercury. However, it is important to recognize that sediment disturbance and the resultant resuspension do not in and of themselves enhance methylation in formerly buried sediment for two reasons. First, resuspension generally contributes little chemical re-partitioning of mercury from the sediment to the aqueous phase (Heyes et al., 2004, Kim et al. 2006). Second, methylmercury production and accumulation are enhanced in anoxic environments (such as buried sediment) relative to oxic environments (such as the water column). Therefore, the principal concern with disturbance of subsurface sediment is associated with downstream transport and redeposition of mercury in locations that are conducive to methylation.

In general, wetlands and other areas in which decreased flow velocity results in the settling of fine grained sediment and/or degradable organic materials are conducive to methylation. Such areas enhance methylation because mercury is typically associated with the organic materials that deposit with fine grained sediment, and because deposition of fine grained sediment and organic matter contributes to the development of anoxic conditions at shallow sediment depths. Thus, redeposition of mercury may enhance bacterial methylation of mercury within the biologically active zone of the sediment under conditions typified by the St. Clair River delta and Lake St. Clair.

6.2.2.1 Vessel Traffic

Significant vessel traffic passes through the St. Clair River annually[8], and the effect of vessel traffic on the redistribution of shoreline sediment warrants thorough consideration. Locations in which subsurface sediment is at risk of disturbance include areas in the vicinity of docks and piers, as well as locations in which there is evidence of propeller scour or the effect of ice jams. Figure 6-7 presents the National Oceanic and Atmospheric Administration's (NOAA's) navigational chart for the portion of the St. Clair River that includes the AOI. This figure highlights the principal navigational channel in the St. Clair River, as well as the dock structures at the north end of the AOI and north of the mouth of Talfourd Creek. Both of these general docking locations are characterized by elevated subsurface concentrations of mercury, and represent locations in which vessel traffic could significantly disturb sediment. Although the main navigational channel highlighted in Figure 6-7 passes to the west of Stag Island, and should therefore limit the potential for large vessel-related resuspension events east of the island, marked ferry routes and dock structures are present east of Stag Island. Further stability analysis of these areas, including radiometric and/or shear stress analysis of collected cores, is recommended. An assessment of bed shear velocity has been conducted for the upper St. Clair River and may provide useful information regarding sediment resuspension potential in these areas of resuspension concern.

Further complicating this assessment is a lack of understanding of whether current conditions in the river define a balance (i.e., equilibrium) between historical inputs of mercury and on-going vessel disturbances. That is, in the absence of on-going chemical discharge to the St. Clair River, it is not known whether those locations likely to experience resuspension events (such as in the vicinity of commercial docks) are already characterized by the redistribution of what buried chemicals were likely to redistribute. In this context, the question of sediment stability is more appropriately redefined as a question of chemical stability, and requires a more thorough understanding of changes to shipping patterns (including passage of increasing tonnage vessels), background sedimentation rates (providing burial and dilution of chemically impacted sediment), and the extent to which current chemical distribution patterns are representative of steady state conditions.

6.2.2.2 Ice Scour

Ice scour is also an important factor that may disturb subsurface sediment. The presence of floating or grounded ice may significantly affect stream velocity by temporarily altering the cross-sectional area through which water flows. During the formation and/or breakup of ice jams, the change in flow velocity typically results in the scouring and resuspension of sediment from channel banks and shallow depositional areas (e.g., Milburn and Prowse 1996). In the St. Clair River, major ice build up appears principally limited to periods in which ice is driven into the river by northerly winds off Lake Huron (Derecki and Quinn 1986). As reported by the United States

[8] http://www.greatlakes-seaway.com/en/seaway/facts/traffic/index.html (for statistics) and http://boatnerd.com/vessel passage (for photographs)

Army Corps of Engineers (USACE), significant ice jams in the St. Clair River occurred in 1942, 1952, 1984, 1987, and 2003.[9] In other years, ice accumulation within the upper river has been characterized as transitory by both Derecki and Quinn (1986) and the USACE ice jam database. Thus, ice-related sediment scour in the St. Clair River is most likely to be a concern in locations where shallow water sediment deposits exist. An example of such a deposit is located south of Talfourd Creek, where the NOAA navigation chart (Figure 6-8) and site data indicate the presence of a coarse-grained (less than 10% silt and clay) sandy deposit. Because subsurface sediment at this location is characterized by elevated concentrations of mercury, a more refined assessment of sediment stability in this area is recommended.

6.2.2.3 Methylation Potential

Mercury methylation increases risks associated with mercury in subsurface sediment because methylmercury is the more toxic and bioaccumulative form of mercury. Because methylmercury may be transported from upgradient locations, as well as produced *in situ*, it is difficult to predict methylation potential (and, therefore identify locations of heightened methylation potential) from either total sediment mercury concentration or sediment methylmercury concentration.

The rate and extent of methylmercury accumulation in a given location is a function of the quality and quantity of available microbial substrate, the concentration of pore water inorganic mercury available for methylation, and the background geochemistry that controls oxidation/reduction dynamics. Geochemically, the dominant environmental factor that controls the depth distribution of methylmercury in sediment is the depth-dependent balance between oxygen diffusion into the sediment and oxygen consumption by sediment bacteria and chemical reactions. As noted above, because oxygen penetration is limited by fine grained sediment and bacterial respiration, sediment that is organically enriched and/or dominated by finer grained particles suggest an increased potential for mercury methylation within the biologically active zone of sediment. Regardless of the depth in the sediment that mercury is methylated, methylmercury produced within the sediment may subsequently diffuse to the water column (or a shallower sediment depth), become bound or sorbed to sediment organic matter, be taken up by benthic organisms, or be demethylated and converted back to inorganic mercury. The extent to which this process presents a subsurface exposure risk depends on the characteristics and stability of overlying sediment, as well as the concentration of microbially-available inorganic mercury in sediment porewater. These factors define a location's methylation potential.

Methylation potential can be quantified with numerical models that assess the site-specific balance between methylmercury sequestration and exposure (e.g., Johannessen et al. 2005). Sequestration typically results from sedimentation, whereas exposure may result from ongoing diffusion or advection of porewater toward the sediment surface, as well as sediment mixing. Application of such a rate-based model to St. Clair River sediment is outside of the current scope of work. However, such modeling may help define locations in the AOI characterized by

[9] https://rsgis.crrel.usace.army.mil/icejam/

enhanced methylation potential in sediment that is susceptible to disturbance, as well as stable sediment deposits.

An example of an area that warrants consideration for methylation potential is just upstream of the mouth of Talfourd Creek, where surface sediment methylmercury concentrations are elevated relative to other locations along the river (Figure 6-7). Because there are structures in this area that may slow water flow and enhance the deposition of organic matter and/or fine grained sediment, elevated surface sediment methylmercury concentrations may result from enhanced capture and sequestration of materials transported from upgradient sources, enhanced *in situ* production, or a combination of these two processes.

In an effort to better understand the cause of elevated concentrations of methylmercury in this area, ENVIRON evaluated sediment trap data collected in the vicinity of Talfourd Creek (Station 143) and downstream of Talfourd Creek (Station 100) (Richman 2008b). Sediment within the traps for these stations was significantly enriched in fines (69.5% at Station 143 and 60.5% at Station 100) relative to surface sediment samples collected in the vicinity of these sediment traps. Trap sediment was only moderately enriched in TOC (2.9% at Station 143 and 2.8% at Station 100) and methylmercury (0.0107 mg/kg at Station 143 and 0.0086 mg/kg at Station 100). By way of comparison, for the 11 surface sediment samples collected in the vicinity of Station 143 at the same sampling interval (2006) as the sediment trap deployments, the mean percent fines is 15.2%, the mean percent TOC is 2.0% and the mean concentration of methylmercury is 0.0078 mg/kg. For the eight surface sediment samples collected in the vicinity of Station #100 at the same sampling interval (2006) as the sediment trap deployments, the mean percent fines is 5.4%, the mean percent TOC is 1.6% and the mean concentration of methylmercury is 0.0070 mg/kg. This relative lack of enrichment in TOC and methylmercury in trap sediment versus surface sediment suggests that methylmercury is more likely associated with the organic fraction of sediment than with the fine-grained inorganic sediment matrix. Because methylmercury may be both transported with TOC and generated in the presence of elevated TOC concentrations, sediment management decisions should consider the relative influence of these two mechanisms at any given location within the AOI.

Although the sediment trap data set is too small to define with certainty whether *in situ* production is primarily responsible for the methylmercury measured at these locations, results highlight the significance of TOC in controlling the fate and transport of methylmercury. Thus, another location of conceptually similar concern with respect to mercury methylation is in the vicinity of Stag Island, where the NOAA navigational chart highlights the presence of sewer structures on the river bottom (Figure 6-7). Because sewer outfalls may contribute both mercury and organic enrichment to water bodies, it should be confirmed whether these structures serve as secondary contributing sources of chemical or organic matter inputs to the river, or exist as physical impediments to water flow that have contributed to localized chemical deposition. Although TOC is not elevated in the sediment of this area, the sediment is characterized by elevated surface and subsurface concentrations of mercury. A more refined understanding of site-specific methylation potential should focus on porewater (dissolved phase) geochemistry, as well as site-specific diffusion, advection, and sedimentation rates.

6.3 Uncertainty Analysis

A critical element of any risk-based evaluation is the identification and evaluation of factors that contribute to uncertainty in individual LOEs, as well as in overall conclusions. It is important to identify sources of uncertainty so that margins of safety can be built into risk management decisions that rely on the risk analyses. In general and as detailed below, the data available for the St. Clair River AOI are sufficient to characterize the four LOEs and to delineate and prioritize zones within the AOI where sediment management is warranted to mitigate risks. The following subsections discuss key data gaps and sources of uncertainty associated with each of the four LOEs, as well as with the analysis of subsurface sediment risk.

6.3.1 Uncertainty Associated with Risk from Biomagnification

Uncertainty associated with the risk from biomagnification LOE primarily relates to the use of literature-derived toxicity thresholds and exposure assumptions to predict whether fish, birds, and mammals are likely to be at risk from consumption of mercury and octachlorostyrene in prey from the AOI.

6.3.1.1 Uncertainty Associated with Risk of Biomagnification for Fish

Fish were initially predicted to be at risk based on the literature-based evaluation. In order to better understand the implications of those literature-based predictions, field collected data on sex ratios and fitness were evaluated. Sex ratios are skewed for smallmouth bass and yellow perch in the St. Clair River relative to other waterbodies in the region. Skewed sex ratios are correlated with mercury tissue concentrations in freshwater drum, smallmouth bass, northern pike, and yellow perch. Biologically significant effects on fitness were not observed. Thus, the site-specific sex ratio data support the findings of the literature-based predictions for fish.

The main source of uncertainty in the sex ratio findings relates to potential confounding factors. That is, factors other than mercury exposure tissue concentrations—such as natural variability, sampling design, and the presence of co-contaminants—may also influence sex ratios. Sufficient data are not currently available to support year-by-year analyses that would elucidate the natural variability in sex ratios in these species. Sampling design could plausibly affect sex ratio results if sampling occurred during spawning for a particular species, given that male and female fish may congregate in a non-random fashion for spawning. We tested for an interaction between sex ratios and timing of fish sampling, and no effect was evident. We also tested for dose-response relationships between sex ratios and octachlorostyrene, hexachlorobenzene, and hexachlorobutadiene and found no significant interactions. Although data limitations preclude rigorous testing, other chemicals present in the system at low concentrations could have endocrine disrupting effects that would affect sex ratios. However, if co-contaminants are affecting sex ratios, sediment management designed to mitigate risks from mercury is also expected to address chemicals that co-occur with mercury in sediment. For these reasons, confounding factors are unlikely to significantly affect overall conclusions or recommendations stemming from this analysis

6.3.1.2 Uncertainty Associated with Risk of Biomagnification for Wildlife

In general, the evaluation of birds and mammals employs sufficient conservatism to ensure that risks are more likely to be overestimated than underestimated. Given that double-crested cormorants, herring gulls, and raccoons are not predicted to be adversely affected by mercury and octachlorostyrene in prey caught in the AOI, any uncertainties associated with wildlife exposure or TRVs are unlikely to affect the overall conclusions. The use of an AUF of 1.0 for all wildlife ROIs is an example of a conservative assumption that is used to compensate for unavoidable uncertainty and variability in wildlife behaviours that influence exposure. It is likely that some double-crested cormorants, herring gulls, and raccoons derive at least some of their aquatic prey from outside of the AOI. Nonetheless, use of an AUF of 1.0 helped ensure that risks to these ROIs are more likely to be overestimated than underestimated.

Uncertainty in the evaluation of risk to cormorants and herring gulls is also associated with the use of a TRV derived from a study on mallards (Heinz 1979). A recent egg injection study by the same author (Heinz 2008) suggests that double-crested cormorants may be less sensitive than mallards and herring gulls may be more sensitive than mallards to the toxicological effects of mercury. The author has cautioned against using the 2008 study as a basis for quantitative interspecies extrapolation factors, and no other reliable source has been identified for that purpose. For double-crested cormorants, the added conservatism of extrapolating from the mallard study would not change the overall conclusion of no significant risk. The higher sensitivity of herring gulls, however, could result in underestimation of risk to this species. To address that concern, concentrations of mercury in herring gull eggs collected from the St. Clair River and nearby waterbodies were compared to egg-based TRV specific to gulls. As detailed in Section 2.4.2.2, that analysis supported the conclusion that herring gulls foraging in the St. Clair River are not at risk due to mercury.

6.3.2 Uncertainty Associated with Sediment Chemistry

Data gaps and uncertainties associated with the sediment chemistry LOE primarily relate to: 1) the presence and effect of chemicals in sediment that were not evaluated in this report; 2) changes in the spatial distribution of chemicals in sediment as a result of disturbance, resuspension, downstream transport, and deposition; 3) interpolation of concentrations in unsampled areas; and 4) the limited ability of SQGs for mercury to predict adverse effects in benthic invertebrates.

As illustrated in Appendix A and Tables 3-1 and 3-2, many chemicals in addition to mercury and octachlorostyrene have been detected in AOI sediment. Based on previous work (e.g., Milani et al. 2007, Moran et al. 2005) that concluded that mercury and octachlorostyrene were most likely to drive risks in sediment, ENVIRON was contracted to specifically focus on these two chemicals. Consequently, the spatial distribution of other chemicals in AOI sediment has not been characterized, although data are sufficient to support such an effort for many chemicals.

There is unavoidable uncertainty associated with the temporal representativeness of analytical results collected during a fixed time period within a dynamic system. As discussed in Section

6.2, sediment disturbance and mobilization in the St. Clair River is expected, given the river's use by ships, winter icing, and physical structures that enhance erosion and deposition. Additionally, as source areas are controlled, chemical concentrations in sediment inputs to the system are expected to decrease over time, resulting in burial of more contaminated material with cleaner sediment. Thus, the nature and extent of sediment contamination is expected to change over time. Consequently, the representativeness of historical sediment samples will decrease over time.

Although spatial coverage of the AOI for sediment chemistry is quite robust, it is not practical or cost-effective to sample every metre of the AOI. Concentrations of mercury, methylmercury, octachlorostyrene, organic carbon, and grain size in unsampled areas of the AOI were estimated using anisotropic interpolation in a flow-oriented coordinate system. This method was employed because it can account for the greater variability of physical and habitat characteristics transverse to river flow, as opposed to along the longitudinal axis of the river. In other words, river-bottom sediment is typically deposited in the direction of river flow. Therefore, an unsampled location is better predicted by a sample located in the direction of river flow rather than one located transverse to river flow. According to Merwade (2006), performing anisotropic interpolation in a flow-oriented coordinate system as opposed to an x,y coordinate system can reduce the RMSE by as much as 40%. In this analysis, the anisotropic factor, or ratio of the length of the y-axis to length of the x-axis, was adjusted to minimize the RMSE as much as possible. For riverine sites such as the AOI, anisotropic interpolation is expected to introduce less uncertainty into the spatial depiction of chemical concentrations than isotropic methods. Thus, the use of anisotropic interpolation is expected to reduce uncertainty in the overall analysis.

All areas of the AOI have total mercury concentrations exceeding the SQG-low (i.e., the LEL of 0.2 mg/kg) and many areas of the AOI have total mercury concentrations exceeding the SQG-high (i.e., the SEL of 2 mg/kg). However, these screening values were developed using a co-occurrence approach, where data from biological monitoring at a large number of sites (e.g., information on the presence and absence of benthic organisms) are compared to site chemistry data. It is widely accepted that empirical SQGs such as these, do not necessarily represent cause-effect, concentration-response relationships between chemical concentrations and biological effects (Wenning et al. 2005). Indeed, under the COA Framework, biological and toxicity studies are weighed more heavily than comparisons of sediment concentrations to SQGs. This weighting is sufficient to account for the limitations of the SQGs, such that the overall conclusions of this report are not significantly affected by this source of uncertainty.

6.3.3 Uncertainty Associated with Benthos Alteration

Data gaps and uncertainties associated with the benthos alteration LOE primarily relate to the difficulty of defining suitable reference areas. To compensate for this limitation, Milani et al. (2007) compared benthic community structure between upstream and downstream stations on the river. Upstream and downstream were defined relative to the location of the industrial area in Zone 1, upstream of the AOI. The results of this comparison suggest no significant difference in community structure between upstream and downstream sites ($p \leq 0.05$). Comparisons

assessing family diversity, abundances of tubificids, and abundance of chironomids also suggest no significant differences between upstream and downstream sites. Many of the differences between study and reference stations observed by Moran et al. (2005) may be explained by substrate characteristics, a key determinant of benthic community composition. Thus, there is no clear evidence of severe impairment based on this LOE. Even if the benthic community were deemed to be somewhat impaired, the preponderance of toxicity data indicates that toxicity due to chemicals in sediment is not a likely cause of impairment. Thus, uncertainty associated with benthos alteration is not significant with respect to sediment management decision-making.

6.3.4 Uncertainty Associated with Sediment Toxicity

Uncertainties associated with the sediment toxicity LOE primarily relate to the cause of the limited toxicity observed. Under Table 2 of the COA Framework (reproduced as Table 1-1 of this report), the reason for toxicity should be determined in those areas where sediment toxicity was observed, but benthic impairment is not identified. In Milani et al.'s (2007) toxicity testing, there was no apparent correlation between toxicological responses and concentrations of either mercury or methylmercury in sediment. Given the low frequency and severity of the effects observed by Milani et al. (2007), causation was not investigated in detail. Moran et al. (2005) reported more severe and widespread toxicity in the AOI and at an apparently uncontaminated upstream reference location. The uncertainties associated with these inconsistent results may be due to episodic stressor not present during the Milani et al. (2007) sampling events. Toxicity to benthic organisms due to persistent sediment contamination is not indicated.

6.3.5 Uncertainty Associated with Subsurface Sediment Risk

Uncertainty and data gaps associated with the evaluation of subsurface sediment relate to the lack of methylmercury data for subsurface sediment and/or porewater, and the resultant incomplete understanding of the potential for diffusive transfer of methylmercury toward the sediment-water interface. Uncertainty associated with subsurface sediment risks is also related to the question of sediment stability within specific areas of the AOI.

As discussed in Section 6.2.1, subsurface sediment samples collected from within the AOI have been analyzed for total mercury, but not methylmercury. Methylmercury concentrations in porewater also are not available for the AOI. For subsurface risks related to diffusion of aqueous phase methylmercury toward the sediment-water interface, determining the concentration profile of methylmercury in porewater would aid in identifying locations characterized by elevated potential for diffusive porewater transfer. For subsurface sediment risks related to exposure of previously buried methylmercury (such as following natural or anthropogenic disturbance of the sediment), characterization of the concentration and spatial distribution of methylmercury in subsurface sediment would aid in defining zones that would pose potential exposure risks if overlying sediment was disturbed or eroded.

As noted above, the potential for future risks associated with exposure of mercury in subsurface sediment is partly a function of sediment stability. Therefore, for sediment prone to physical

disturbance, an important uncertainty in the subsurface sediment risk analysis is the lack of sediment stability data for specific areas of the AOI where disturbance is reasonably expected, (e.g., marked ferry routes, near docks, areas susceptible to ice scour). ENVIRON understands there may be some bed shear velocity data available for the upper St. Clair River that may be helpful, but examination of that data is outside the scope of the current project. As discussed in Section 6.2.2.1, decisions regarding the need for and extent of sediment management to mitigate subsurface sediment risks are partly a function of whether current conditions in the river define a balance between historical inputs of mercury and on-going sediment disturbances. That is, in the absence of ongoing chemical discharge to the St. Clair River, it is not broadly known whether locations likely to experience resuspension or disturbance events are already characterized by the redistribution of previously buried chemicals. It should be noted as well that current delineation of the depth of sediment contamination is not likely sufficient to support remedy evaluation, design, and costing. .

6.4 Recommendations for Further Investigation

In light of the integrated LOEs presented in Section 6.1, the subsurface sediment risks discussed in Section 6.2, and the data gaps and uncertainties described in Section 6.3, ENVIRON offers several recommendations intended to support sediment management decision-making. Figure 6-8 maps zones of comparable surface and subsurface risk together, to facilitate discussion of related recommendations. Recommendations vary in different reaches of the AOI. The following discussion progresses through the AOI from north to south, with specific reaches numbered as shown in Figure 6-8 and recommendations for specific reaches called out in bold.

The need for sediment management in Reach 1 (i.e., from the northern boundary to the scoured area shown in black in most figures) is driven by risks to fish (Figure 6-8). Figure 6-8 indicates that the docks in Reach 1 also pose a potential subsurface sediment risk due to resuspension. Such risks are likely to be addressed by the management actions taken to address risk to fish. Therefore, no actions are recommended to reduce uncertainty for the northernmost reach.

Reach 2 of the AOI is scoured, as marked in black on most figures depicting the AOI in this report. The intensive scouring has prevented collection of sediment data from this reach. The very limited sediment in that reach therefore does not warrant management and no actions are recommended for this area.

Reach 3 extends from the southern end of the scoured area to adjacent to the northern end of Stag Island. While fairly limited portions of Reach 3 were identified as warranting sediment management to mitigate risks to fish, some of Reach 3 has elevated resuspension risk and elevated methylation risk. The remainder of Reach 3 has elevated potential for ice scour risk. There are elevated concentrations of mercury in subsurface sediment throughout Reach 3. ENVIRON recommends focused evaluation of sediment just north of the mouth of Talfourd Creek (Area 3a) in order to characterize sediment stability and methylation potential. Given the potential for ice scour risk between the mouth of Talfourd Creek and the northern end of Stag Island (Area 3b), sediment stability testing is also recommended in Area 3b. Furthermore,

because Talfourd Creek may be contributing sediment to Area 3b, and because creek discharge may result in localized sediment mixing, it is important to assess the extent to which sediment deposits in Area 3b represent stable river bed features that sequester and potentially dilute chemicals of concern (through new sediment input and/or sediment mixing). Specific recommendations include:

- **ENVIRON recommends review of existing bed shear models to confirm the applicability of existing data for Reach 3**. If modeling results are inconclusive, ENVIRON recommends supplementing existing data with erosion testing, such as via flume-based assessment of sediment resuspension potential. Resuspension assessment may be either laboratory-based (i.e., SEDFLUME) or in situ (i.e., FLUME) (e.g., Ravens 2007).
- **Ice accumulation mapping is recommended** to more narrowly define the spatial significance of this resuspension mechanism.
- **ENVIRON recommends evaluating methylation potential based on mercury and methylmercury analysis of sediment cores sectioned at cm-scale resolution**. High resolution sampling should extend 15 cm to 20 cm downward from the sediment-water interface, so as to include sediment from the 0 cm to 10 cm interval and sediment from greater than 10 cm, as specified in the COA Framework. Mercury and methylmercury concentrations should be analyzed in both the sediment porewater and solid phases within each core section. The depth profile of these analytes will also augment existing coarser-resolution data for assessing the extent to which sediment is stably sequestered versus actively reworked.

Reach 4 parallels Stag Island. Adjacent to the northern half of Stag Island, sediment management is not required to mitigate risks to fish (Area 4a). There is a zone of elevated methylation risk adjacent to the northern tip of Stag Island (Area 4a) that is related to the presence of elevated mercury concentrations as well as the potential for organic enrichment due to existing sewer structures. Although methylation potential could be further evaluated in this reach by analyzing sediment cores at cm-scale resolution, as described above, the lack of risks to fish in Area 4a suggests that the assessment of methylation potential in this area is of lower overall significance. ENVIRON does not consider this analysis to be critical for this area and no action is therefore recommended for Area 4a.

In Area 4b, adjacent to the central part of Stag Island, there is a zone of elevated resuspension risk associated with the ferry crossing. **ENVIRON recommends focused evaluation of sediment in Area 4b to characterize sediment stability.** Again, as described above, sediment stability analysis should include erodibility testing, as well as mapping the extent of ice accumulation in this area.

6.5 Summary and Conclusions

The purpose of this report was to apply the COA Framework to the St. Clair River. The St. Clair River flows 64 km from Lake Huron south to Lake St. Clair and forms the border between the

state of Michigan and Ontario. The COA Framework uses an ecosystem approach to sediment assessment to evaluate potential effects on sediment-dwelling and aquatic organisms, as well as potential for contamination to biomagnify in the food chain, in order to form a rational basis for decision-making. This report focused on an 8.3 km reach of the St. Clair River. Key findings and recommendations of this report follow.

Risk from Biomagnification

Risk from biomagnification is one of the four LOEs used to evaluate sediment quality in this report. For this LOE, concentrations of biomagnifying chemicals in sediment, benthic organisms, and/or predators of those organisms were modeled through to top predators, in order to evaluate ecological risk. ENVIRON conducted a streamlined analysis based on ERA principles and practices, with the goal of refining the current understanding of the risk from biomagnification LOE. Risk from biomagnification was evaluated by: 1) selecting ecological ROIs; 2) characterizing chemical concentrations in aquatic organisms; and 3) comparing chemical concentrations to TRVs derived from the literature.

Risk to Fish

- In general, risks calculated based on comparisons to a literature-derived TRV are age-dependent, with negligible risk predicted for young-of-year fish throughout the St. Clair River, intermediate to high risks predicted for adult sportfish in Blocks 2 and 3, and negligible risks predicted for adult sportfish in Block 1.
- Again, based on TRV comparisons, species-specific risks within the AOI (Block 2) indicate high risks for northern pike and redhorse sucker and intermediate risks for carp, freshwater drum, white sucker, and yellow perch, based on comparisons of mercury tissue concentrations to a literature-derived TRV. Octachlorostyrene is not predicted to adversely affect fish.
- Key sources of uncertainty for fish relate to the use of literature-based TRVs, exposure assumptions, the sampling design, and co-contaminants. However, multiple LOEs suggest these uncertainties are unlikely to affect overall conclusions or recommendations.

Risk to Wildlife

- Mean and 95%UCL concentrations of mercury and octachlorostyrene in prey tissue are below the target concentrations protective of wildlife ROIs, including double-crested cormorants, herring gulls, and raccoons. Thus, negligible risks are predicted for wildlife foraging within the AOI.
- Key sources of uncertainty for wildlife relate to the use of literature-based TRVs, differences in species sensitivity, and exposure assumptions. However, consistent use of conservative assumptions to compensate for uncertainty, as well as evaluation of avian risks based on both dose and measured egg concentrations suggest that these uncertainties are not expected to affect overall conclusions or recommendations presented in this report.

Sediment Chemistry

The sediment chemistry LOE involves the comparison of sediment chemistry data to SQGs and reference conditions. The objective of this LOE is to determine whether: 1) chemicals are present in sediment at concentrations greater than conservative screening levels; and/or 2) chemicals present in sediment could biomagnify and affect the health of biological communities at higher trophic levels.

All sampling stations in the AOI exceed the SQG-low and 61% exceed the SQG-high for total mercury, but exceedances of the mercury SQG are not generally predictive of impairment of the benthic community in the AOI. Concentrations of octachlorostyrene in sediment from all sampling stations in the AOI were below the equilibrium partitioning SQG, indicating that adverse effects on benthic invertebrates from octachlorostyrene are unlikely.

Anisotropic interpolation indicates the two areas of the most significantly elevated concentrations of total mercury in surface sediment occur south of the scoured area and on the northeast side of Stag Island.

Key sources of uncertainty related to: 1) presence and effect of chemicals in sediment that were not evaluated in this report; 2) past and future changes in the spatial distribution of chemicals in sediment; 3) interpolation of concentrations in unsampled areas; and 4) limited ability of mercury SQGs to predict adverse effects in benthic invertebrates. However, consideration of the other three LOEs prevents these uncertainties from significantly affecting the overall conclusions of this report. Recommendations are also offered to help reduce uncertainty.

Benthos Alteration

The objective of the benthos alteration LOE is to determine whether the benthic community structure in the AOI differs significantly from appropriate reference sites. Milani et al. (2007) and Moran et al. (2005) evaluated the benthic community in the AOI. This report summarized those findings, with particular attention given to defining the magnitude and spatial extent of any impairment observed.

- Neither Milani et al. (2007) nor Moran et al. (2005) indicate evidence of impairment in benthic community structure in the AOI.
- Sampling stations represented the full range of TOC concentrations, grain size distribution, and mercury concentrations in the AOI, indicating good spatial representativeness of the survey.
- The primary source of uncertainty relates to identification of appropriate upstream reference stations. However, Milani et al.'s (2007) comparison of upstream and downstream conditions supports the finding of no significant alteration in the AOI's benthic community.

Sediment Toxicity

The objective of the sediment toxicity LOE was to determine whether survival, growth and/or reproduction of sediment-associated invertebrates and minnows are impaired in the St. Clair River AOI. Milani et al. (2007) and Moran et al. (2005) completed a number of toxicity tests using AOI sediment, which are summarized in this report.

- Multiple toxicity tests on invertebrate survival, growth, and reproduction provide no clear indication of strong toxicity or a relationship between toxicological responses and concentrations of total or methylmercury in river sediment.
- Test conditions represented the full range of TOC concentrations, grain size distribution, and mercury concentrations in the AOI, indicating good spatial representativeness of the tests.
- Uncertainty associated with the sediment toxicity LOE primarily relates to the cause of the limited toxicity observed. Given the low frequency and severity of the effects observed by Milani et al. (2007), causation was not investigated in detail. Moran et al. (2005) reported more severe and widespread toxicity in the AOI and at an apparently uncontaminated upstream reference location, possibly due to an episodic or localized stressor not present during the Milani et al. (2007) sampling events.

Sediment Management Recommendations

- Prioritized zones for sediment management based on risks to fish are identified and mapped (Figure 6-4). The most important zones for sediment management to address risks to fish are immediately upstream and downstream of the scoured area.
- Further investigation is recommended to characterize sediment stability, as well as methylation and methylmercury exposure potential for subsurface mercury-contaminated sediment within focused reaches of the AOI, particularly downstream of the scoured area. Specific recommendations include: 1) examination of existing numerical modeling data, as well as potential erodibility analysis of sediment in relevant locations of the AOI; 2) ice accumulation mapping; and 3) mercury and methylmercury analysis of sediment cores sectioned over the top 15 cm to 20 cm of the core at cm-scale resolution.

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Tables

Table 1-1.

Decision Matrix for WOE Categorization. Based on Table 1, see text for explanation; a dash means "or". Separate endpoints can be included within each LOE (e.g., metals, PAHs, PCBs for Chemistry; survival, growth, reproduction for Toxicity; abundance, diversity, dominance for Benthos).

Scenario	Bulk Sediment Chemistry	Overall Toxicity[1]	Benthos Alteration[2]	Biomagnification Potential[3]	Assessment
1	☐	☐	☐	☐	No further actions needed
2	■–◘	☐	☐	☐	No further actions needed
3	○	☐	■–◘	☐	Determine reason(s) for benthos alteration (Section 5.3)
4	☐	■–◘	☐	☐	Determine reason(s) for sediment toxicity (Section 5.3)
5	☐	☐	☐	◘	Fully assess risk of biomagnification (Section 4.3)
6	■–◘	■–◘	☐	☐	Determine reason(s) for sediment toxicity (Section 5.3)
7	☐	☐	■–◘	◘	Determine reason(s) for benthos alteration (Section 5.3) **and** fully assess risk of biomagnification (Section 4.3)
8	■–◘	☐	■–◘	☐	Determine reason(s) for benthos alteration (Section 5.3)
9	■–◘	☐	☐	◘	Fully assess risk of biomagnification (Section 4.3)
10	■–◘	■–◘	☐	◘	Determine reason(s) for sediment toxicity (Section 5.3) **and** fully assess risk of biomagnification (Section 4.3)
11	■–◘	☐	■–◘	◘	Determine reason(s) for benthos alteration (Section 5.3) **and** fully assess risk of biomagnification (Section 4.3)
12	☐	■–◘	☐	◘	Determine reason(s) for sediment toxicity (Section 5.3) **and** fully assess risk of biomagnification (Section 4.3)
13	☐	■–◘	■–◘	☐	Determine reason(s) for sediment toxicity **and** benthos alteration[2] (Section 5.3)

14	□	■–◘	■–◘	◘	Determine reason(s) for sediment toxicity **and** benthos alteration (Section 5.3), **and** fully assess risk of biomagnification (Section 4.3)
15	■–◘	■–◘	■–◘	□	Management actions required[4]
16	■–◘	■–◘	■–◘	◘	Management actions required[4]

[1] Overall toxicity refers to the results of laboratory sediment toxicity tests conducted with a range of test organisms and toxicity endpoints. A positive finding of sediment toxicity may suggest that elevated concentrations of COPC are adversely affecting test organisms. However, toxicity may also occur that is not related to sediment contamination as a result of laboratory error, problems with the testing protocol, or with the test organisms used.

[2] Benthos alteration may be due to other factors, either natural (e.g., competition/predation, habitat differences) or human-related (e.g., water column contamination). Benthos alteration may also be related to sediment toxicity if a substance is present that was not measured in the sediment or for which no sediment quality guidelines exist, or due to toxicity associated with the combined exposure to multiple substances.

[3] Per Table 1, significant biomagnification (■) can typically only be determined in Step 6; Step 3 only allows a determination that there either is negligible biomagnification potential or that there is possible biomagnification potential. However, there may be site-specific situations where sufficient evidence is already available from fish advisories and prior research to consider biomagnification at a site significant; this would be determined in Step 1 (examination of available data). Thus, for example, if significant biomagnification were indicated in Scenario 5, above, management actions would be required. The other three LOE do allow for definitive determinations in prior Steps of this Framework.

[4] Definitive determination possible. Ideally elevated chemistry should be shown to in fact be linked to observed biological effects (i.e., is causal), to ensure management actions address the problem(s). For example, there is no point in removing contaminated sediment if the source of contamination has not been addressed.. Ensuring causality may require additional investigations such as toxicity identification evaluation (TIE) and/or contaminant body residue (CBR) analyses (see Section 5.3). If bulk sediment chemistry, toxicity and benthos alteration all indicate that adverse effects are occurring, further assessments of biomagnification should await management actions dealing with the clearly identified problem of contaminated and toxic sediments adversely affecting the organisms living in those sediments. In other words, deal with the obvious problem, which may obviate the possible problem (e.g., dredging to deal with unacceptable contaminant-induced alterations to the benthos will effectively also address possible biomagnification issues).

Table 2-1. Methylmercury Toxicity Studies for Fish Toxicity Reference Values

Species	Exposure Media	No-Effect Concentration (mg/kg wet weight)	Lowest Effect Concentration (mg/kg wet weight)	Effect Endpoint	Reference
Walleye (*Stizostedion vitreum*)	food	0.060[a]	0.25	Gonadal development	Friedmann et al. 1996
Striped mullet (*Mugil cephalus*)	water	<0.10[a]	0.30	Fin regeneration	Weis and Weis 1978
Fathead minnow (*Pimephales promelas*)	food	0.10[a]	0.39	Reproduction	Hammerschmidt et al. 2002[b]
Mummichog (*Fundulus heteroclitus*)	food	0.20	0.47	Lethality[c]	Matta et al. 2001
Golden shiner (*Notemigonus crysoleucas*)	food	0.23	0.52	Predator avoidance behaviour	Webber and Haines 2003
Fathead minnow (*Pimephales promelas*)	food	0.068[a]	0.71	Reproduction and related behaviour	Sandheinrich and Miller 2006
Fathead minnow (*Pimephales promelas*)	food	0.079[a]	0.86	Reproduction	Drevnick and Sanderheinrich 2003
Brook trout (*Salvelinus fontinalis*)	water	2.7	5.0	Lethality[c]	McKim et al. 1976
Mosquitofish (*Gambusia holbrooki*)	mesocosm sediment & food web	2.0	6.9	Population decline, lack of juveniles	Tatara et al. 1999

a. No-effect concentration represents control fish
b. Concentrations converted from dry weight
c. Reproduction was also measured but was a less sensitive endpoint than mortality
mg/kg: milligrams per kilogram

Table 2-2. Hexachlorobenzene Toxicity Studies for Avian Toxicity Reference Values

Test Species	Life stage	Effect	Exposure Matrix or Route	Exposure Frequency and /or Duration	Measurement endpoint	Concentration (ppm)	Test-species Dose (a) (mg/kg-day)	Reference
Japenese quail (*Coturnix coturnix*)	Adult	Reproduction; egg hatchability and egg volume	Dietary	90 days (critical life stage)	NOAEC	5	0.67	Vos et al. 1971
Japenese quail (*Coturnix coturnix*)	Adult	Reproduction and survival of chicks	Dietary	90 days	LOAEC	20	3	Schwetz et al. 1974
Japenese quail (*Coturnix coturnix*)	Adult	Reproduction; egg hatchability and egg volume	Dietary	90 days (critical life stage)	LOAEC	20	2.67	Vos et al. 1971
American kestrel (*Falco sparverius*)	Adult	Mortality and histological damage	In live food (mice)	65 days	LOAEC	20	3	Vos et al. 1971
Chickens (*Gallus sp.*)	Eggs, chicks, and adult	Reproduction: Fertility and hatchability and development	Dietary	Adults 25 weeks; chicks 6 months	NOAEC	100	6.25	Avrahami and Steele 1972

LOAEC: lowest observed adverse effect concentration
LOAEL: lowest observed adverse effect level
mg/kg-day: milligrams per kilogram bodyweight per day
NOAEC: no observed adverse effect concentration
NOAEL: no observed adverse effect level
ppm: parts per million

Table 2-3. Methylmercury Toxicity Studies for Mammalian Toxicity Reference Values

Test Species	Effect	Exposure Matrix or Route	Exposure duration (days)	Concentration of in diet (mg/kg)	Daily intake (mg/kg-day)	Reference
Mink (*Mustela vison*)	Acceptable reproduction and health for ranch production	Incorporated in fish	91	0.5	0.12	Kirk 1971
Mink (*Mustela vison*)	Mortality	Incorporated in fish	60	1	0.23	Kirk 1971
Mink (*Mustela vison*)	No clinical signs of toxicity	Incorporated in fish	145	0.33	0.077	Wobeser et al. 1976a
Mink (*Mustela vison*)	Tendency to move slowly	Added to food	93	1.1	0.26	Wobeser et al. 1976b
Mink (*Mustela vison*)	No mortality	Added to food	184	1.0	0.10 (males)	Wren et al. 1987a
Mink (*Mustela vison*)	Mortality	Added to food	81	1.0	0.18 (females)	Wren et al. 1987a
Mink (*Mustela vison*)	No significant reproductive effect (but low sample size)	Added to food	103	1.0 (administered every other day)[a]	0.090 (females)	Wren et al. 1987a,b
Mink (*Mustela vison*)	No mortality or reproductive effects, two generation study	Incorporated in fish	400	0.1	0.023	Dansereau et al. 1999
Mink (*Mustela vison*)	50% reduction in whelping of mated females	Incorporated in fish	400	0.5	0.12	Dansereau et al. 1999
Mink (*Mustela vison*)	Mortality	Incorporated in fish	400	1.0	0.23	Dansereau et al. 1999

a. After 81 days exposure at 0.18 mg/kg-day, exposure was decreased to half for remaining 103 days to prevent further mortality
mg/kg: milligrams per kilogram
mg/kg-day: milligrams per kilogram bodyweight per day

Table 2-4. Hexachlorobenzene Toxicity Studies for Mammalian Toxicity Reference Values

Test Species	Life stage	Effect	Exposure Matrix or Route	Exposure Frequency and /or Duration	Measurement endpoint	Concentration in Diet (mg/kg)	Test-species Dose (a) (mg/kg-day)	Reference
Domestic pig	not specified	Hepatic toxicity	Oral	90 days	NOAEL	-	0.05	den Tonkelaar et al. 1978
Monkey (*cynomolgus; Macaca sp* .)	Adult females	Reproductive effects: cellular degeneration	Oral	90 days	LOAEL	-	0.1	Babineau et al. 1991
Monkey (*cynomolgus; Macaca sp* .)	5 year old females	Reproductive effects: suppressed P4 levels	Gelatin capsules	13 weeks	LOAEL	-	0.1	Foster et al. 1992a
Monkey (*cynomolgus; Macaca sp* .)	not specified	Reproductive effects	Gelatin capsules	90 days	LOAEL	-	0.1	Jarrell et al. 1993
Monkey (*cynomolgus; Macaca sp* .)	Mature females	Reproductive effects	Gelatin capsules	12 wks, 7 day/wk 1/xday	LOAEL	-	0.1	Sims et al. 1991
Mink (*Mustela vison*)	Kits 0-17 wks	Body weight, hepatic and renal function	Perinatal and dietary	331 day (maternal); 6 wks (kits)	NOAEC	5	1.11	Rush et al. 1983
Mink (*Mustela vison*)	Adult females and males	Reduction in litter size and reduction in live births	Dietary	331 days	LOAEC	25	5.56	Bleavins et al. 1984
Mink (*Mustela vison*)	Adult females and males	Reduction in litter size and reduction in live births	Dietary	331 days	NOAEC	5	1.11	Bleavins et al. 1984
Mink (*Mustela vison*)	Kits 0-6 wks	44% kit mortality	Dietary	331 day (maternal); 6 wks (kits)	LOAEC	1	0.22	Bleavins et al. 1984
Mink (*Mustela vison*)	Kits 0-6 wks	Kit body weight	Dietary	331 day (maternal); 6 wks (kits)	NOAEC	1	0.22	Bleavins et al. 1984
Rat (*Rattus sp.*)	Male and female (30 days)	Survival, reproduction and pup viability	Dietary	130 wks	NOAEC	8	1	Arnold et al. 1985
Mink (*Mustela vison*)	Kits 0-6 wks	Kit body weight	Dietary	331 day (maternal); 6 wks (kits)	LOAEC	5	1.11	Bleavins et al. 1984
Ferrets (*Mustela putorius furo*)	Adult females and males	Reduction in live births	Dietary	331 days	NOAEC	5	1.11	Bleavins et al. 1984
Dog (*Canis familiaris*)	7-10 month (6-10kg) Beagle	Reduced growth, increased mortality	Gelatin capsules	12 months	NOAEC	10	1.25	Gralla et al. 1977
Rat (*Rattus sp.*)	4 generations	Reproduction maternal mortality, reduction in litter size, and reduced birth weights	Dietary	4 generations	NOAEC	20	2	Grant et al. 1977

Table 2-4. Hexachlorobenzene Toxicity Studies for Mammalian Toxicity Reference Values

Test Species	Life stage	Effect	Exposure Matrix or Route	Exposure Frequency and /or Duration	Measurement endpoint	Concentration in Diet (mg/kg)	Test-species Dose (a) (mg/kg-day)	Reference
Rat (*Rattus sp.*)	Adult females	Developmental effects: neurotoxicity	Gavage	4 days	LOAEL	-	2.5	Goldey & Taylor 1992
Rat (*Rattus sp.*)	Male and female (30 days)	Survival, reproduction and pup viability	Dietary	130 wks	LOAEC	40	3	Arnold et al. 1985
Rat (*Rattus sp.*)	4 generations	Reproduction maternal mortality, reduction in litter size and reduced birth weights	Dietary	4 generations	LOAEC	40	3	Grant et al. 1977
Hamster (*Mesocricetus auratus*)	6-wk	Survival	Dietary	Lifespan	LOAEL	-	4	Cabral et al. 1977
Rat (*Rattus sp.*)	Male and female	Sublethal toxic signs	Dietary	4 months	NOAEC	100	5	Kimbrough & Linder 1974
Rat (*Rattus sp.*)	1 generation females	Developmental effects	Dietary	1 generation	LOAEL	_	5	Kitchen et al. 1982
Ferrets (*Mustela putorius furo*)	Adult females and males	Mortality	Dietary	331 days	NOAEC	25	5.56	Bleavins et al. 1984
Ferrets (*Mustela putorius furo*)	Adult females and males	Reduction in live births	Dietary	331 days	LOAEC	25	5.56	Bleavins et al. 1984
Mink (*Mustela vison*)	Adult females and males	Mortality	Dietary	331 days	NOAEC	25	5.56	Bleavins et al. 1984
Ferrets (*Mustela putorius furo*)	Adult females and males	Reduction in live births	Dietary	331 days	LOAEC	25	5.56	Bleavins et al. 1984
Rat (*Rattus sp.*)	Adult female	Reproductive effects	Oral	149 days	NOAEL	-	6.5	Mendoza et al. 1979
Rat (*Rattus sp.*)	6 wk old male and female	Growth, mortality, clinical signs of toxicity	Dietary	15 wks	NOAEL	-	8	Kuiper-Goodman 1977
Rat (*Rattus sp.*)	100-125 g males and females	Mortality	Dietary	80 days	LOAEC	100	9	Cuomo et al. 1991
Rat (*Rattus sp.*)	not specified	Mortality	Oral	96 days	LD50	100	9	Kitchin et al. 1982
Rabbit (*Lepus sp.*)	Gestating adults	Sublethal toxicity signs	Dietary	27 days	NOAEL	-	10	Villaneuve et al. 1974
Mouse (*Mus sp.*)	6-7 wks (female and male)	Growth and survival of females	Dietary	15 wks	LOAEL	50	10	Cabral et al. 1979
Rat (*Rattus sp.*)	not specified	Mortality	Oral	96 days	LD50	140	12	Kitchin et al. 1982
Dog (*Canis familiaris*)	7-10 month (6-10kg) Beagle	Reduced growth, increased mortality	Gelatin capsules	12 months	LOAEC	100	12.5	Gralla et al. 1977
Mink (*Mustela vison*)	Adult females and males	Mortality	Dietary	331 days	LOAEC	125	27.5	Bleavins et al. 1984

Table 2-4. Hexachlorobenzene Toxicity Studies for Mammalian Toxicity Reference Values

Test Species	Life stage	Effect	Exposure Matrix or Route	Exposure Frequency and /or Duration	Measurement endpoint	Concentration in Diet (mg/kg)	Test-species Dose (a) (mg/kg-day)	Reference
Ferrets (*Mustela putorius furo*)	Adult females and males	Mortality	Dietary	331 days	LOAEC	125	27.5	Bleavins et al. 1984
Rat (*Rattus sp.*)	Adult female	Teratogenic effects; maternal toxicity, fetal skeletal abnormality	Oral	singe dose on Gd 6-9, 10-13, 6-16, or 6-21	NOAEL	-	60	Khera 1974
Rat (*Rattus sp.*)	15 Adult males	Teratogenic effects (successful impregnation of females)	Oral	10 days	NOAEL	-	60	Khera 1974
Monkey (*cynomolgus; Macaca sp*.)	not specified	Developmental effects	Gavage	60 days	LOAEL	-	64	Bailey et al. 1980
Rat (*Rattus sp.*)	Adult female	Teratogenic effects maternal toxicity, fetal skeletal abnormality	Oral	singe dose on Gd 6-9, 10-13, 6-16, or 6-21	LOAEL	-	80	Khera 1974
Dog (*Canis familiaris*)	Adult female Beagle	Mortality, growth, clinical signs	Gelatin capsules	21 days	NOAEL	-	150	Sundlof et al. 1981
Rat (*Rattus sp.*)	200 g females	Growth lesions	Dietary	4 wks	LOAEC	2,000	171	Gajdos & Gajdos-Torok 1961
Rat (*Rattus sp.*)	Female Wistar (100-200g)	Systematic: hepatic effects (increased cytochrome P-450 content)	Gavage	3 days	LOAEL	-	250	Ariyoshi et al. 1975
Rat (*Rattus sp.*)	198-300 g male and female adults	Mortality	Oral dose	16 days	LOAEL	-	500	Villaneuve & Newsome 1975
Guinea pig (*Cavia cobava*)	520-800 g adults	Mortality	Oral doses	16 days	LD100	-	500	Villaneuve & Newsome 1975
Deer mice (*Peromyscus maniculatus*)	Wild trapped adults	Mortality	Oral in diet (wheat seeds)	3 days of treatment	LD50	-	1,250	Schafer et al. 1985
Rat (*Rattus sp.*)	Male	Mortality	Oral	Acute	LD50	-	1,250	-
Cat (*Felis domesticus*)	not specified	Mortality	Oral	not specified	LD50	-	1,700	Savitski 1965
Mink (*Mustela vison*)	Adult males	Mortality	Dietary	Single	NOAEL	-	2,000	Bleavins et al. 1984
Mouse (*Mus sp.*)	not specified	Mortality	Oral	Single	LD0	-	2,000	-
Rabbit (*Oryctolagus sp.*)	not specified	Mortality	Oral	Acute	LD50	-	2,600	-

Table 2-4. Hexachlorobenzene Toxicity Studies for Mammalian Toxicity Reference Values

Test Species	Life stage	Effect	Exposure Matrix or Route	Exposure Frequency and /or Duration	Measurement endpoint	Concentration in Diet (mg/kg)	Test-species Dose (a) (mg/kg-day)	Reference
Guinea pig (*Cavia cobava*)	not specified	Mortality	Oral	Single	LD0	-	3,000	-
Rat (*Rattus sp.*)	not specified	Mortality	Oral	not specified	LD50	-	3,500-10,000	Booth & McDowell 1975
Rat (*Rattus sp.*)	not specified	Mortality	Oral	Single dose	LD50	-	10,000	Ben-Dyke et al. 1970
Sheep (*Ovis aries*)	Lambs	Growth, clinical signs	Oral	90 days	NOAEC	1	-	Mull et al. 1978

a. Test-species dose derived, if necessary, using generic exposure parameter values from USEPA 1993.

ATSDR: Agency for Toxic Substances and Disease Registry
g: grams
LD50: lethal to 50% of the population studied
LOAEC: lowest observed adverse effect concentration
LOAEL: lowest observed adverse effect level
mg/kg-day: milligrams per kilogram body weight per day
NOAEC: no observed adverse effect concentration
NOAEL: no observed adverse effect level
ppm: parts per million
USEPA: U.S. Environmental Protection Agency
wks: weeks

Table 2-5. Raccoon Food Ingestion Rate Exposure Parameters

Variable	Abbreviation	Units	Point Estimate	Source
Body weight	BW	kg	5.80	Sanderson 1984, Nagel 1943, Johnson 1970, Hamilton 1936
Food preferences	Pi	unitless		
Aquatic invertebrates	Pai	unitless	0.16	Alexander 1977, Stuewer 1943
Terrestrial invertebrates	Pti	unitless	0.1	
Plants	Pp	unitless	0.24	
Fish	Pf	unitless	0.14	
Birds and Mammals	Pbm	unitless	0.19	
Amphibians and Reptiles	Par	unitless	0.17	
Free metabolic rate	FMR	kJ/day	2185	
Slope	a	unitless	6.03	Nagy et al. 1999
Power	b	unitless	0.68	
Gross energy	Gi	kcal/kg		
Aquatic invertebrates	Gai	kcal/kg	950	Cummins and Wuycheck 1971, Golley 1961, Tyler 1973, Collopy 1975, Jorgenson et al. 1991, Pierotti and Annette 1987, Minnich 1982, Thayer et al. 1973
Terrestrial invertebrates		kcal/kg	1300	Cummins and Wuycheck 1971, Thayer et al. 1973, Collopy 1975, Bell 1990
Plants		kcal/kg	1300	Davis and Golley 1963, Drozdz 1968
Fish	Gf	kcal/kg	1600	Thayer et al. 1973, Ashwell-Erickson and Elsner 1981, Miller 1978
Birds and Mammals	Gm	kcal/kg	1800	Cummins and Wuycheck 1971, Collopy 1975, Gorecki 1975, Koplin et al. 1980, Odum et al. 1965, Duke et al. 1987, Congdon et al. 1982
Amphibians and Reptiles	Gar	kcal/kg	1300	Gorecki 1975, Koplin et al. 1980, Congdon et al. 1982
Assimilation efficiency	AEi	unitless		
Aquatic invertebrates	AEai	unitless	0.87	Grodzinski and Wunder 1975, Barrett and Stueck 1976,
Terrestrial invertebrates	Aeti	unitless	0.87	Grodzinski and Wunder 1975, Barrett and Stueck 1976,
Plants	Aep	unitless	0.78	
Fish	AEf	unitless	0.91	Nagy 1987
Birds and Mammals	Aebm	unitless	0.84	Litvaitis and Mautz 1976, Vogtsberger and Barrett 1973, Grodzinski and Wunder 1975
Amphibians and Reptiles	Aear	unitless	0.84	Litvaitis and Mautz 1976, Vogtsberger and Barrett 1973, Grodzinski and Wunder 1975
Food ingestion rate	FIR	kg/day	0.45	$FIR = (FMR \times CF) / \sum_{i=1}^{n} (AEi \times Gi \times Pi)$

kcal/kg: kilocalories per kilogram
kg/day: kilograms per day
kJ/day: kiloJoules per day
$FMR = aBW^{b}$
CF: 0.239 kcal/kJ
i: prey item type (unitless)

Table 2-6. Target Aquatic Prey Tissue Concentrations Protective of Each Wildlife Receptor of Interest

Chemical	Receptor	NOAEL (mg/kg-day)	LOAEL (mg/kg-day)	TRV (mg/kg-day)	Body Weight (kg)	Food Ingestion Rate (kg/day)	Area Use Factor (unitless)	Proportion of Diet, Aquatic Prey (unitless)	Target Aquatic Prey Concentration (mg/kg)
Methylmercury	Herring gull	0.039	0.078	0.055	1.135	0.34	1.0	0.85	0.22
Methylmercury	Double-crested cormorant	0.039	0.078	0.055	1.96	0.32	1.0	1.0	0.34
Methylmercury	Raccoon	0.023	0.12	0.053	5.8	0.45	1.0	0.30	2.3
Octachlorostyrene	Herring gull	0.67	2.67	1.3	1.135	0.34	1.0	0.85	5.3
Octachlorostyrene	Double-crested cormorant	0.67	2.67	1.3	1.96	0.32	1.0	1.0	8.2
Octachlorostyrene	Raccoon	0.039	0.22	0.093	5.8	0.45	1.0	0.30	4.0

kg/day: kilograms per day
kg: kilograms
LOAEL: lowest observed adverse effect level
mg/kg: milligrams per kilogram
mg/kg-day: milligrams per kilogram body weight per day
NOAEL: no observed adverse effect level
TRV: toxicity reference value

$$C_{aqprey} = \frac{TRV \times BW}{FIR \times AUF \times P_{aqprey}}$$

Table 2-7. Distribution of Fish Tissue Samples Used to Evaluate Risk to Fish

Block 1[a]					
		Mercury		Octachlorostyrene	
Location	Species	Number of Samples	Mean Length (cm)	Number of Samples	Mean Length (cm)
Adult Sportfish					
Upper St. Clair River	Alewife	1	24	2	24
Upper St. Clair River	Brown Bullhead	13	25	22	24
Upper St. Clair River	Carp	15	57	4	37
Upper St. Clair River	Freshwater Drum	5	47	1	36
Upper St. Clair River	Largemouth Bass	6	32	9	29
Upper St. Clair River	Northern Pike	1	67		
Upper St. Clair River	Redhorse Sucker	5	38	3	36
Upper St. Clair River	Rock Bass	9	20	15	21
Upper St. Clair River	Shad	10	29	17	24
Upper St. Clair River	Smallmouth Bass	5	36	5	36
Upper St. Clair River	Walleye	11	46	5	38
Upper St. Clair River	White Bass	10	30	15	27
Upper St. Clair River	White Sucker	20	38	5	32
Upper St. Clair River	Yellow Perch	20	20	22	22
Young-of-Year					
CAN #1_C	Goby	2	10	5	11
CAN #2_C	Goby	2	10	5	10
CAN #3_C	Goby	2	8	4	9
St. Clair R. - Sarnia Bay	Bluntnose Minnow	5	5	5	5
St. Clair R. - Sarnia Bay	Sand Shiner	16	5	15	5
St. Clair R. - Sarnia Bay	Spottail Shiner	6	6	6	6
St. Clair River - u/s Bluewater Bridge	Emerald Shiner	12	5	12	5
St. Clair River - u/s Bluewater Bridge	Sand Shiner	1	6	1	6

Table 2-7. Distribution of Fish Tissue Samples Used to Evaluate Risk to Fish

Block 2[b]					
		Mercury		Octachlorostyrene	
Location	Species	Number of Samples	Mean Length (cm)	Number of Samples	Mean Length (cm)
Adult Sportfish					
Middle St. Clair River	Carp	17	61		
Middle St. Clair River	Freshwater Drum	3	46	1	40
Middle St. Clair River	Northern Pike	9	69		
Middle St. Clair River	Redhorse Sucker	5	42	2	40
Middle St. Clair River	Rock Bass	16	20	27	21
Middle St. Clair River	Shad	1	22	3	22
Middle St. Clair River	Smallmouth Bass	4	21	10	20
Middle St. Clair River	Walleye	4	47	1	39
Middle St. Clair River	White Bass	1	22	3	22
Middle St. Clair River	White Sucker	20	42	4	37
Middle St. Clair River	Yellow Perch	22	23	20	26
Young-of-Year					
CAN #4_C	Goby	1	8	2	8
CAN #5_C	Goby	2	10	4	10
CAN #6_C	Goby	1	7	1	7
CAN #7_C	Goby	2	11	5	11
CAN #8_C	Goby	2	13	6	13
St. Clair R. - Suncor	Spottail Shiner	2	5	2	5
St. Clair R.- Talfourd Cr. mouth	Bluntnose Minnow	5	6	5	6
St. Clair R.- Talfourd Cr. mouth	Emerald Shiner	11	5	11	5
St. Clair R.- Talfourd Cr. mouth	Spottail Shiner	14	6	14	6
St. Clair River - d/s Corunna	Emerald Shiner	5	5	5	5
St. Clair River - d/s Corunna	Spottail Shiner	6	5	5	5
St. Clair River - Stag Island	Emerald Shiner	5	4	5	4
St. Clair River - Stag Island	Spottail Shiner	4	5	4	5
St.ClairR.-N.Tip Stag Is. Mainland	Spottail Shiner	1	6		

Table 2-7. Distribution of Fish Tissue Samples Used to Evaluate Risk to Fish

Block 3[c]					
		Mercury		Octachlorostyrene	
Location	Species	Number of Samples	Mean Length (cm)	Number of Samples	Mean Length (cm)
Adult Sportfish					
Lower St. Clair River	Black Crappie	5	23	13	23
Lower St. Clair River	Bluegill	8	16	24	16
Lower St. Clair River	Brown Bullhead	5	27	9	27
Lower St. Clair River	Carp	21	62	1	38
Lower St. Clair River	Freshwater Drum	15	37	12	35
Lower St. Clair River	Largemouth Bass	5	29	10	21
Lower St. Clair River	Northern Pike	10	53	1	41
Lower St. Clair River	Redhorse Sucker	6	43	1	38
Lower St. Clair River	Rock Bass	18	19	13	22
Lower St. Clair River	Shad	9	35	12	32
Lower St. Clair River	Smallmouth Bass	2	23	5	23
Lower St. Clair River	Walleye	6	54	1	40
Lower St. Clair River	White Sucker	2	34	2	25
Lower St. Clair River	Yellow Perch	17	21	32	20
Young-of-Year					
CAN #9_C	Goby	2	8	4	9
St. Clair River - Lambton G.S.	Spottail Shiner	23	6	23	6
St. Clair River - Sombra	Spottail Shiner	7	5	7	5

cm: centimeter

a. Block 1 is located upstream of the Area of Interest (AOI)

b. Block 2 is the AOI

c. Block 3 is located downstream of the AOI

Table 2-8. Distribution of Prey Samples Used to Evaluate Risk to Double-Crested Cormorants

Chemical	Prey Type	Block 1[a]		Block 2[b]		Block 3[c]	
		Number of Samples	Mean Length (cm)	Number of Samples	Mean Length (cm)	Number of Samples	Mean Length (cm)
Mercury							
	All Fish	**139**	**20**	**116**	**15**	**117**	**20**
	Alewife	1	24				
	Black Crappie					5	23
	Bluegill					8	16
	Bluntnose Minnow	5	5	5	6		
	Brown Bullhead	13	25			5	27
	Carp	4	37			1	38
	Emerald Shiner	12	5	21	5		
	Freshwater Drum	1	36	1	40	12	35
	Goby	6	10	8	10	2	8
	Largemouth Bass	6	32			4	24
	Northern Pike					1	41
	Redhorse Sucker	3	36	2	40	1	38
	Rock Bass	9	20	16	20	18	19
	Sand Shiner	17	5				
	Shad	8	25	1	22	9	35
	Smallmouth Bass	5	36	4	21	2	23
	Spottail Shiner	6	6	27	5	30	6
	Walleye	5	38	1	39	1	40
	White Bass	10	30	1	22		
	White Sucker	8	29	9	35	1	25
	Yellow Perch	20	20	22	23	17	21
Octachlorostyrene							
	All Fish	**116**	**20**	**93**	**14**	**99**	**20**
	Alewife	1	24				
	Black Crappie					5	23
	Bluegill					8	16
	Bluntnose Minnow	5	5	5	6		
	Brown Bullhead	9	24			5	27
	Carp	4	37			1	38
	Emerald Shiner	12	5	21	5		
	Freshwater Drum	1	36	1	40	12	35
	Goby	6	10	8	10	2	8
	Largemouth Bass	6	32			4	24
	Northern Pike					1	41
	Redhorse Sucker	3	36	2	40	1	38
	Rock Bass	5	21	10	22	5	22
	Sand Shiner	16	5				
	Shad	8	25	1	22	9	35
	Smallmouth Bass	5	36	4	21	2	23
	Spottail Shiner	6	6	25	5	30	6
	Walleye	5	38	1	39	1	40
	White Bass	10	30	1	22		
	White Sucker	4	34	4	37	1	25
	Yellow Perch	10	24	10	27	12	21

cm: centimeter

a. Block 1 is located upstream of the Area of Interest (AOI)

b. Block 2 is the AOI

c. Block 3 is located downstream of the AOI

Table 2-9. Distribution of Prey Samples Used to Evaluate Risk to Herring Gulls

Chemical	Prey Type	Block 1[a] Number of Samples	Block 1[a] Mean Length (cm)	Block 2[b] Number of Samples	Block 2[b] Mean Length (cm)	Block 3[c] Number of Samples	Block 3[c] Mean Length (cm)
Mercury							
	All Fish	**61**	**21**	**46**	**20**	**60**	**20**
	Alewife	1	23.9				
	Black Crappie					5	23
	Bluegill					8	16
	Brown Bullhead	13	25			4	26
	Goby	3	11	4	12	1	11
	Largemouth Bass	2	24			3	19
	Rock Bass	9	20	16	20	18	19
	Shad	7	24	1	22	2	24
	Smallmouth Bass			3	19	2	23
	White Bass	3	22	1	22		
	White Sucker	5	24	1	30	1	25
	Yellow Perch	18	19	20	22	16	20
	All Invertebrates	**13**		**36**		**7**	
	Invertebrates	10		30		6	
	Mussels	3		6		1	
Octachlorostyrene							
	All Fish	**39**	**22**	**27**	**21**	**42**	**21**
	Alewife	1	24				
	Black Crappie					5	23
	Bluegill					8	16
	Brown Bullhead	9	24			4	26
	Goby	3	11	4	12	1	11
	Largemouth Bass	2	24			3	19
	Rock Bass	5	21	10	22	5	22
	Shad	7	24	1	22	2	24
	Smallmouth Bass			3	19	2	23
	White Bass	3	22	1	22		
	White Sucker	1	27			1	25
	Yellow Perch	8	22	8	26	11	20
	All Invertebrates	**3**		**6**		**1**	
	Mussels	3		6		1	

cm: centimeter

a. Block 1 is located upstream of the Area of Interest (AOI)

b. Block 2 is the AOI

c. Block 3 is located downstream of the AOI

Table 2-10. Distribution of Prey Samples Used to Evaluate Risk to Raccoons

Chemical	Prey Type	Block 1[a] Number of Samples	Block 1[a] Mean Length (cm)	Block 2[b] Number of Samples	Block 2[b] Mean Length (cm)	Block 3[c] Number of Samples	Block 3[c] Mean Length (cm)
Mercury							
	All Fish	**38**	**18**	**37**	**17**	**46**	**18**
	Black Crappie					3	21
	Bluegill					8	16
	Brown Bullhead	4	21				
	Goby	5	10	7	11	1	11
	Largemouth Bass	1	22			3	19
	Rock Bass	9	20	13	19	15	18
	Shad	2	21	1	22	1	23
	Smallmouth Bass			3	19	1	21
	White Bass	2	21	1	22		
	White Sucker	1	23				
	Yellow Perch	14	17	12	19	14	19
	All Invertebrates	**13**		**36**		**7**	
	Invertebrates	10		30		6	
	Mussels	3		6		1	
Octachlorostyrene							
	All Fish	**23**	**18**	**20**	**17**	**29**	**18**
	Black Crappie					3	21
	Bluegill					8	16
	Brown Bullhead	4	21				
	Goby	5	10	6	11	1	11
	Largemouth Bass	4	22			3	19
	Rock Bass	5	21	7	20	3	20
	Shad	2	21	1	22	1	23
	Smallmouth Bass			3	19	1	21
	White Bass	2	21	1	22		
	Yellow Perch	4	18	2	21	9	18
	All Invertebrates	**3**		**6**		**1**	
	Mussels	3		6		1	

cm: centimeter

a. Block 1 is located upstream of the Area of Interest (AOI)

b. Block 2 is the AOI

c. Block 3 is located downstream of the AOI

Table 2-11 Comparison of Total Mercury Concentrations in Whole Body Fish Tissue Within, Upstream, and Downstream of the Area of Interest

	Number of Samples	Minimum Detected Concentration (mg/kg)	Maximum Detected Concentration (mg/kg)	Mean (mg/kg)	95th Percentile (mg/kg)	TRV (mg/kg)	Samples Exceeding the TRV (%)
Block 1[a]							
Young-of-Year	46	0.020	0.070	0.028	0.057	0.20	0
Adult Sportfish[d]	131	0.016	0.68	0.11	0.23	0.20	10
All Fish	177	0.016	0.68	0.086	0.23	0.20	7
Block 2[b]							
	Number of Samples	**Minimum Detected Concentration (mg/kg)**	**Maximum Detected Concentration (mg/kg)**	**Mean (mg/kg)**	**95th Percentile (mg/kg)**	**TRV (mg/kg)**	**Samples Exceeding the TRV (%)**
Young-of-Year	61	0.020	0.16	0.049	0.09	0.20	0
Adult Sportfish[e]	102	0.030	0.47	0.17	0.32	0.20	31
All Fish	163	0.020	0.47	0.13	0.29	0.20	20
Block 3[c]							
	Number of Samples	**Minimum Detected Concentration (mg/kg)**	**Maximum Detected Concentration (mg/kg)**	**Mean (mg/kg)**	**95th Percentile (mg/kg)**	**TRV (mg/kg)**	**Samples Exceeding the TRV (%)**
Young-of-Year	32	0.030	0.12	0.056	0.07	0.20	0
Adult Sportfish[f]	129	0.023	0.54	0.16	0.35	0.20	25
All Fish	161	0.023	0.54	0.14	0.32	0.20	20

mg/kg: milligrams per kilogram
TRV: toxicity reference value protective of fish
a. Block 1 is located upstream of the Area of Interest (AOI)
b. Block 2 is the AOI
c. Block 3 is located downstream of the AOI
d. Alewife, brown bullhead, carp, freshwater drum, largemouth bass, northern pike, redhorse sucker, rock bass, shad, smallmouth bass, walleye, white bass, white sucker, yellow perch
e. Carp, freshwater drum, northern pike, redhorse sucker, rock bass, shad, smallmouth bass, walleye, white bass, white sucker, yellow perch
f. Black crappie, bluegill, brown bullhead, carp, freshwater drum, largemouth bass, northern pike, redhorse sucker, rock bass, shad, smallmouth bass, walleye, white sucker, yellow perch

Table 2-12. Total Mercury Concentrations in Whole Body Fish Tissue by Sampling Location

Block 1[a]								
	Location	**Number of Samples**	**Minimum Detected Concentration (mg/kg)**	**Maximum Detected Concentration (mg/kg)**	**Mean (mg/kg)**	**95th Percentile (mg/kg)**	**TRV (mg/kg)**	**Samples Exceeding the TRV (%)**
Young-of-Year								
	CAN #1_C	2	0.023	0.057	0.040	0.056	0.20	0
	CAN #2_C	2	0.038	0.054	0.046	0.053	0.20	0
	CAN #3_C	2	0.039	0.047	0.043	0.047	0.20	0
	St. Clair R. - Sarnia Bay	27	0.020	0.060	0.028	0.047	0.20	0
	St. Clair River - u/s Bluewater Bridge	13	0.020	0.070	0.020	0.052	0.20	0
Adult Sportfish[d]								
	Upper St. Clair River	131	0.016	0.68	0.11	0.23	0.20	10
Block 2[b]								
	Location	**Number of Samples**	**Minimum Detected Concentration (mg/kg)**	**Maximum Detected Concentration (mg/kg)**	**Mean (mg/kg)**	**95th Percentile (mg/kg)**	**TRV (mg/kg)**	**Samples Exceeding the TRV (%)**
Young-of-Year								
	CAN #4_C	1	0.13	0.13	0.13	0.13	0.20	0
	CAN #5_C	2	0.047	0.066	0.057	0.065	0.20	0
	CAN #6_C	1	0.094	0.094	0.094	0.094	0.20	0
	CAN #7_C	2	0.067	0.16	0.11	0.16	0.20	0
	CAN #8_C	2	0.065	0.086	0.075	0.085	0.20	0
	St. Clair R. - Suncor	2	0.060	0.070	0.065	0.070	0.20	0
	St. Clair R.- Talfourd Cr. mouth	30	0.020	0.13	0.041	0.086	0.20	0
	St. Clair River - d/s Corunna	11	0.030	0.080	0.050	0.075	0.20	0
	St. Clair River - N. Tip Stag Island Mainland	1	0.053	0.053	0.053	0.053	0.20	0
	St. Clair River - Stag Island	9	0.020	0.070	0.034	0.062	0.20	0
Adult Sportfish[e]								
	Middle St. Clair River	102	0.030	0.47	0.17	0.32	0.20	31

Table 2-12. Total Mercury Concentrations in Whole Body Fish Tissue by Sampling Location

Block 3[c]								
	Location	Number of Samples	Minimum Detected Concentration (mg/kg)	Maximum Detected Concentration (mg/kg)	Mean (mg/kg)	95th Percentile (mg/kg)	TRV (mg/kg)	Samples Exceeding the TRV (%)
Young-of-Year								
	CAN #9_C	2	0.075	0.12	0.095	0.113	0.20	0
	St. Clair River - Lambton G.S.	23	0.030	0.070	0.050	0.060	0.20	0
	St. Clair River - Sombra	7	0.060	0.070	0.063	0.070	0.20	0
Adult Sportfish[f]								
	Lower St. Clair River	129	0.023	0.54	0.16	0.35	0.20	25

mg/kg: milligrams per kilogram

TRV: toxicity reference value protective of fish

a. Block 1 is located upstream of the Area of Interest (AOI)

b. Block 2 is the AOI

c. Block 3 is located downstream of the AOI

d. Alewife, brown bullhead, carp, freshwater drum, largemouth bass, northern pike, redhorse sucker, rock bass, shad, smallmouth bass, walleye, white bass, white sucker, yellow perch

e. Carp, freshwater drum, northern pike, redhorse sucker, rock bass, shad, smallmouth bass, walleye, white bass, white sucker, yellow perch

f. Black crappie, bluegill, brown bullhead, carp, freshwater drum, largemouth bass, northern pike, redhorse sucker, rock bass, shad, smallmouth bass, walleye, white sucker, yellow perch

Table 2-13. Total Mercury Concentration in Whole Body Fish Tissue by Sampling Location and Species

Block 1[a]									
	Location	Species	Number of Samples	Minimum Detected Concentration (mg/kg)	Maximum Detected Concentration (mg/kg)	Mean (mg/kg)	95th Percentile (mg/kg)	TRV (mg/kg)	Samples Exceeding the TRV (%)
Young-of-Year									
	CAN #1_C	Goby	2	0.023	0.057	0.040	0.056	0.2	0
	CAN #2_C	Goby	2	0.038	0.054	0.046	0.053	0.2	0
	CAN #3_C	Goby	2	0.039	0.047	0.043	0.047	0.2	0
	St. Clair R. - Sarnia Bay	Bluntnose Minnow	5	0.020	0.030	0.026	0.030	0.2	0
		Sand Shiner	16	0.020	0.060	0.033	0.053	0.2	0
		Spottail Shiner	6	0.020	0.030	0.019	0.028	0.2	0
	St. Clair River - u/s Bluewater Bridge	Emerald Shiner	12	0.020	0.040	0.015	0.035	0.2	0
		Sand Shiner	1	0.070	0.070	0.070	0.070	0.2	0
Adult Sportfish									
	Upper St. Clair River	Alewife	1	0.023	0.023	0.023	0.023	0.2	0
		Brown Bullhead	13	0.016	0.030	0.022	0.030	0.2	0
		Carp	15	0.023	0.19	0.10	0.18	0.2	0
		Freshwater Drum	5	0.073	0.68	0.37	0.65	0.2	80
		Largemouth Bass	6	0.049	0.21	0.13	0.20	0.2	17
		Northern Pike	1	0.15	0.15	0.15	0.15	0.2	0
		Redhorse Sucker	5	0.043	0.14	0.077	0.13	0.2	0
		Rock Bass	9	0.079	0.23	0.13	0.21	0.2	11
		Shad	10	0.023	0.049	0.032	0.049	0.2	0
		Smallmouth Bass	5	0.16	0.30	0.23	0.30	0.2	60
		Walleye	11	0.085	0.45	0.16	0.34	0.2	27
		White Bass	10	0.079	0.22	0.13	0.19	0.2	10
		White Sucker	20	0.023	0.18	0.086	0.17	0.2	0
		Yellow Perch	20	0.036	0.18	0.075	0.14	0.2	0

Table 2-13. Total Mercury Concentration in Whole Body Fish Tissue by Sampling Location and Species

Block 2[b]									
	Location	Species	Number of Samples	Minimum Detected Concentration (mg/kg)	Maximum Detected Concentration (mg/kg)	Mean (mg/kg)	95th Percentile (mg/kg)	TRV (mg/kg)	Samples Exceeding the TRV (%)
Young-of-Year									
	CAN #4_C	Goby	1	0.13	0.13	0.13	0.13	0.2	0
	CAN #5_C	Goby	2	0.047	0.066	0.06	0.065	0.2	0
	CAN #6_C	Goby	1	0.094	0.094	0.09	0.094	0.2	0
	CAN #7_C	Goby	2	0.067	0.16	0.11	0.16	0.2	0
	CAN #8_C	Goby	2	0.065	0.086	0.08	0.085	0.2	0
	St. Clair River - d/s Corunna	Emerald Shiner	5	0.030	0.040	0.034	0.040	0.2	0
		Spottail Shiner	6	0.050	0.080	0.063	0.078	0.2	0
	St. Clair River - Stag Island	Emerald Shiner	5	0.02	0.02	0.02	0.020	0.2	0
		Spottail Shiner	4	0.04	0.07	0.0525	0.067	0.2	0
	St. Clair River - N. Tip Stag Island Mainland	Spottail Shiner	1	0.053	0.053	0.053	0.053	0.2	0
	St. Clair R. - Suncor	Spottail Shiner	2	0.06	0.07	0.065	0.070	0.2	0
	St. Clair R.- Talfourd Cr. mouth	Bluntnose Minnow	5	0.040	0.13	0.072	0.12	0.2	0
		Emerald Shiner	11	0.0050	0.030	0.015	0.025	0.2	0
		Spottail Shiner	14	0.020	0.090	0.051	0.077	0.2	0
Adult Sportfish									
	Middle St. Clair River	Carp	17	0.11	0.38	0.18	0.31	0.2	24
		Freshwater Drum	3	0.18	0.47	0.28	0.44	0.2	33
		Northern Pike	9	0.14	0.29	0.24	0.29	0.2	89
		Redhorse Sucker	5	0.20	0.35	0.25	0.33	0.2	80
		Rock Bass	16	0.061	0.33	0.15	0.32	0.2	13
		Shad	1	0.030	0.030	0.03	0.030	0.2	0
		Smallmouth Bass	4	0.085	0.14	0.11	0.13	0.2	0
		Walleye	4	0.073	0.18	0.14	0.18	0.2	0
		White Bass	1	0.061	0.061	0.06	0.061	0.2	0
		White Sucker	20	0.036	0.28	0.16	0.27	0.2	40
		Yellow Perch	22	0.049	0.38	0.15	0.29	0.2	23

Table 2-13. Total Mercury Concentration in Whole Body Fish Tissue by Sampling Location and Species

Block 3[c]									
	Location	Species	Number of Samples	Minimum Detected Concentration (mg/kg)	Maximum Detected Concentration (mg/kg)	Mean (mg/kg)	95th Percentile (mg/kg)	TRV (mg/kg)	Samples Exceeding the TRV (%)
Young-of-Year									
	CAN #9_C	Goby	2	0.075	0.115	0.095	0.113	0.2	0
	St. Clair River - Lambton G.S.	Spottail Shiner	23	0.03	0.07	0.050	0.060	0.2	0
	St. Clair River - Sombra	Spottail Shiner	7	0.06	0.07	0.063	0.070	0.2	0
Adult Sportfish									
	Lower St. Clair River	Black Crappie	5	0.043	0.18	0.09	0.17	0.2	0
		Bluegill	8	0.073	0.14	0.095	0.13	0.2	0
		Brown Bullhead	5	0.036	0.28	0.100	0.24	0.2	20
		Carp	21	0.079	0.32	0.19	0.30	0.2	43
		Freshwater Drum	15	0.085	0.46	0.21	0.42	0.2	47
		Largemouth Bass	5	0.067	0.472	0.193	0.429	0.2	40
		Northern Pike	10	0.103	0.219	0.142	0.209	0.2	10
		Redhorse Sucker	6	0.043	0.22	0.149	0.21	0.2	17
		Rock Bass	18	0.08	0.39	0.18	0.31	0.2	33
		Shad	9	0.023	0.07	0.05	0.06	0.2	0
		Smallmouth Bass	2	0.091	0.15	0.12	0.15	0.2	0
		Walleye	6	0.131	0.54	0.32	0.54	0.2	50
		White Sucker	2	0.131	0.131	0.068	0.125	0.2	0
		Yellow Perch	17	0.06	0.36	0.13	0.33	0.2	12

mg/kg: milligrams per kilogram
TRV: toxicity reference value protective of fish
a. Block 1 is located upstream of the Area of Interest (AOI)
b. Block 2 is the AOI
c. Block 3 is located downstream of the AOI

Table 2-14. Comparison of Double-Crested Cormorant Prey Concentrations to Target Tissue Concentrations[a]

Chemical	Prey Type	Number of Samples	Minimum Detected Concentration	Maximum Detected Concentration	Mean Concentration	95%UCL	Target Prey Concentration	Exceedence of Target Prey Concentration
Block 1[b]								
Mercury (mg/kg)	All Fish	139	0.016	0.30	0.064	0.073	0.34	No
Octachlorostyrene (mg/kg)	All Fish	116	0.0005	0.013	0.0010	0.0014	8.2	No
Block 2[c]								
Mercury (mg/kg)	All Fish	118	0.02	0.38	0.093	0.11	0.34	No
Octachlorostyrene (mg/kg)	All Fish	93	0.0005	0.037	0.0068	0.0082	8.2	No
Block 3[d]								
Mercury (mg/kg)	All Fish	117	0.023	0.40	0.11	0.12	0.34	No
Octachlorostyrene (mg/kg)	All Fish	99	0.0005	0.021	0.0039	0.0049	8.2	No

95%UCL: 95% upper confidence limit of the arithmetic average; calculated using the BCA Bootstrap method with 10,000 bootstrap iterations.
mg/kg: milligrams per kilogram

Mean concentrations and 95%UCLs of prey are weighted based on the proportion of each prey type in the diet. Weighted means and UCLs are summed for total prey concentrations. Target prey concentrations are shown in Table 2-6.

a. See Table 2-8 for distribution of prey samples by species.
b. Block 1 is located upstream of the Area of Interest (AOI)
c. Block 2 is the AOI
d. Block 3 is located downstream of the AOI

Table 2-15. Comparison of Herring Gull Prey Concentrations to Target Tissue Concentrations[a]

Block 1[b]									
Chemical	**Prey Type**	**Number of Samples**	**Minimum Detected Concentration**	**Maximum Detected Concentration**	**Percent of Prey in Aquatic Diet**	**Weighted Mean Concentration**	**Weighted 95%UCL**	**Target Aquatic Prey Concentration**	**Exceedence of Target Prey Concentration**
Mercury (mg/kg)[e]									
	All Fish	61	0.016	0.23	81%	0.047	0.055		
	All Invertebrates	13	0.0003	0.025	19%	0.0021	0.0028		
	Total	**74**	**0.0003**	**0.23**	**100%**	**0.049**	**0.058**	0.22	No
Octachlorostyrene (mg/kg)									
	All Fish	39	0.0005	0.013	81%	0.00070	NC		
	All Invertebrates	3	0.30	1.7	19%	0.14	NC		
	Total	**42**	**0.0005**	**1.7**	**100%**	**0.14**	**0.0**	5.3	No
Block 2[c]									
Chemical	**Prey Type**	**Number of Samples**	**Minimum Detected Concentration**	**Maximum Detected Concentration**	**Percent of Prey in Aquatic Diet**	**Weighted Mean Concentration**	**Weighted 95% UCL**	**Target Aquatic Prey Concentration**	**Exceedence of Target Prey Concentration**
Mercury (mg/kg)[e]									
	All Fish	46	0.030	0.33	81%	0.11	0.12		
	All Invertebrates	36	0.0079	0.15	19%	0.0082	0.010		
	Total	**82**	**0.0079**	**0.33**	**100%**	**0.11**	**0.13**	0.22	No
Octachlorostyrene (mg/kg)									
	All Fish	27	0.0005	0.0080	81%	0.0011	0.0017		
	All Invertebrates	6	1.0	3.6	19%	0.43	0.56		
	Total	**33**	**0.0005**	**3.6**	**100%**	**0.43**	**0.56**	5.3	No

Table 2-15. Comparison of Herring Gull Prey Concentrations to Target Tissue Concentrations[a]

Block 3[d]									
Chemical	**Prey Type**	**Number of Samples**	**Minimum Detected Concentration**	**Maximum Detected Concentration**	**Percent of Prey in Aquatic Diet**	**Weighted Mean Concentration**	**Weighted 95%UCL**	**Target Aquatic Prey Concentration**	**Exceedence of Target Prey Concentration**
Mercury (mg/kg)[e]									
	All Fish	60	0.023	0.39	81%	0.098	0.11		
	All Invertebrates	7	0.0012	0.073	19%	0.0046	0.0082		
	Total	**67**	**0.0012**	**0.39**	**100%**	**0.10**	**0.12**	0.22	No
Octachlorostyrene (mg/kg)									
	All Fish	42	0.0005	0.004	81%	0.00059	NC		
	All Invertebrates	1	0.30	0.30	19%	0.056	NC		
	Total	**43**	**0.0005**	**0.30**	**100%**	**0.057**	**0.0**	5.3	No

95%UCL: 95% upper confidence limit of the arithmetic average; calculated using the BCA Bootstrap method with 10,000 bootstrap iterations.
mg/kg: milligrams per kilogram
NC: Not calculated due to small sample size or lack of variability.
Mean concentrations and 95%UCLs of prey are weighted based on the proportion of each prey type in the aquatic portion of the diet. Weighted means and UCLs are summed for total prey concentrations. Target prey concentrations are shown in Table 2-6.
a. See Table 2-9 for distribution of prey samples by species.
b. Block 1 is located upstream of the Area of Interest (AOI)
c. Block 2 is the AOI
d. Block 3 is located downstream of the AOI
e. Mercury concentrations are methylmercury. Methylmercury concentrations were used for invertebrates when available. Total mercury concentrations were used for mussels as methylmercury concentrations were unavailable.

Table 2-16. Comparison of Racoon Prey Concentrations to Target Tissue Concentrations[a]

Chemical / Prey Type	Number of Samples	Minimum Detected Concentration	Maximum Detected Concentration	Percent of Prey in Aquatic Diet	Weighted Mean Concentration	Weighted 95%UCL	Target Aquatic Prey Concentration	Exceedence of Target Prey Concentration
Block 1[b]								
Mercury (mg/kg)[e]								
All Fish	38	0.016	0.235	47%	0.032	0.039		
All Invertebrates	13	0.0003	0.025	53%	0.0060	0.0081		
Total	**51**	**0.0003**	**0.23**	**100%**	**0.038**	**0.047**	2.3	No
Octachlorostyrene (mg/kg)								
All Fish	23	0.0005	0.0067	47%	0.00040	NC		
All Invertebrates	3	0.30	1.7	53%	0.40	NC		
Total	**26**	**0.0005**	**1.65**	**100%**	**0.400**	**0.0**	4.0	No
Block 2[c]								
Mercury (mg/kg)[e]								
All Fish	37	0.030	0.32	47%	0.050	0.058		
All Invertebrates	36	0.0079	0.15	53%	0.023	0.029		
Total	**73**	**0.0079**	**0.32**	**100%**	**0.073**	**0.09**	2.3	No
Octachlorostyrene (mg/kg)								
All Fish	20	0.0005	0.019	47%	0.0014	0.0025		
All Invertebrates	6	1	3.6	53%	1.2	1.6		
Total	**26**	**0.0005**	**3.60**	**100%**	**1.2**	**1.6**	4.0	No

Table 2-16. Comparison of Racoon Prey Concentrations to Target Tissue Concentrations[a]

Block 3[d]									
Chemical	**Prey Type**	**Number of Samples**	**Minimum Detected Concentration**	**Maximum Detected Concentration**	**Percent of Prey in Aquatic Diet**	**Weighted Mean Concentration**	**Weighted 95%UCL**	**Target Aquatic Prey Concentration**	**Exceedence of Target Prey Concentration**
Mercury (mg/kg)[e]									
	All Fish	46	0.030	0.39	47%	0.058	0.068		
	All Invertebrates	7	0.0012	0.073	53%	0.013	0.023		
	Total	**53**	**0.0012**	**0.39**	**100%**	**0.071**	**0.091**	2.3	No
Octachlorostyrene (mg/kg)									
	All Fish	29	0.0005	0.004	47%	0.00031	NC		
	All Invertebrates	1	0.30	0.30	53%	0.16	NC		
	Total	**30**	**0.0005**	**0.30**	**100%**	**0.16**	**NC**	4.0	No

95%UCL: 95% upper confidence limit of the arithmetic average; calculated using the BCA Bootstrap method with 10,000 bootstrap iterations.
mg/kg: milligrams per kilogram
NC: Not calculated due to small sample size or lack of variability.

Mean concentrations and 95%UCLs of prey are weighted based on the proportion of each prey type in the aquatic portion of the diet. Weighted means and UCLs are summed for total prey concentrations. Target prey concentrations are shown in Table 2-6.

a. See Table 2-10 for distribution of prey samples by species
b. Block 1 is located upstream of the Area of Interest (AOI)
c. Block 2 is the AOI
d. Block 3 is located downstream of the AOI
e. Mercury concentrations are methylmercury. Methylmercury concentrations were used for invertebrates when available. Total mercury concentrations were used for mussels as methylmercury concentrations were unavailable.

Table 3-1. Surface[a] Sediment Chemistry Summary Statistics for the Area of Interest

Analyte	Number of Detected Samples		Number of Samples	Frequency of Detection %	Minimum Detected Concentration	Maximum Detected Concentration	Mean	95%UCL	Units
Nutrients and Metals									
Acid Iron	83	/	83	100	5,200	22,000	8,633	9,192	mg/kg
Acid Manganese	83	/	83	100	90	370	178	189	mg/kg
Acid Mercury	83	/	83	100	0.58	41	4.2	5.8	mg/kg
Acid Phosphorus	83	/	83	100	130	540	254	272	mg/kg
Aluminum (AL)	5	/	5	100	2,680	3,080	2,826	NC	mg/kg
Arsenic (As)	5	/	5	100	2	3	2.6	NC	mg/kg
Barium (Ba)	5	/	5	100	10	13	12	NC	mg/kg
Boron (B)	1	/	5	20	5	5	3	NC	mg/kg
Calcium (Ca)	5	/	5	100	46,200	60,500	52,600	NC	mg/kg
Chromium (Cr)	5	/	5	100	6	8	7.2	NC	mg/kg
Cobalt (Co)	5	/	5	100	3	4	3.6	NC	mg/kg
Copper (Cu)	5	/	5	100	10	27	15	NC	mg/kg
Iron (Fe)	90	/	90	100	5,200	22,000	8,634	9,164	mg/kg
Lead (Pb)	5	/	5	100	6	102	34	NC	mg/kg
Magnesium (Mg)	5	/	5	100	13,700	18,800	15,780	NC	mg/kg
Manganese (Mn)	90	/	90	100	90	370	178	188	mg/kg
Methyl Mercury (MeHg)	92	/	93	99	0.0020	0.12	0.011	0.014	mg/kg
Molybdenum (Mo)	5	/	5	100	1	2	1.2	NC	mg/kg
Nickel (Ni)	5	/	5	100	7	11	8.6	NC	mg/kg
Potassium (K)	5	/	5	100	570	750	644	NC	mg/kg
Sodium (Na)	5	/	5	100	110	150	128	NC	mg/kg
Strontium (Sr)	5	/	5	100	29	40	34	NC	mg/kg
Titanium (Ti)	5	/	5	100	109	207	160	NC	mg/kg
Total Phosphorus (TP)	88	/	88	100	130	540	251	268	mg/kg
Total Kjeldahl Nitrogen (TKN)	85	/	86	99	4	4,480	976	1,136	mg/kg
Total Mercury (Hg)	120	/	121	99	0.58	41	4	5.5	mg/kg
Vanadium (V)	5	/	5	100	10	17	12	NC	mg/kg
Zinc (Zn)	5	/	5	100	40	56	45	NC	mg/kg
Zirconium (Zr)	5	/	5	100	3	3	3	NC	mg/kg

Table 3-1. Surface[a] Sediment Chemistry Summary Statistics for the Area of Interest

Analyte	Number of Detected Samples		Number of Samples	Frequency of Detection %	Minimum Detected Concentration	Maximum Detected Concentration	Mean	95%UCL	Units
Organics									
1,2,4,5-Tetrachlorobenzene	4	/	5	80	0.005	0.021	0.011	NC	mg/kg
1-Methylnapthalene	5	/	5	100	0.08	0.24	0.14	NC	mg/kg
2-Methylnapthalene	5	/	5	100	0.07	0.18	0.11	NC	mg/kg
Acenaphthene	4	/	5	80	0.08	0.4	0.16	NC	mg/kg
Acenaphthylene	5	/	5	100	0.06	0.61	0.21	NC	mg/kg
Anthracene	5	/	5	100	0.07	0.48	0.17	NC	mg/kg
Benzo(a)anthracene	5	/	5	100	0.08	0.56	0.18	NC	mg/kg
Benzo(a)pyrene	5	/	5	100	0.06	0.41	0.14	NC	mg/kg
Benzo(b)fluoranthene	5	/	5	100	0.07	0.36	0.14	NC	mg/kg
Benzo(ghi)perylene	3	/	5	60	0.06	0.17	0.070	NC	mg/kg
Biphenyl	4	/	5	80	0.2	0.5	0.23	NC	mg/kg
Chrysene	5	/	5	100	0.07	0.48	0.16	NC	mg/kg
Dibenzo(a,h)anthracene	1	/	5	20	0.14	0.14	0.048	NC	mg/kg
Fluoranthene	5	/	5	100	0.18	0.51	0.26	NC	mg/kg
Fluorene	5	/	5	100	0.08	0.47	0.18	NC	mg/kg
Hexachlorobenzene (HCB)	105	/	105	100	0.003	1.8	0.081	0.13	mg/kg
Hexachlorobutadiene (HCBD)	93	/	105	89	0.01	0.4	0.040	0.051	mg/kg
Indeno(1,2,3-cd)pyrene	1	/	5	20	0.11	0.11	0.042	NC	mg/kg
Naphthalene	5	/	5	100	0.09	0.43	0.20	NC	mg/kg
Octachlorostyrene (OCS)	105	/	105	100	0.004	1.4	0.057	0.100	mg/kg
PAHs	5	/	5	100	1.4	6.9	2.8	NC	mg/kg
Pentachlorobenzene (QCB)	3	/	5	60	0.009	0.035	0.012	NC	mg/kg
Phenanthrene	5	/	5	100	0.28	1.1	0.51	NC	mg/kg
Pyrene	5	/	5	100	0.26	0.99	0.41	NC	mg/kg

Table 3-1. Surface[a] Sediment Chemistry Summary Statistics for the Area of Interest

Analyte	Number of Detected Samples		Number of Samples	Frequency of Detection %	Minimum Detected Concentration	Maximum Detected Concentration	Mean	95%UCL	Units
Polychlorinated Biphenyls									
PCBs	13	/	17	76	0.01	0.4	0.070	0.13	mg/kg
Aroclor 1254	5	/	5	100	0.012	0.19	0.076	NC	mg/kg
Physical Parameters									
Clay	14	/	14	100	4.6	30.9	11	15	%
Sand	14	/	14	100	8.7	72.4	48	57	%
Silt	14	/	14	100	20.4	69	40	48	%
Silt & Clay	82	/	83	99	0.21	78.1	12	15	%
Total Solids	5	/	5	100	68	76	73	NC	%
Total Organic Carbon (TOC)	122	/	122	100	0.42	4.3	1.5	1.6	%
Moisture	102	/	102	100	17	74	36	38	%

a. Surface sediment defined as 0-15 centimetres; statistics are calculated on sediment results from 2005-2008.
95%UCL: 95% upper confidence limit of the arithmetic mean; calculated using the BCA Bootstrap method with 10,000 bootstrap iterations
mg/kg: milligrams per kilogram

Table 3-2. Subsurface[a] Sediment Chemistry Summary Statistics for the Area of Interest

Analyte	Number of Detected Samples		Number of Samples	Frequency of Detection (%)	Minimum Detected Concentration	Maximum Detected Concentration	Mean	95%UCL	Units
Nutrients and Metals									
Iron	5	/	5	100	7,800	15,050	11,123	NC	mg/kg
Manganese	5	/	5	100	160	250	205	NC	mg/kg
Total Kjeldahl Nitrogen	5	/	5	100	359	762	623	NC	mg/kg
Total Mercury	104	/	106	98	0.07	190	18	24	mg/kg
Organics									
Hexachlorobenzene	92	/	98	94	0.003	2.2	0.27	0.34	mg/kg
Hexachlorobutadiene	90	/	98	92	0.008	9.4	0.27	0.60	mg/kg
Octachlorostyrene	92	/	97	95	0.002	5.3	0.44	0.64	mg/kg
Polychlorinated Biphenyls									
Polychlorinated Biphenyls	87	/	93	94	0.04	3.9	0.43	0.55	mg/kg
Physical Parameters									
Sand	5	/	5	100	42	68	54	NC	%
Silt & Clay	28	/	28	100	11	100	65	72.4	%
Silt	5	/	5	100	26	40	35	NC	%
Clay	5	/	5	100	6	17	11	NC	%
Total Organic Carbon	95	/	95	100	0.7	6.7	2.7	3.0	%
Moisture	5	/	5	100	26	30	28	NC	%

a. Subsurface sediment defined as >15 centimetres; statistics are calculated on sediment results from 2000-2008.

95%UCL: 95% upper confidence limit of the arithmetic mean; calculated using the BCA Bootstrap method with 10,000 bootstrap iterations.
mg/kg: milligrams per kilogram
NC: Not calculated due to small sample size

Table 3-3. Summary Statistics for Mercury and Octachlorostyrene Concentrations in Surface Sediment for Area of Interest

Analyte	Number Detected		Number of Samples	Frequency of Detection (%)	Minimum Detected Concentration	Maximum Detected Concentration	Mean Concentration	Detection Limit[a]	95% UCL[b]	LEL	Percentage of Samples Exceeding LEL	SEL	Percentage of Samples Exceeding SEL
Total Mercury (mg/kg)	120	/	121	99	0.58	41	4.3	0.0050	5.5	0.2	100	2.0	61

Analyte	Number Detected		Number of Samples	Frequency of Detection (%)	Minimum Detected Concentration	Maximum Detected Concentration	Mean Concentration	Detection Limit[a]	95% UCL[b]	Average TOC Concentration (%)	Sediment Quality Guideline (SQG)[c]	Percentage of Samples Exceeding SQG
Octachlorostyrene (mg/kg)	105	/	105	100	0.004	1.4	0.057	0.0050	0.099	1.5	650	0

95%UCL: 95% of the upper confidence level of the arithmetic average
LEL: lowest effects level
mg/kg: milligrams per kilogram
SEL: severe effects level
SQG: sediment quality guideline
TOC: total organic carbon
a. Detection limit applies to samples collected by Pollutech. Detection limit was not provided for samples collected by Environment Canada.
b. 95%UCL calculated using non-parametric BCA Bootstrap Method with 10,000 iterations.

Table 4-1. Probabilities of Test Sites Belonging to 1 of 6 Great Lakes Faunal Groups Using a Revised BEAST Model (2001 sites only)

Site	Probability of Group Membership (%)					
	Group 1	Group 2	Group 3	Group 4	Group 5	Group 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[a]	0.346	0.084	**0.530**	0.039	0.000	0.000
6666[a]	0.301	0.086	**0.586**	0.027	0.000	0.000
6667[a]	0.305	0.070	**0.604**	0.020	0.000	0.000
6668[a]	0.321	0.073	**0.549**	0.056	0.000	0.000
6669[a]	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

Highest probability for each site is bolded
Source: Milani et al. 2007; Table 8
a. denotes AOI stations

Table 4-2. 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: AOI Sites

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

Families expected to be at test sites that are absent are highlighted
a. QA/QC site numbers represent the average of three field replicates.
Source: Milani et al. 2007; Table 9c

Table 4-3. Benthic Macroinvertebrate Results Summary

Number of Taxa

Location	1	2	3	4	5	6	7	8	9
Rep 1	31	19	16	17	13	20	12	29	17
Rep 2	29	21	6	12	11	18	14	29	14
Rep 3	32	24	7	19	16	16	18	25	11
Average	30.7	21.3	9.7	16.0	13.3	18.0	14.7	27.7	14.0

Location	U.S. - 1	U.S. - 2	U.S. - 3	U.S. - 4	U.S. - 5	U.S. - 6	U.S. - 7	U.S. - 8
Rep 1	25	21	23	23	22	36	41	28
Rep 2	23	28	31	24	26	30	36	27
Rep 3	22	41	32	22	24	33	30	30
Average	23.3	30.0	28.7	23.0	24.0	33.0	35.7	28.3

Abundance

Location	1	2	3	4	5	6	7	8	9
Rep 1	276	113	136	333	167	624	38	179	226
Rep 2	312	121	58	144	37	542	50	139	376
Rep 3	366	114	38	539	95	223	42	150	58
Average	318.0	116.0	77.3	338.7	99.7	463.0	43.3	156.0	220.0

Location	U.S. - 1	U.S. - 2	U.S. - 3	U.S. - 4	U.S. - 5	U.S. - 6	U.S. - 7	U.S. - 8
Rep 1	233	120	223	955	466	1071	1377	854
Rep 2	459	323	382	872	849	415	866	815
Rep 3	367	400	267	395	1034	612	385	470
Average	353.0	281.0	290.7	740.7	783.0	699.3	876.0	713.0

Source: Moran et al. 2005: Table 4.5.1

Table 5-1. Summary of Invertebrate Toxicity Results for the Area of Interest and Upstream Reference Sites

Station*	*Hyalella azteca*[a]		*Chironomus tentans*[b]		*Chironomus riparius*[c]		*Hexagenia spp.*[d]		*Tubifex tubifex*[e]				Reference
	Growth (mg)	Survival (%)	Growth (mg)	Survival (%)	Growth (mg)	Survival (%)	Growth (mg)	Survival (%)	Survival (%)	Cocoons Hatched (%)	No. Cocoons/ Adult	No. Young/ Adult	
Upstream Reference													
6660	0.49	91	--	--	0.46	95	3.2	100	100	62	12	28	Milani et al. 2007
CAN #1_C	0.31	***52***	3.7	***86***	--	--	--	--	--	--	--	--	Moran et al. 2005
6648	0.70	93	--	--	0.34	85	9.8	100	100	54	12	31	Milani et al. 2007
6697	0.56	97	--	--	0.38	83	6.0	98	100	57	12	28	Milani et al. 2007
6661	0.64	76	--	--	0.36	87	7.1	98	100	59	12	37	Milani et al. 2007
6698	0.70	84	--	--	0.58	95	8.3	96	100	53	13	36	Milani et al. 2007
Area of Interest													
6665	0.86	99	--	--	0.50	97	5.1	100	100	59	12	27	Milani et al. 2007
CAN #4_C	0.19	***24***	5.4	100	--	--	--	--	--	--	--	--	Moran et al. 2005
66M76	0.53	92	--	--	0.37	96	8.2	100	100	53	12	29	Milani et al. 2007
CAN #5_C	0.14	84	5.0	94	--	--	--	--	--	--	--	--	Moran et al. 2005
6699	0.69	93	--	--	0.48	95	6.6	100	100	53	12	26	Milani et al. 2007
66M262	0.42	95	--	--	0.48	88	1.6	100	100	56	9	22	Milani et al. 2007
66M272	0.38	87	--	--	0.32	92	7.5	100	100	53	11	25	Milani et al. 2007
6666	0.67	95	--	--	0.38	91	2.1	***76***	100	53	11	20	Milani et al. 2007
66M253	0.60	98	--	--	0.39	84	7.7	100	100	52	10	28	Milani et al. 2007
66M271	0.34	92	--	--	0.40	92	1.0	92	100	51	10	35	Milani et al. 2007
66M144	0.26	81	--	--	0.30	85	2.5	98	100	53	***5***	6	Milani et al. 2007
CAN #6_C	0.21	100	4.1	88	--	--	--	--	--	--	--	--	Moran et al. 2005
6667	0.57	89	--	--	0.39	95	8.3	98	100	55	12	27	Milani et al. 2007
CAN #7_C	0.18	***16***	***2.3***	***66***	--	--	--	--	--	--	--	--	Moran et al. 2005
66M80	0.69	95	--	--	0.36	93	7.7	100	100	54	12	34	Milani et al. 2007
66M269	0.55	91	--	--	0.26	89	9.1	98	100	48	11	23	Milani et al. 2007
CAN #8_C	0.08	***18***	3.8	86	--	--	--	--	--	--	--	--	Moran et al. 2005
6668	0.61	97	--	--	0.46	73	6.8	100	100	56	12	24	Milani et al. 2007
66M264	0.47	95	--	--	0.45	89	7.2	100	100	48	8	15	Milani et al. 2007
6669	0.60	94	--	--	0.39	92	7.9	99	100	56	11	32	Milani et al. 2007

a. 14-day test for Moran et al. 2005; 28-day test for Milani et al. 2007
b. 10-day test
c. 10-day test
d. 21-day test
e. 28-day test
* Stations are listed in order, upstream to downstream.
-- not tested
Bold and italic values indicate a significant inhibitive effect.

Table 5-2. Fathead Minnow *In Situ* Toxicity Test Results - Percent Survival and Average Lengths and Weights

Monitoring Location Number	Repetition	% Survival	Average Length (mm)	Average Weight (g)
1	1	100	27.5	0.2244
	2	90	28.8	0.2338
	3			
	Average	95	28.1	0.2291
2	1	90	33.8	0.3989
	2	90	33.3	0.4008
	3	100	31.9	0.3475
	Average	93.3	33.0	0.3824
3	1	100	25.5	0.1920
	2	100	30.5	0.2937
	3	90	33.4	0.4146
	Average	96.7	29.8	0.3001
4	1	100	25.9	0.1905
	2	80	31.0	0.3247
	3	80	30.6	0.2995
	Average	86.7	29.2	0.2715
5	1	90	27.7	0.2245
	2	80	27.4	0.2004
	3	70	32.6	0.3613
	Average	80.0	29.2	0.2621
6	1	60	29.8	0.2513
	2	90	27.7	0.2101
	3	50	35.6	0.4604
	Average	66.7	31.0	0.3073
7	1	80	30.6	0.3154
	2	90	26.4	0.2061
	3	70	31.3	0.3061
	Average	80.0	29.5	0.2759
8	1			
	2	100	29.3	0.2408
	3	70	29.0	0.2435
	Average	85.0	29.2	0.2421
9	1	100	28.3	0.2474
	2	90	34.3	0.4557
	3	100	29.1	0.2825
	Average	95.0	31.7	0.3691

The cage was damaged. Therefore, the data has been omitted

Source: Moran et al. 2005

g: gram

mm: millimetre

Table 6-1. Derivation of Site-specific Invertebrate-to-Fish Biomagnification Factor for Mercury

Area	Concentration of Mercury in Redhorse Sucker (mg/kg)	Concentration of Mercury in Northern Pike (mg/kg)	Concentration of Methylmercury in Oligochaete (mg/kg)	Concentration of Methylmercury in Chironomid (mg/kg)	BMF: Oliochaete to Fish		BMF: Chironomid to Fish	
					Redhorse Sucker	Northern Pike	Redhorse Sucker	Northern Pike
Sarnia[a]	0.08	0.15	0.0014	0.017	55	110	4.4	9
Stag Island	0.25	0.24	0.015	0.072	16	15	3.5	3.3
Port Lambton[b]	0.15	0.14	0.011	0.018	14	13	8.5	8.1

a. Due to the low oligochaete methylmercury concentrations measured in the Sarnia reference area, these values were not used in the determination of the site specific BMF
b. The interbrate samples were collected from a location 7 kilometres north of Port Lambton
BMF: biomagnification factor

Table 6-2. Derivation of Target Oligochaete Tissue Concentrations in the Area of Interest

Oligochaete to Fish BMF		Target Fish Tissue Concentration (mg/kg)	Target Oligochaete Tissue Concentrations (mg/kg MeHg)[a]	Oligochaete Tissue SWAC[b]	Oligochaete Tissue Concentration Defining Remediation Zone[c]	Area Requiring Remediation to Achieve Target Oligochaete Concentration (m^2)
Low End	13	0.20	0.0154	0.020	0.027	47,100
High End	16	0.20	0.0125	0.020	0.025	69,700

BMF: biomagnification factor
MeHg: methylmercury
SWAC: spatially weighted average concentration
m^2: square metres

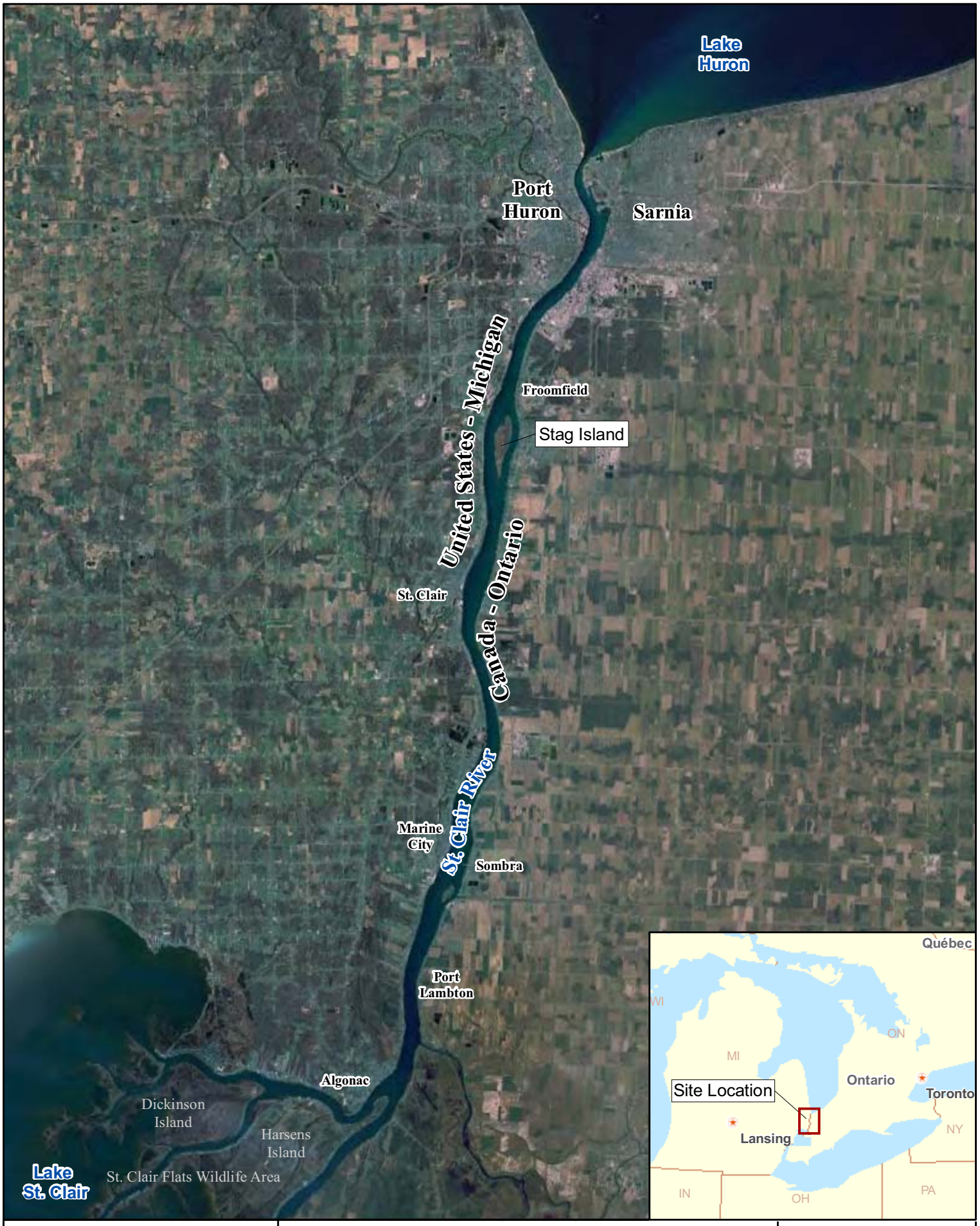
a. Target oligochaete tissue concentration = Target fish tissue concentration / BMF

b. SWAC calculation based on an interpolated surface, where the concentration of each pixel is multiplied by the area of each pixel using the following equation:

$$SWAC = \frac{\sum Ci \times Ai}{\sum Ai}$$ where Ci = concentration in oligochaete tissue and Ai = area

c. Concentration calculated by iteratively replacing higher tissue concentrations with zero until the oligochaete tissue SWAC < target tissue concentration

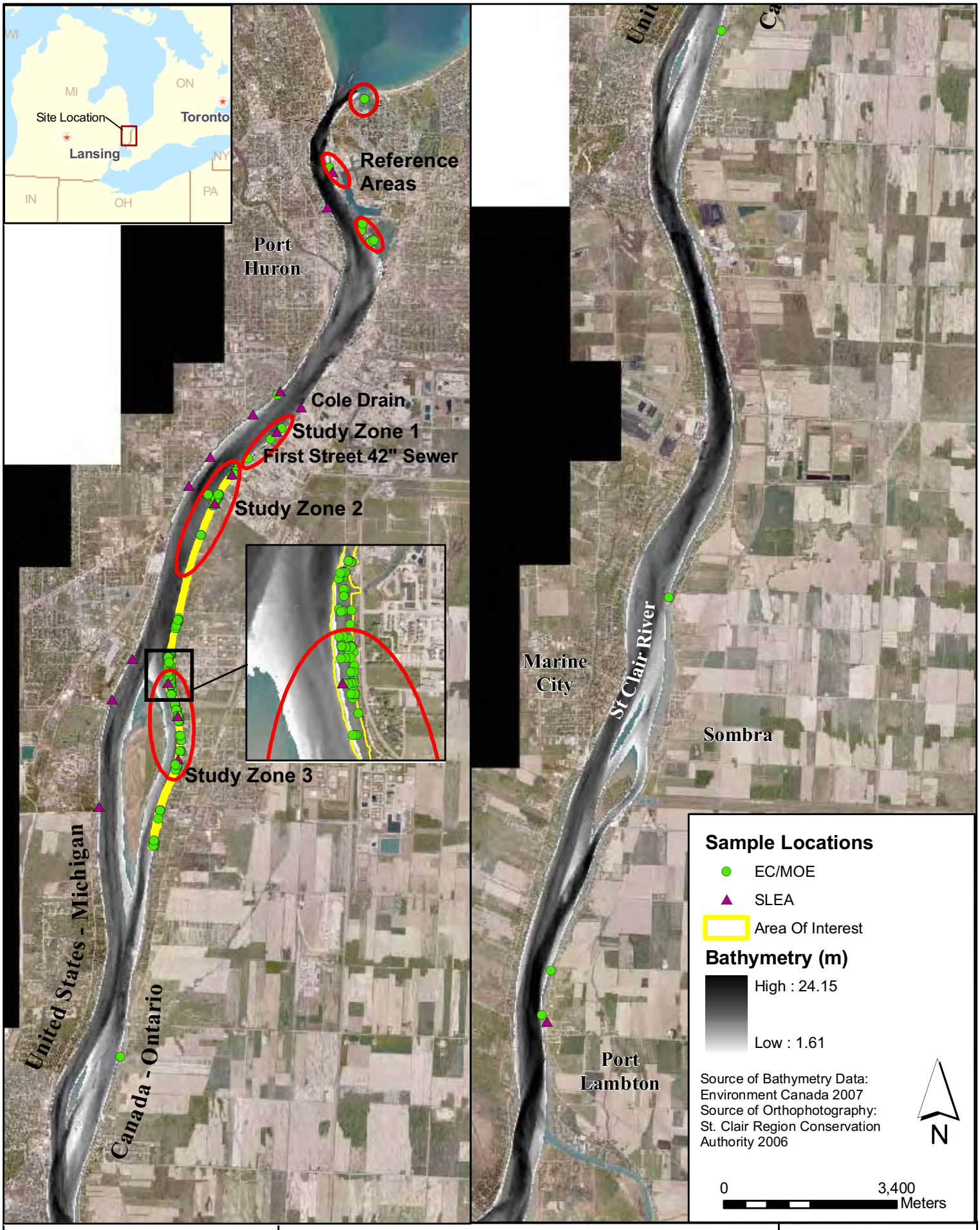
Figures



ENVIRON

St. Clair River Location

Figure 1-1



ENVIRON

St. Clair River Zones and Sampling Stations (2000-2008)

Figure 1-2

Thursday, February 19, 2009 2:37:55 PM
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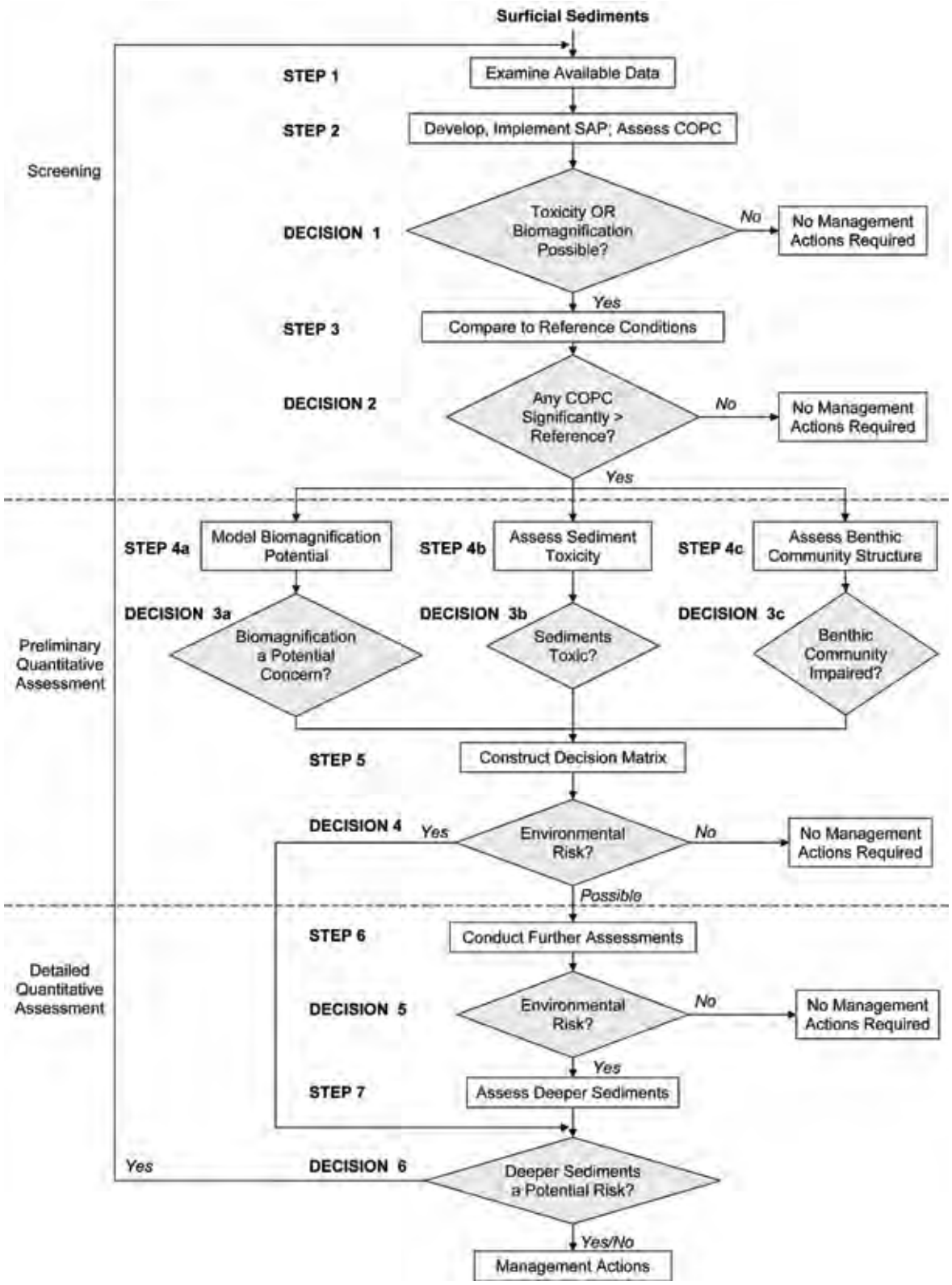
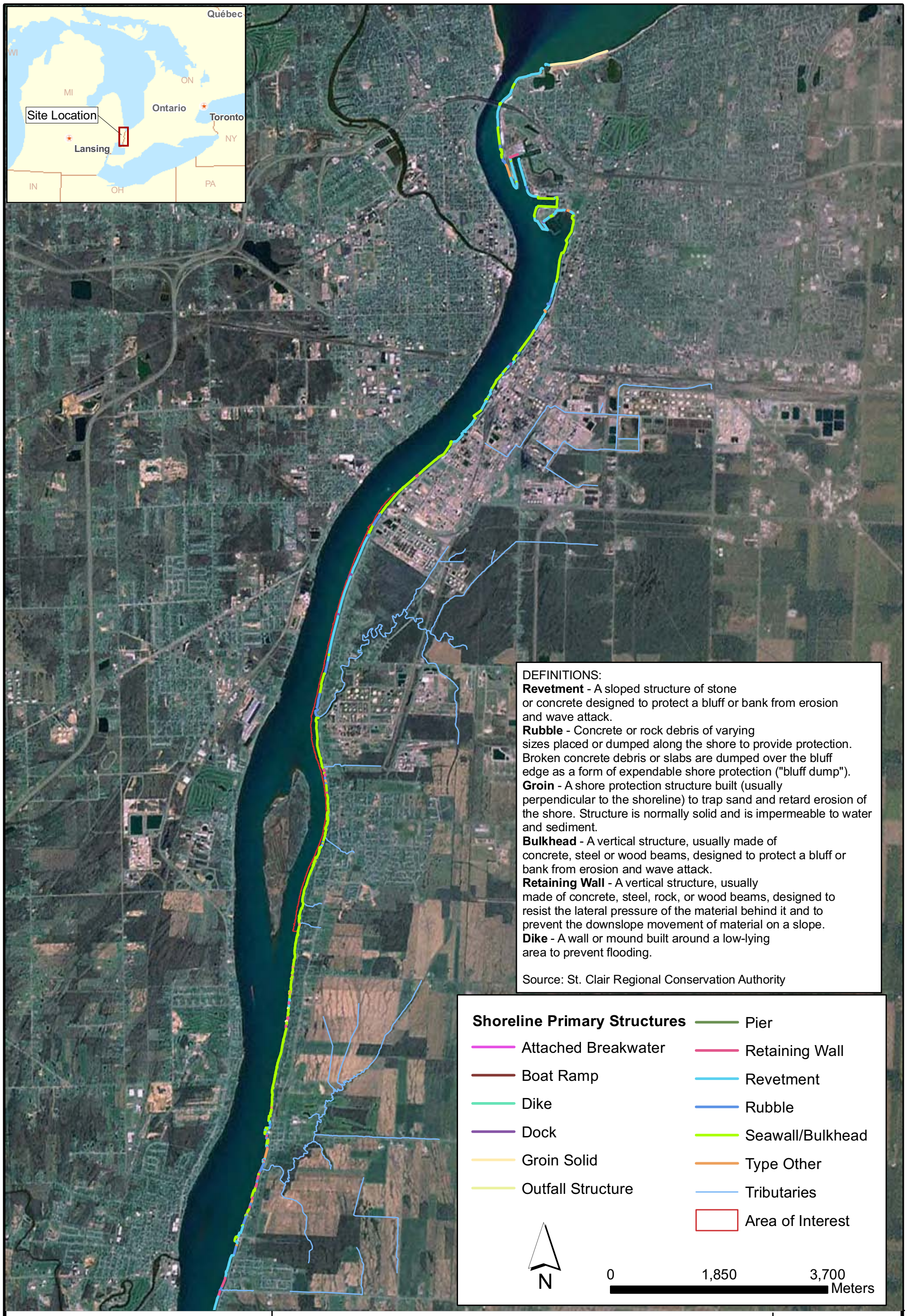


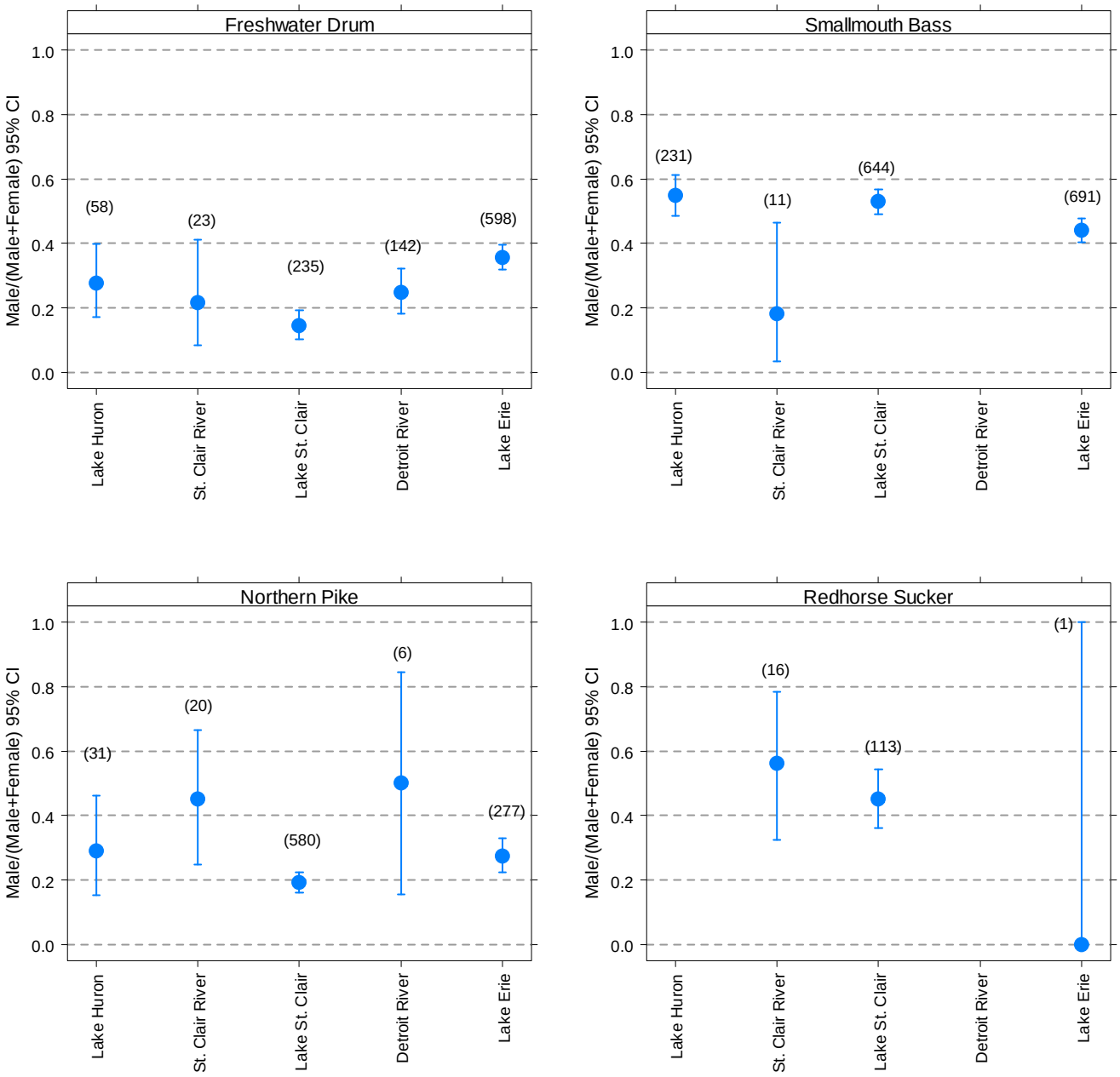
Figure 1-3. Canada-Ontario Decision-Making Framework for Assessment of Great Lakes Contaminated Sediment



ENVIRON

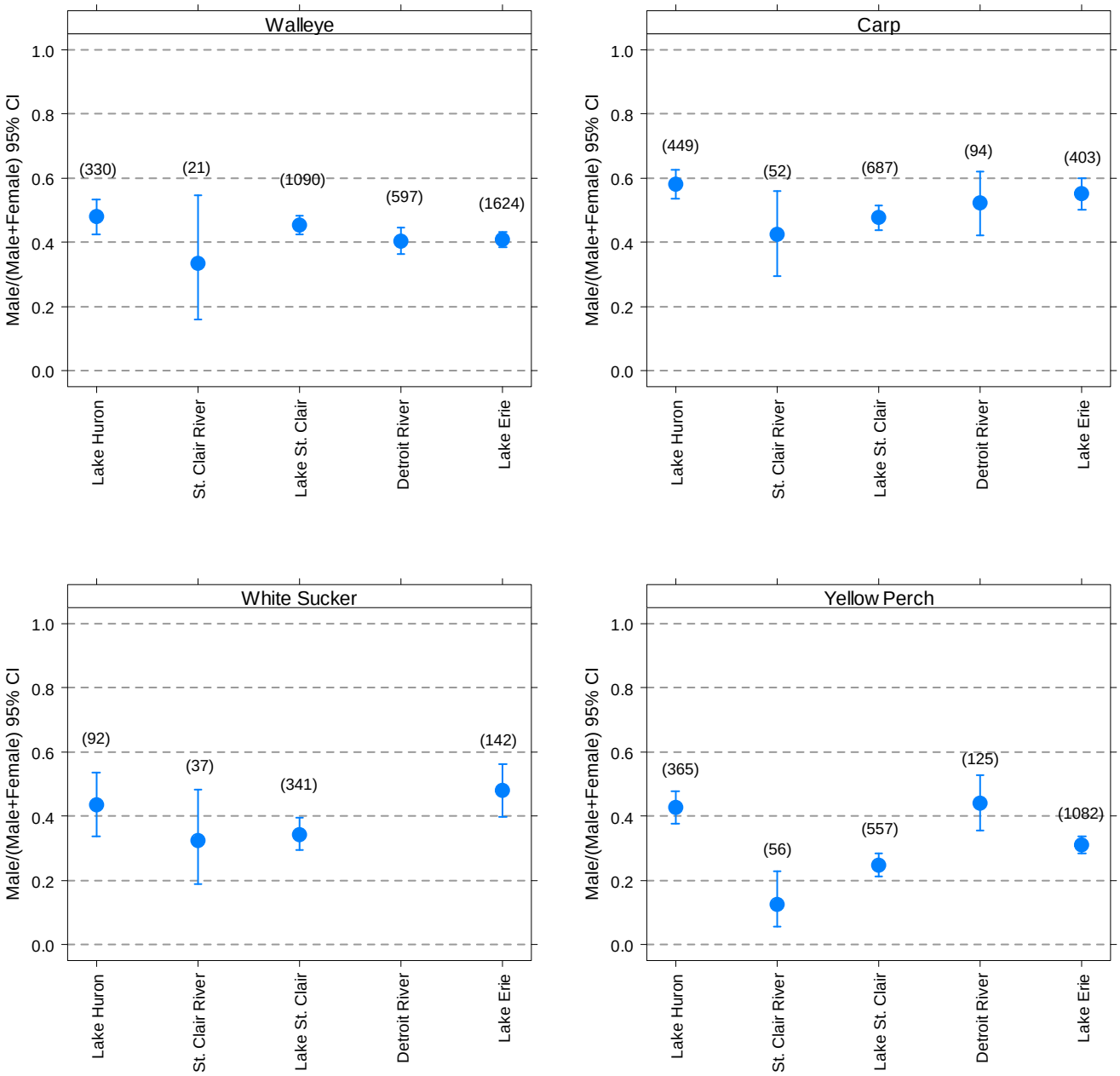
Shoreline Structures Along the Canadian Side of the St. Clair River

Figure 2-1



Note: Values in parentheses are sample sizes

ENVIRON	Comparison of Average Sex Ratios and 95% Confidence Intervals in Fish by Water Body	Figure 2-2 Page 1 of 3

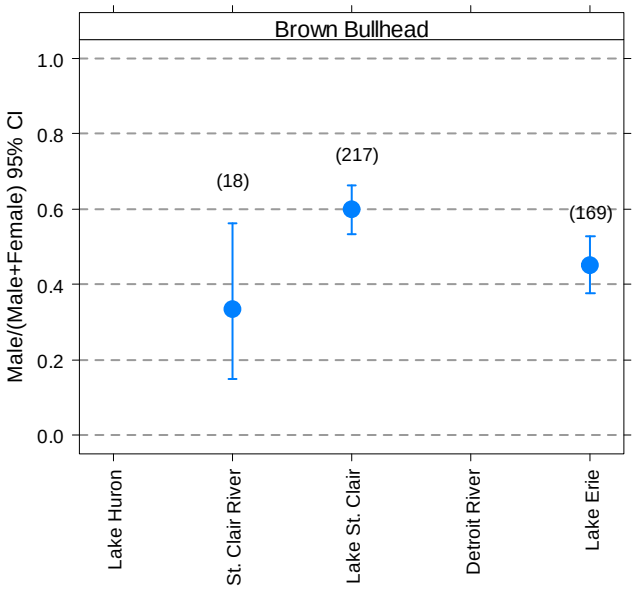


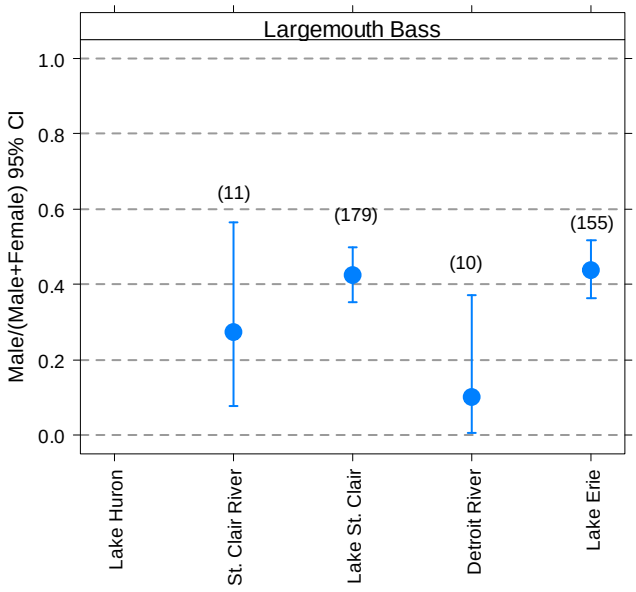
Note: Values in parentheses are sample sizes

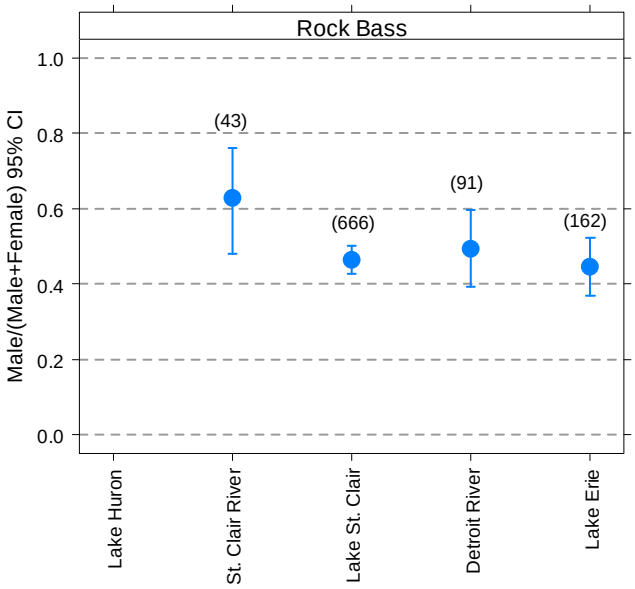
ENVIRON

Comparison of Average Sex Ratios and 95% Confidence Intervals in Fish by Water Body

Figure 2-2





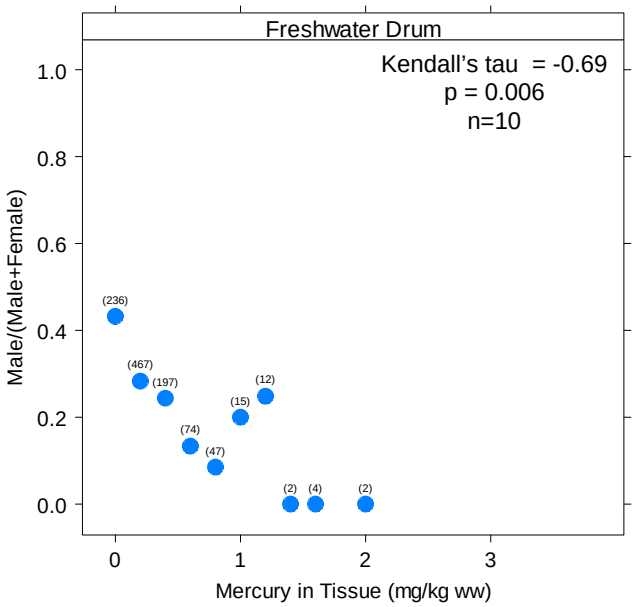


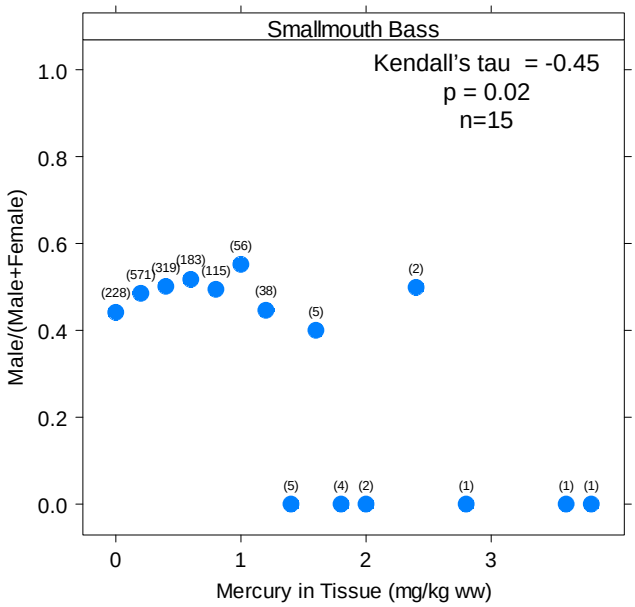
Note: Values in parentheses are sample sizes

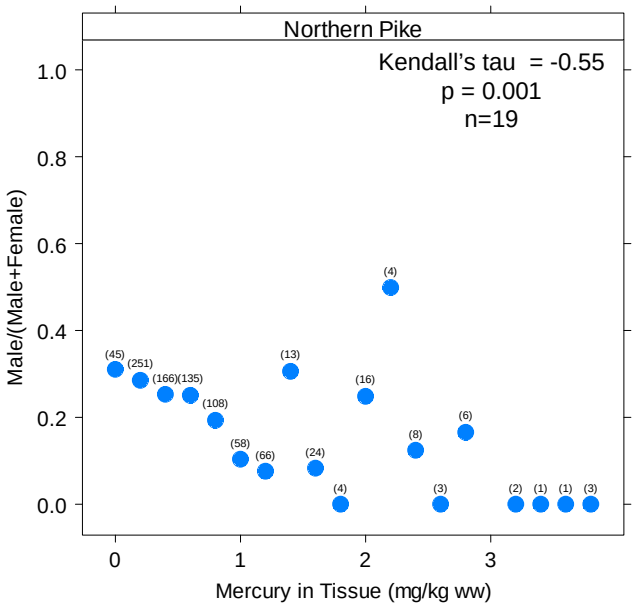
ENVIRON

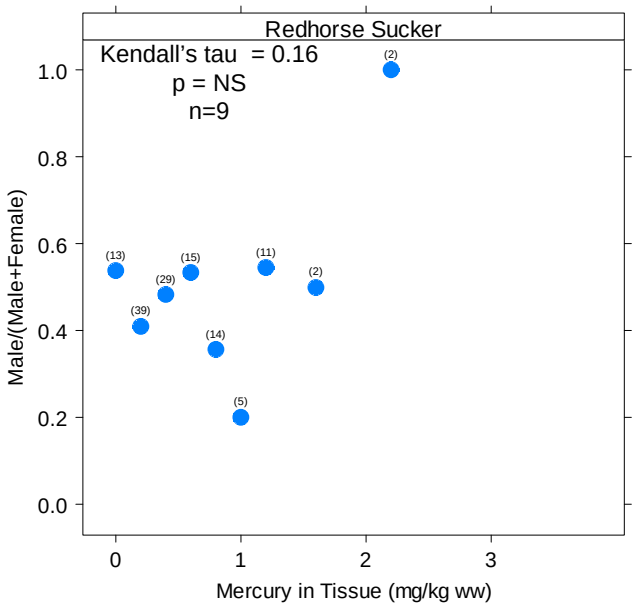
Comparison of Average Sex Ratios and 95% Confidence Intervals in Fish by Water Body

Figure 2-2







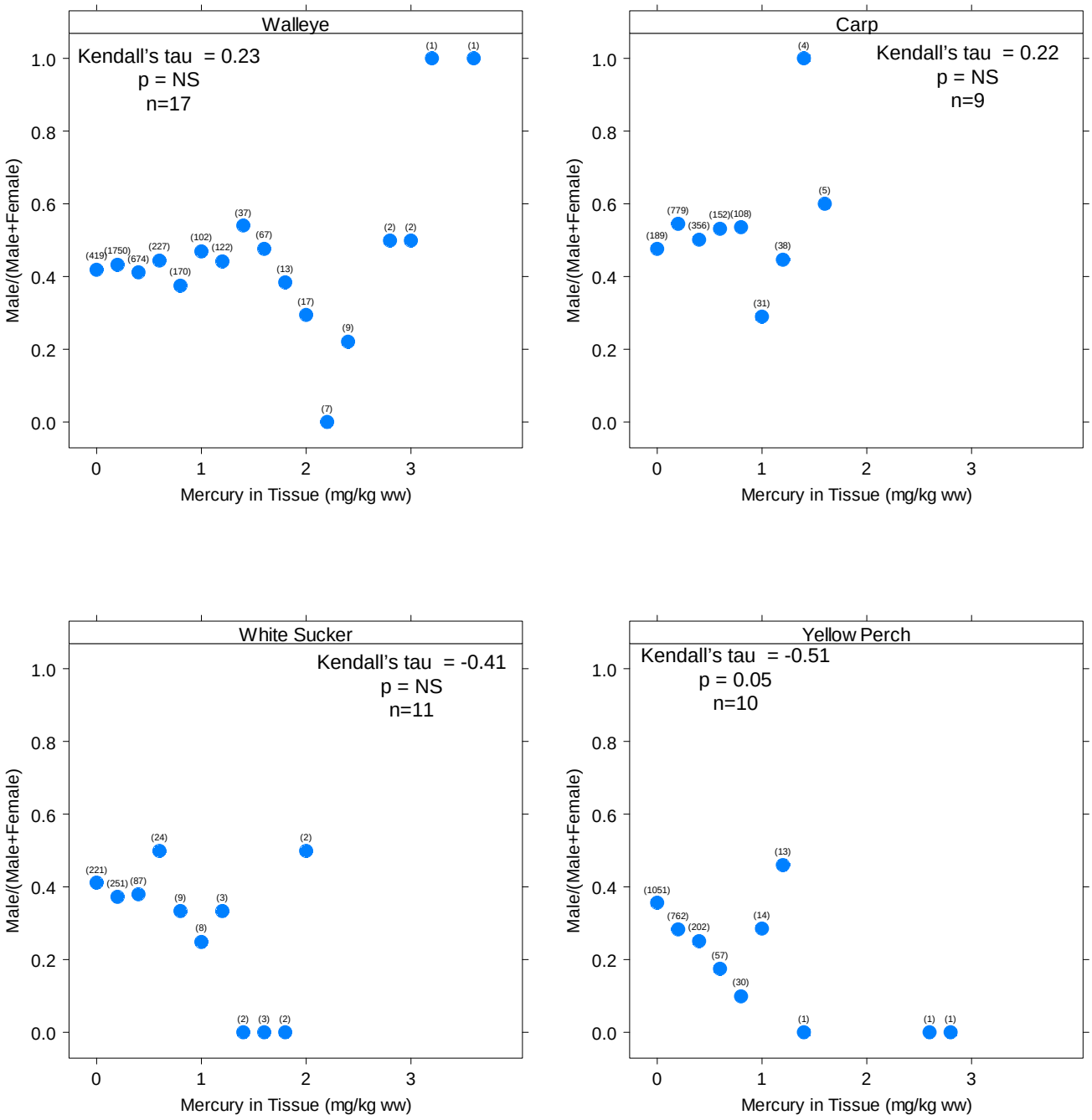


Note: n refers to the number of bins, while values in parentheses refer to the numbers of samples per bin

ENVIRON

Comparison of Sex Ratios to Fish Tissue Mercury Concentrations By Species

Figure 2-3

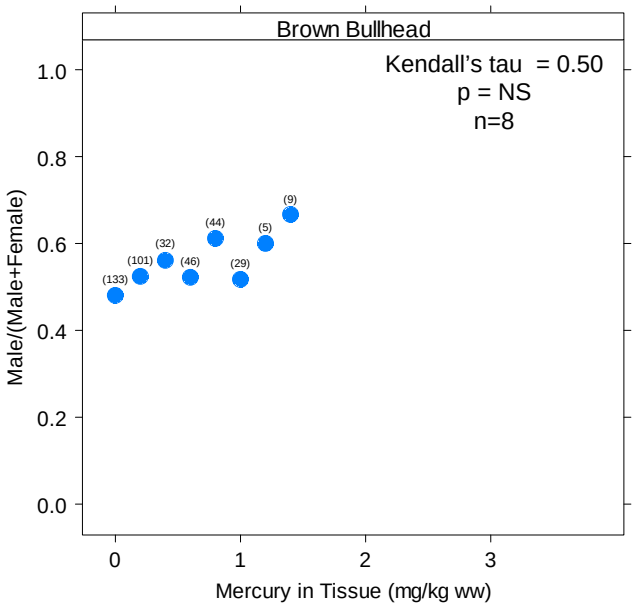


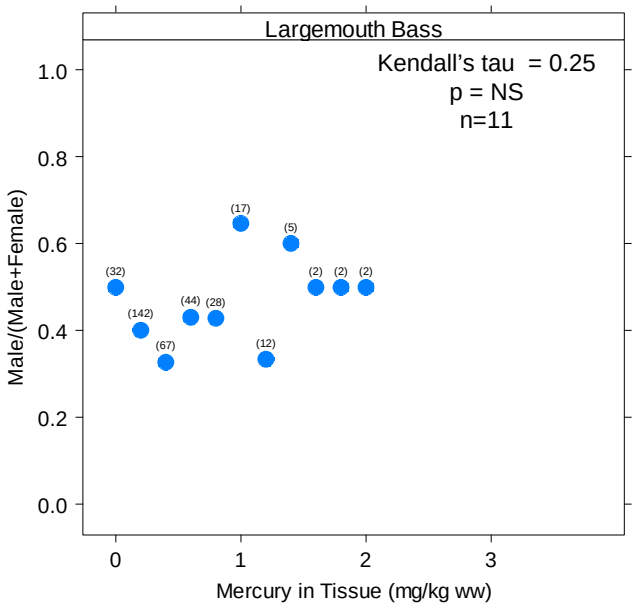
Note: n refers to the number of bins, while values in parentheses refer to the numbers of samples per bin

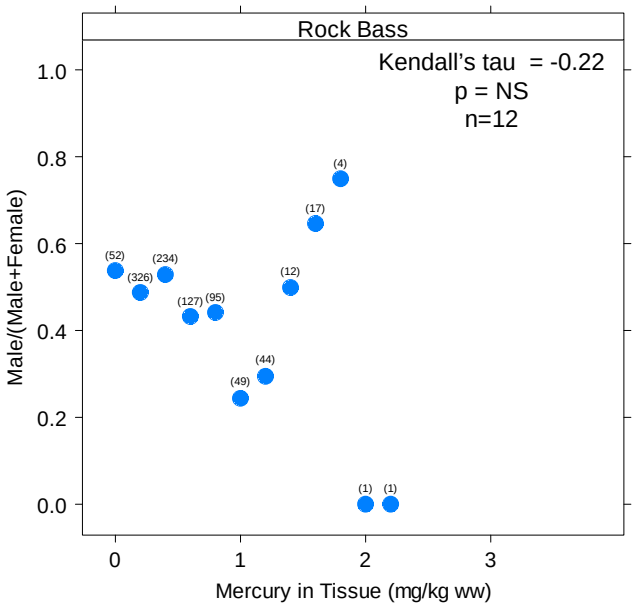
ENVIRON

Comparison of Sex Ratios to Fish Tissue Mercury Concentrations By Species

Figure 2-3





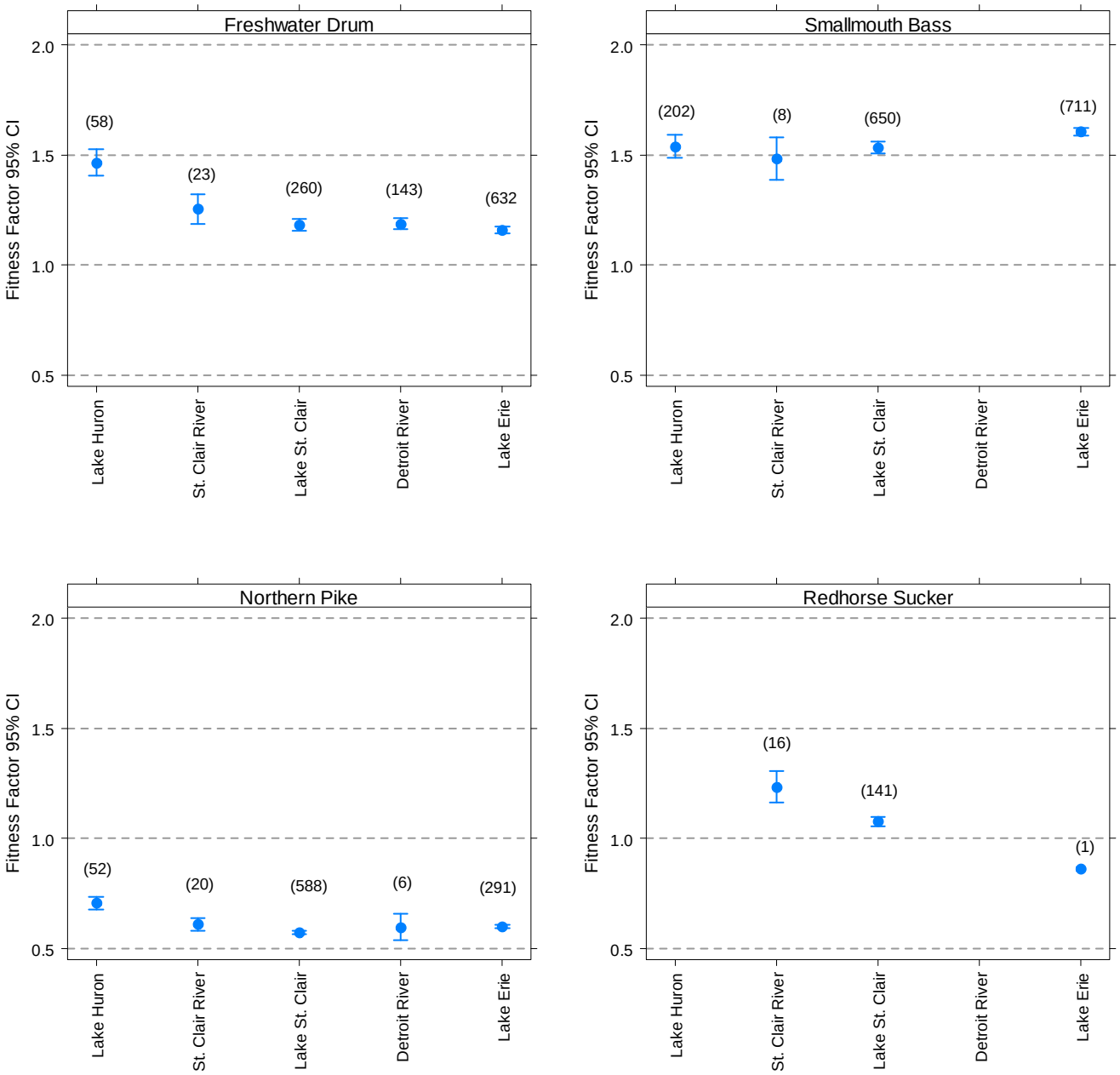


Note: n refers to the number of bins, while values in parentheses refer to the numbers of samples per bin

ENVIRON

Comparison of Sex Ratios to Fish Tissue Mercury Concentrations By Species

Figure 2-3

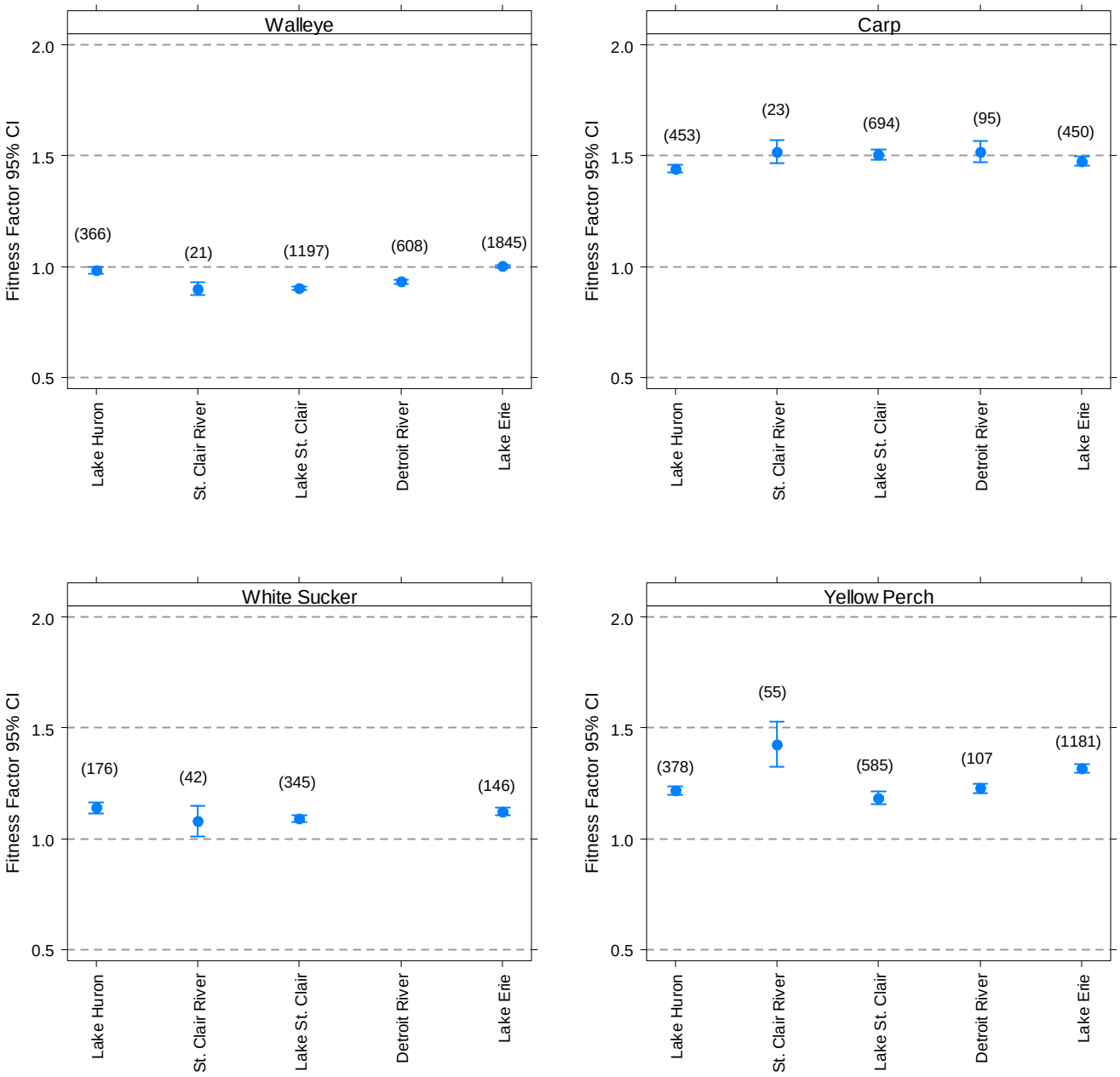


Note: Values in parentheses are sample sizes

ENVIRON

Comparison of Fitness Factors and 95% Confidence Intervals in Fish by Water Body

Figure 2-4

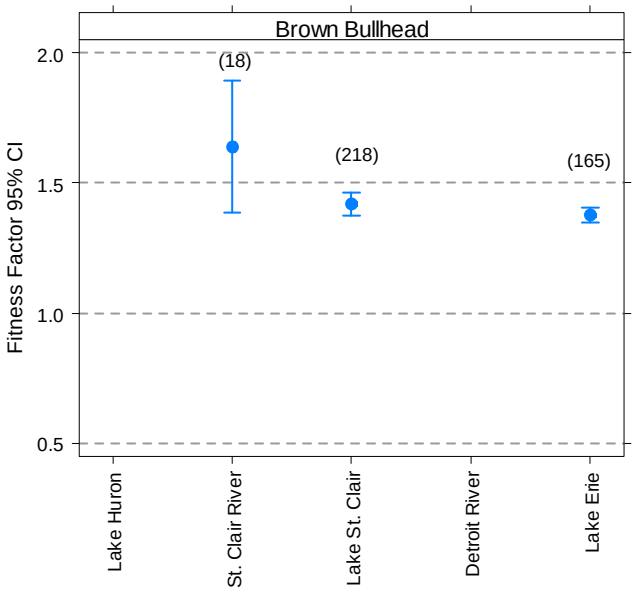


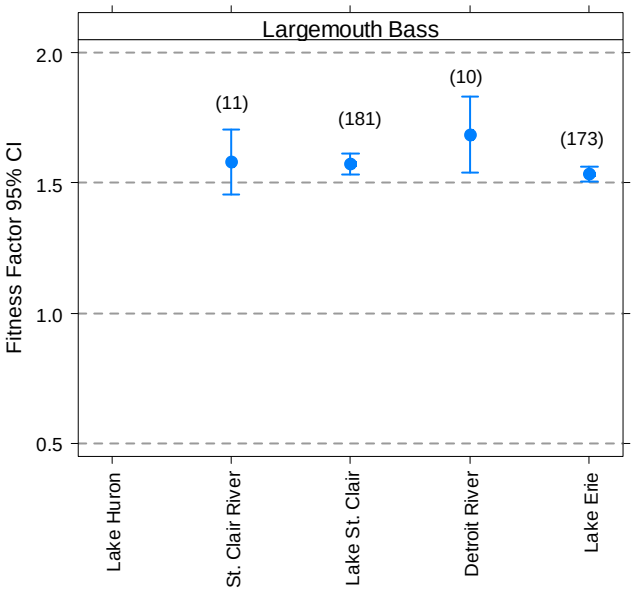
Note: Values in parentheses are sample sizes

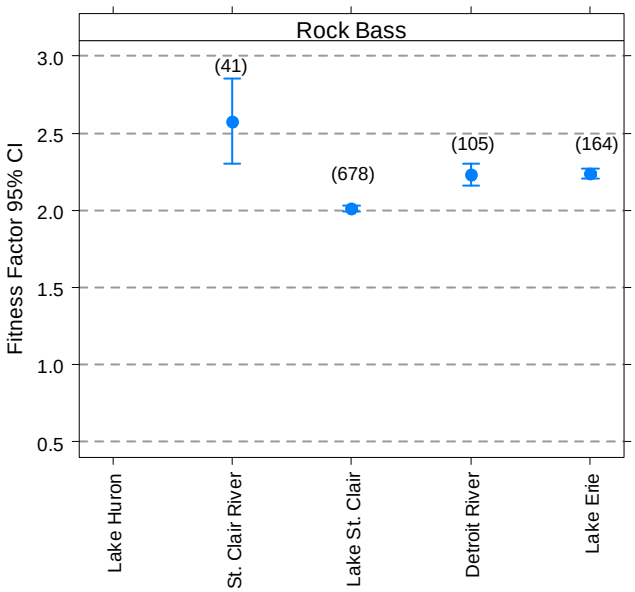
ENVIRON

Comparison of Fitness Factors and 95% Confidence Intervals in Fish by Water Body

Figure 2-4

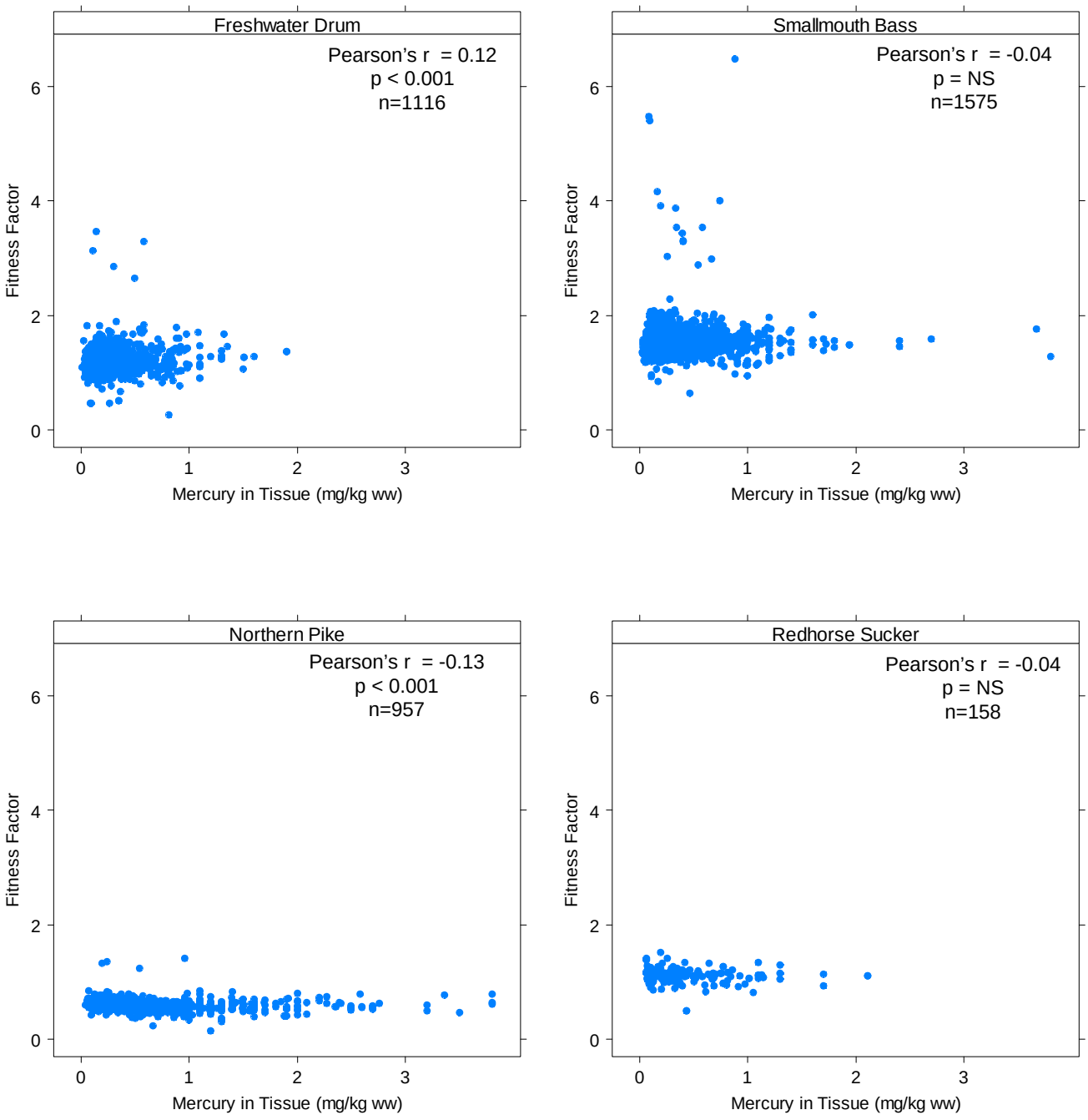






Note: Values in parentheses are sample sizes

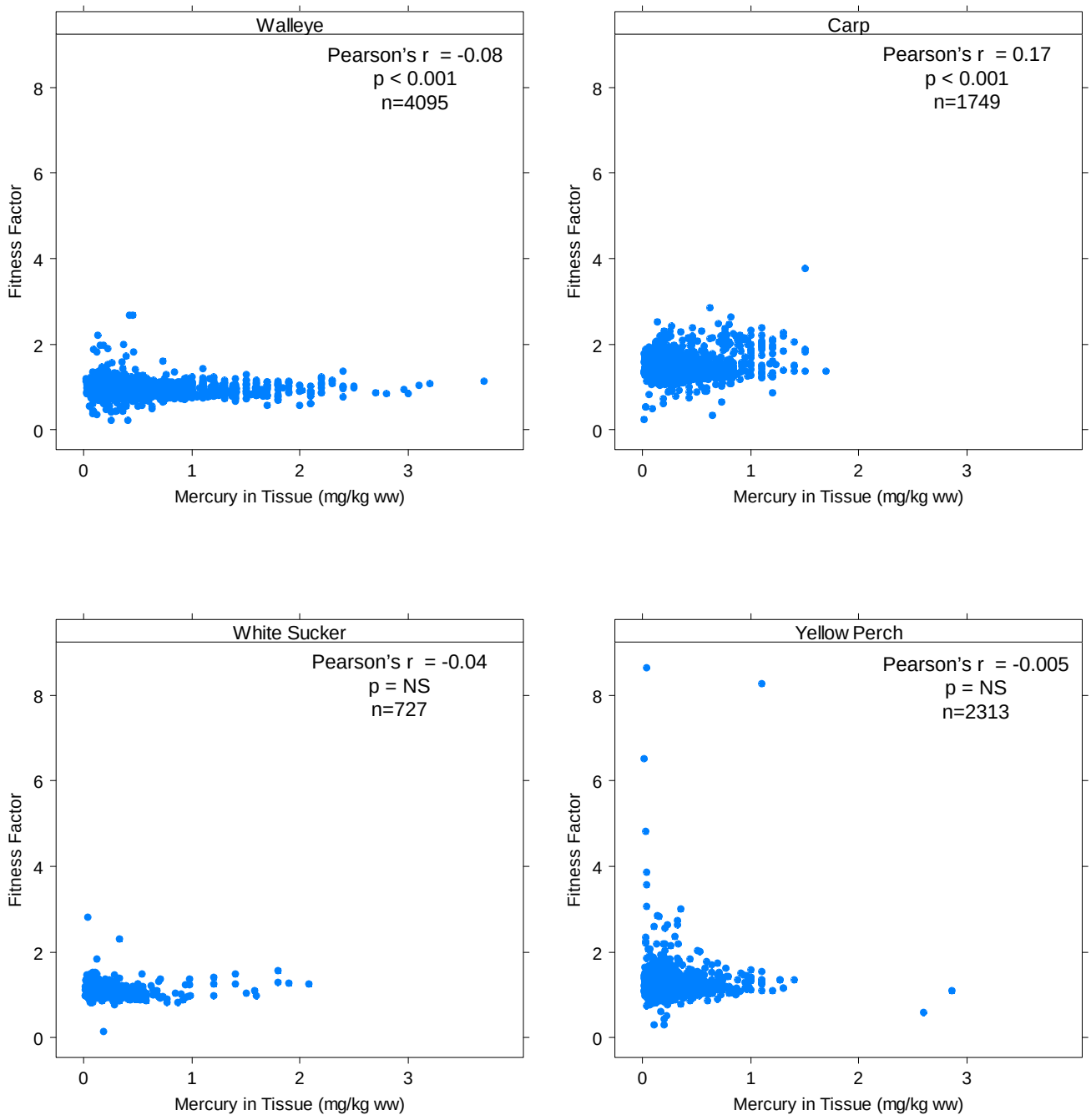
ENVIRON	Comparison of Fitness Factors and 95% Confidence Intervals in Fish by Water Body	Figure 2-4 Page 3 of 3



ENVIRON

Comparison of Fitness Factors to Fish Tissue Mercury Concentrations by Species

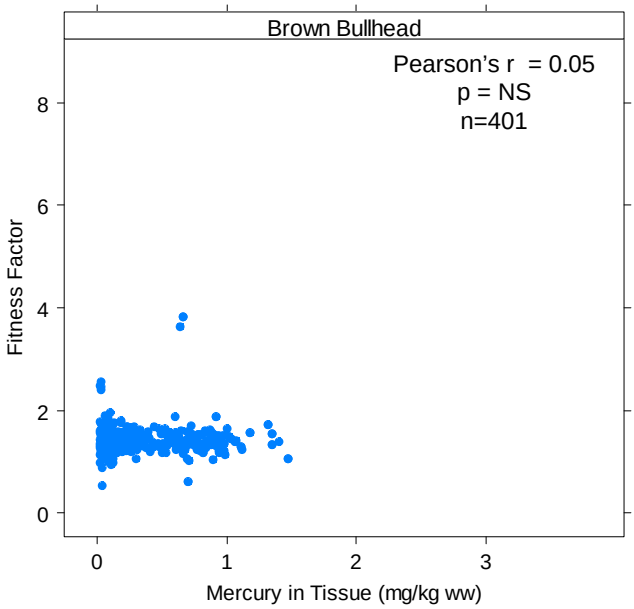
Figure 2-5

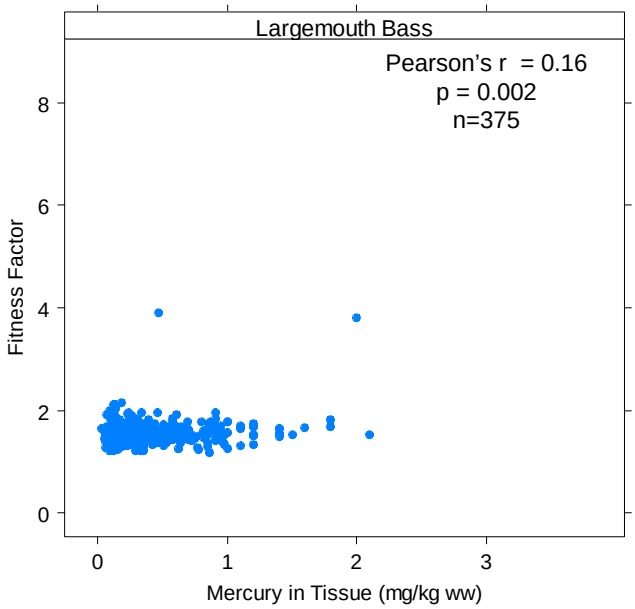


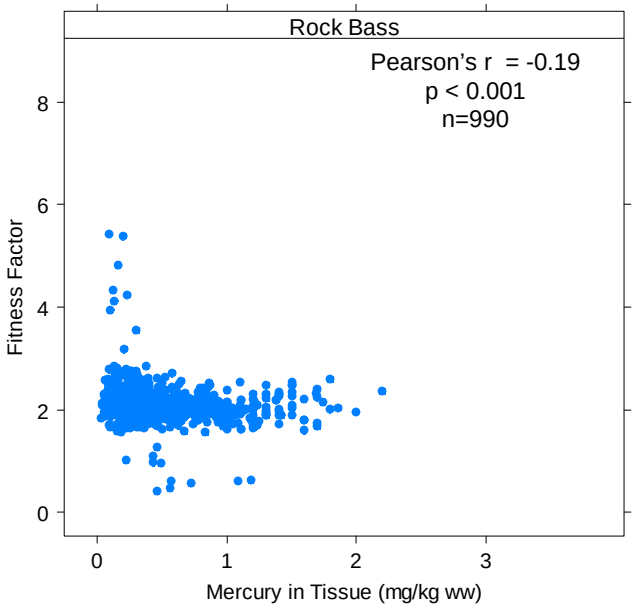
ENVIRON

Comparison of Fitness Factors to Fish Tissue Mercury Concentrations by Species

Figure 2-5



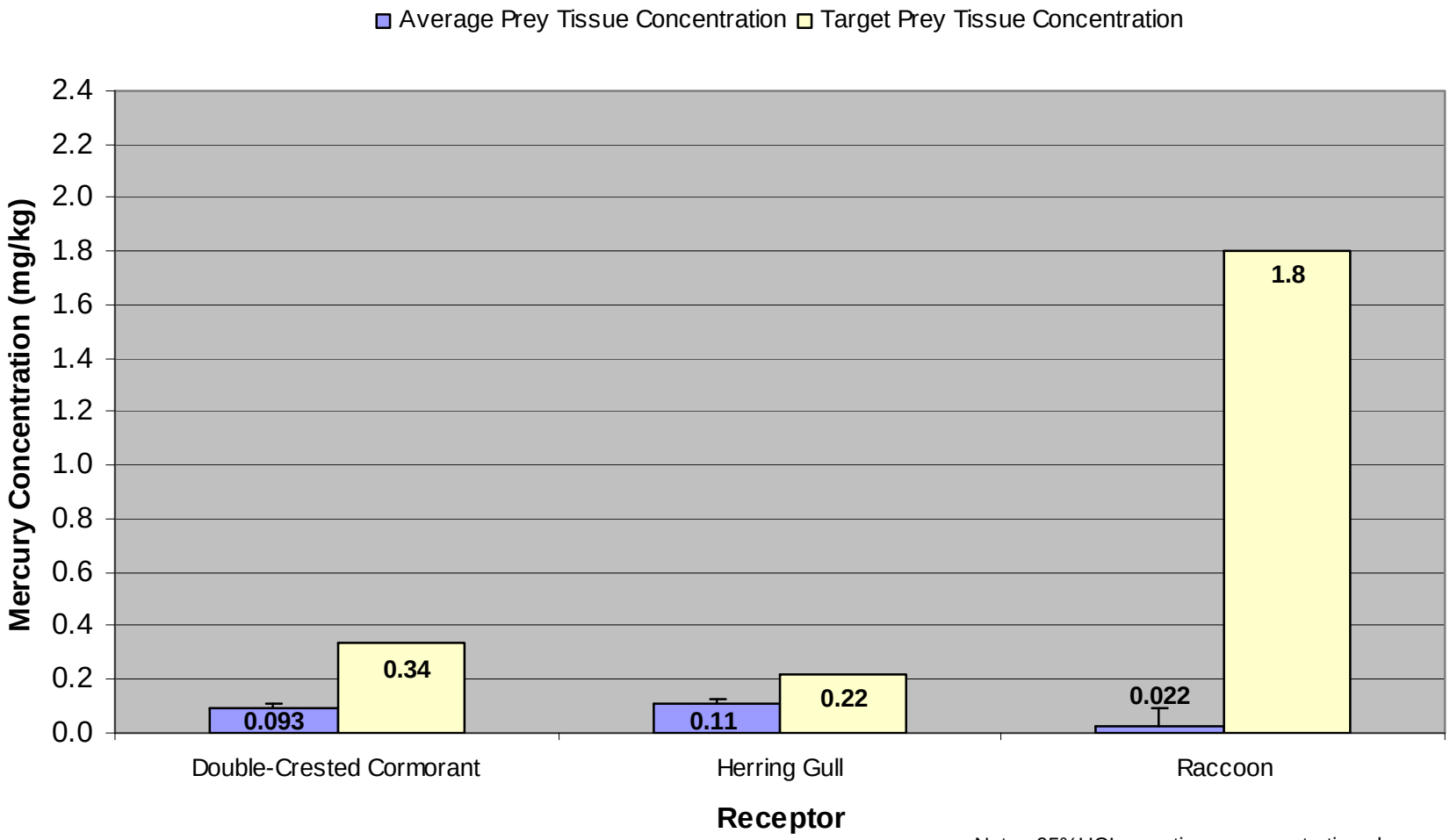




ENVIRON

Comparison of Fitness Factors to Fish Tissue
Mercury Concentrations by Species

Figure
2-5

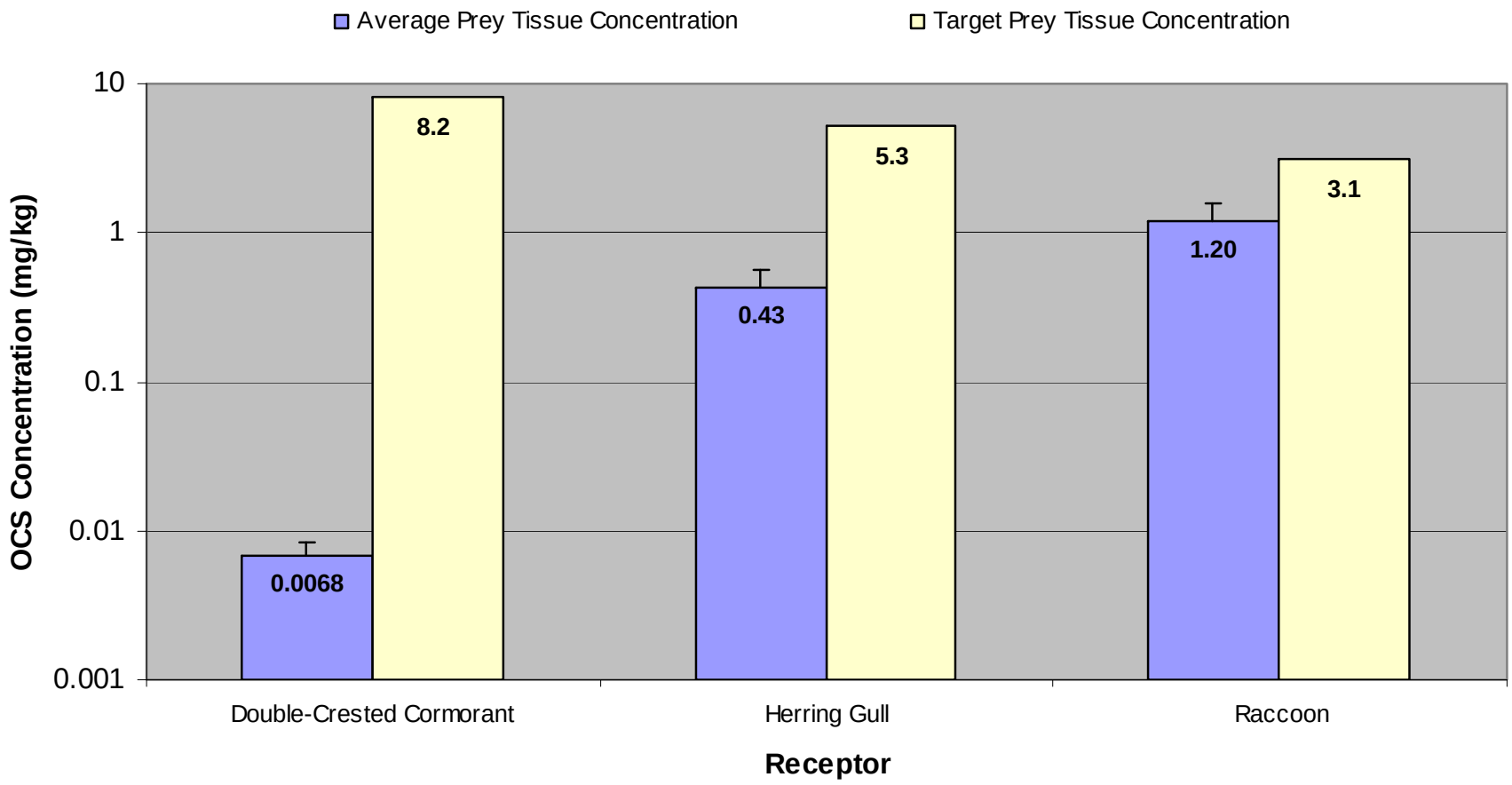


Note: 95%UCL prey tissue concentration shown as a "whisker" on each bar.

ENVIRON

Target Prey Concentrations Compared to Measured Mercury Prey Tissue Concentrations in the Area of Interest

Figure 2-6

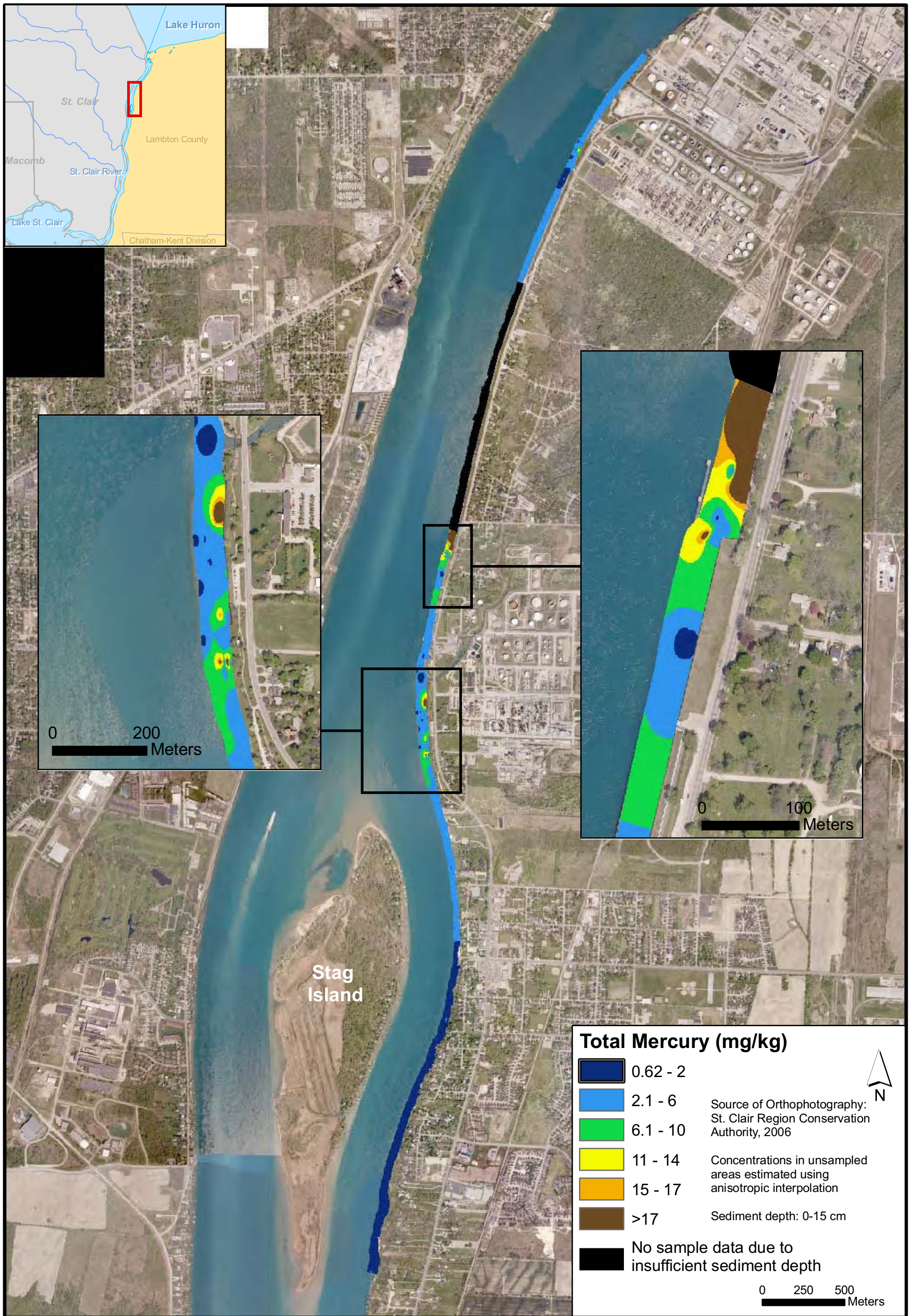


Note: 95%UCL prey tissue concentration shown as a "whisker" on each bar.

ENVIRON

Target Prey Concentrations Compared to Measured Octachlorostyrene Prey Tissue Concentrations in the Area of Interest

Figure 2-7



ENVIRON

Spatial Trends in Total Mercury Concentrations in Surface Sediment (2005-2008)

Figure 3-1

Thursday, March 5, 2009 4:07:17 PM
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0 100 Meters

0 100 Meters

0 100 Meters

0 100 Meters

Stag Island

Lake Huron
St. Clair
Lambton County
Macomb
St. Clair River
Lake St. Clair
Chatham-Kent Division

No sample data due to insufficient sediment depth

Methylmercury (mg/kg)

- ≤0.003
- 0.003-0.005
- 0.0051-0.010
- 0.011-0.020
- 0.021-0.030
- 0.031-0.040
- 0.041-0.050
- >0.05

Source of Orthophotography: St. Clair Region Conservation Authority, 2006

Concentrations in unsampled areas estimated using anisotropic interpolation

Sediment depth: 0-15 cm

N

0 500 Meters

ENVIRON

Spatial Trends in Methylmercury Concentrations in Surface Sediment (2005-2008)

Figure 3-2

Thursday, March 5, 2009 4:39:48 PM
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0 100 Meters

0 100 Meters

0 100 Meters

Stag Island

Lake Huron
St. Clair
Lambton County
Macomb
St. Clair River
Lake St. Clair
Chatham-Kent Division

No sample data due to insufficient sediment depth

Octachlorostyrene (mg/kg)

- 0.004 - 0.04
- 0.041 - 0.1
- 0.11 - 0.2
- 0.21 - 0.4
- 0.41 - 0.6
- 0.61 - 1.4

Source of Orthophotography: St. Clair Region Conservation Authority, 2006

Concentrations in unsampled areas estimated using anisotropic interpolation

Sediment depth: 0-15 cm

N

0 800 Meters

ENVIRON

Spatial Trends in Octachlorostyrene Concentrations in Surface Sediment (2005-2008)

Figure 3-3

Friday, March 6, 2009 8:50:38 AM
\\mesrv02\Client_Files\St Clair\GIS\MXD\Figure3-3_OCSOC_SurfaceSed_IDW_11x17.mxd

0 100 Meters

0 100 Meters

0 200 Meters

Stag Island

Lake Huron
St. Clair
Lambton County
Macomb
St. Clair River
Lake St. Clair
Chatham-Kent Division

No sample data due to insufficient sediment depth

TOC (%)

- 0.42 - 1.0
- 1.0 - 1.5
- 1.5 - 2.0
- 2.0 - 2.5
- 2.5 - 3.0
- 3.0 - 3.5
- >3.5

Source of Orthophotography: St. Clair Region Conservation Authority, 2006

Concentrations in unsampled areas estimated using anisotropic interpolation

Sediment depth: 0-15 cm

N

0 820 Meters

ENVIRON

Spatial Trends in Total Organic Carbon Concentrations in Surface Sediment (2005-2008)

Figure 3-4

Thursday, March 5, 2009 1:38:37 PM
\\mesrv02\Client_Files\St Clair\GIS\MXD\Figure3-4_TOC_SurfaceSed_IDW_11x17.mxd

0 100 Meters

0 100 Meters

0 100 Meters

0 100 Meters

Stag Island

Lake Huron
St. Clair
Lambton County
Macomb
St. Clair River
Lake St. Clair
Chatham-Kent Division

No sample data due to insufficient sediment depth

Percent Fines (Silt & Clay)

- 0.21 - 10
- 11 - 20
- 21 - 30
- 31 - 40
- 41 - 50
- 51 - 60
- 61 - 91

Source of Orthophotography: St. Clair Region Conservation Authority, 2006

Concentrations in unsampled areas estimated using anisotropic interpolation

Sediment depth: 0-15 cm

N

0 350 700 Meters

ENVIRON

Spatial Trends in Grain Size Distribution in Surface Sediment (2005-2008)

Figure 3-5

Thursday, March 5, 2009 4:03:15 PM
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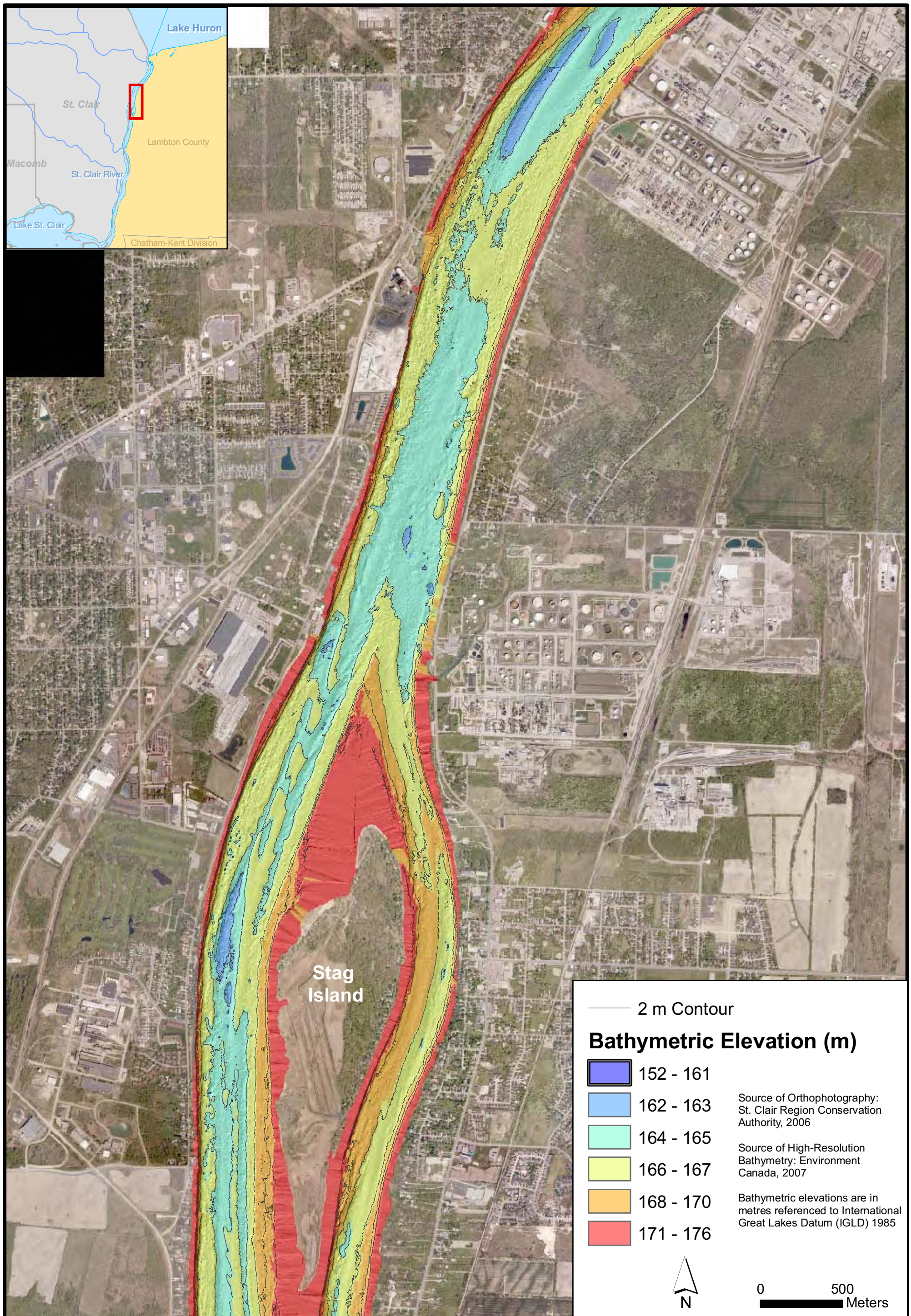

ENVIRON

Bathymetry in the St. Clair River Area of Interest

Figure 3-6

Tuesday, February 17, 2009 12:04:14 PM
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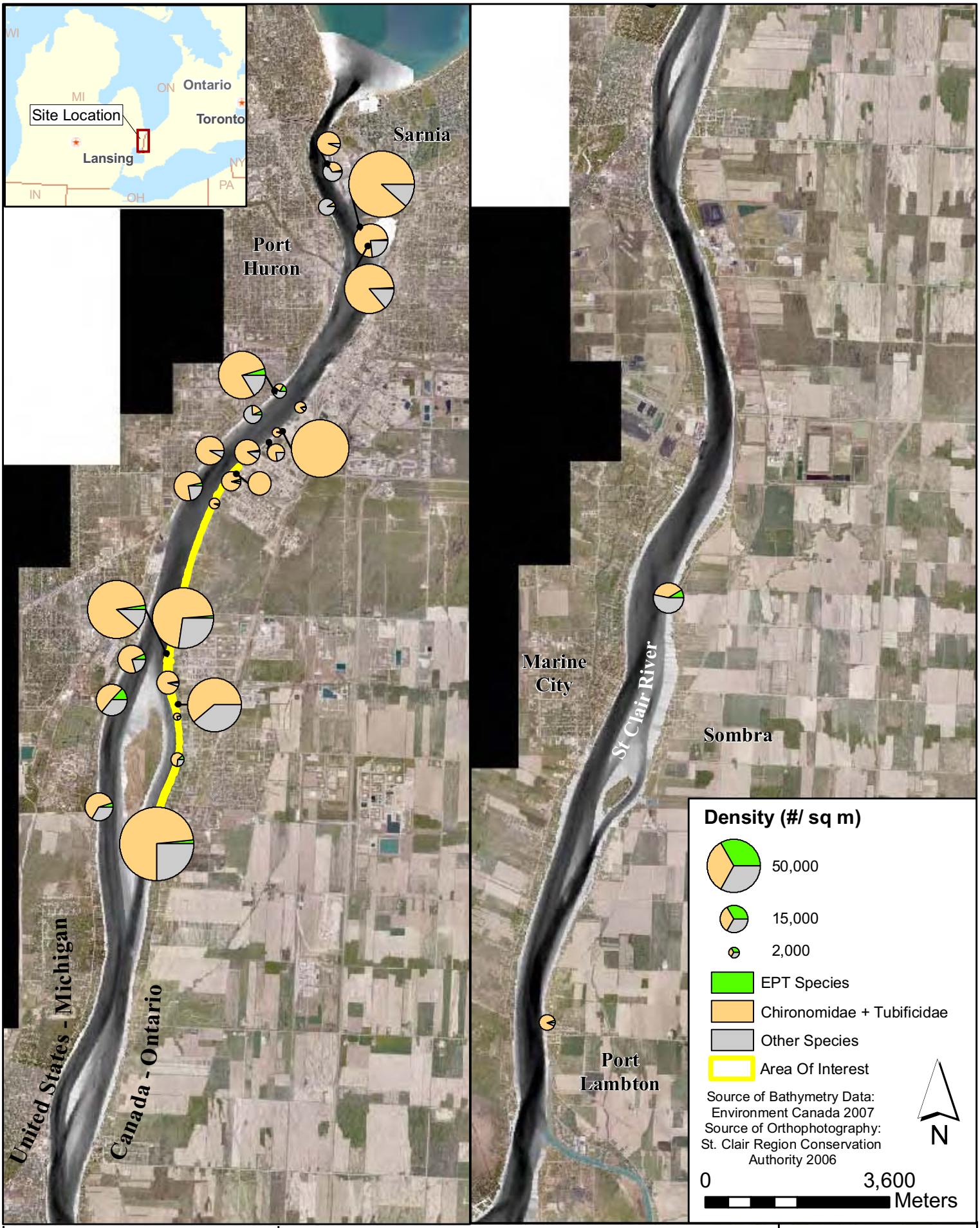

ENVIRON

Spatial Trends in Benthic Community Structure

Figure 4-1

Tuesday, March 10, 2009 2:45:55 PM
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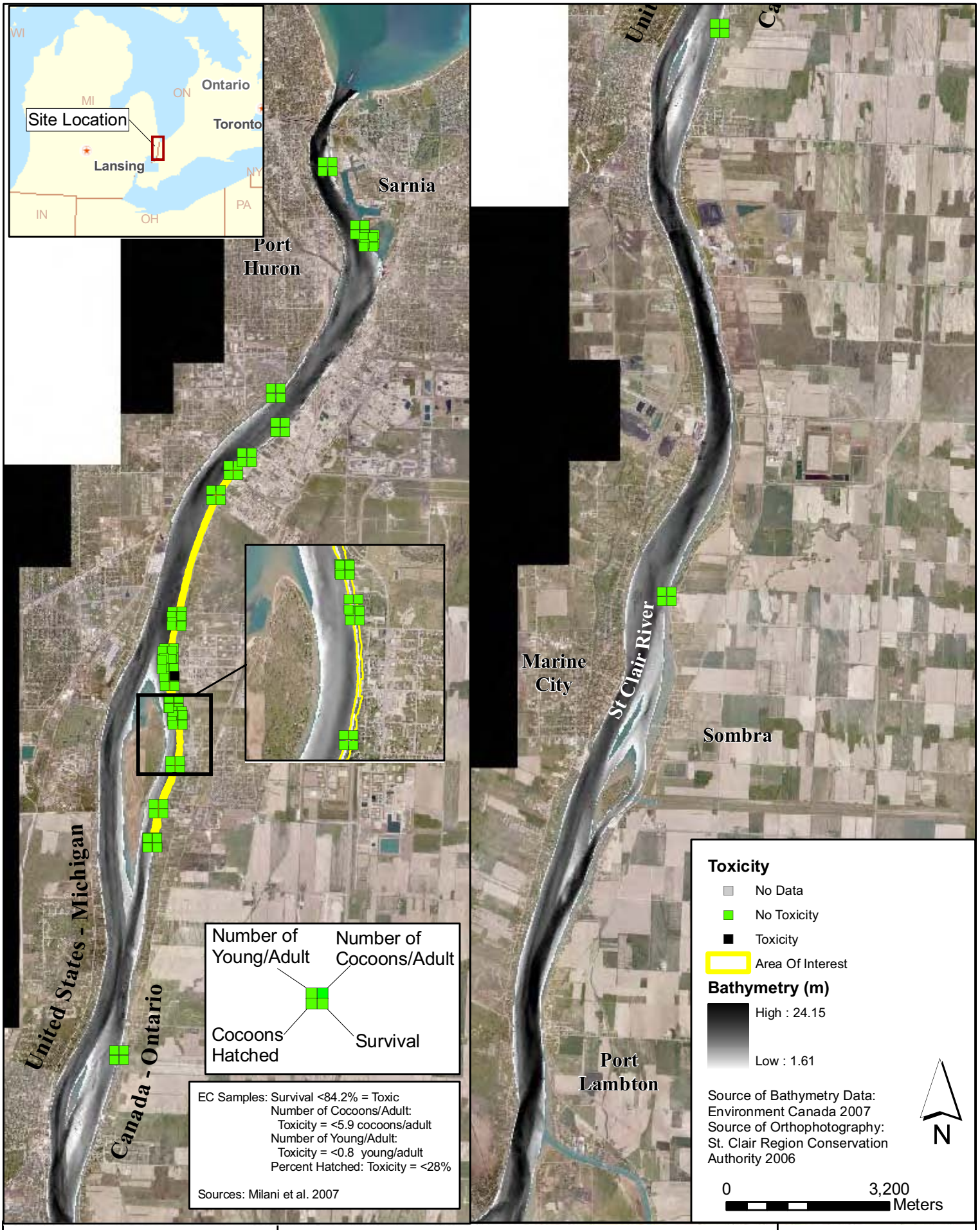

ENVIRON

Spatial Trends in Oligochaete Toxicity

Figure 5-1

Wednesday, March 11, 2009 8:37:14 AM
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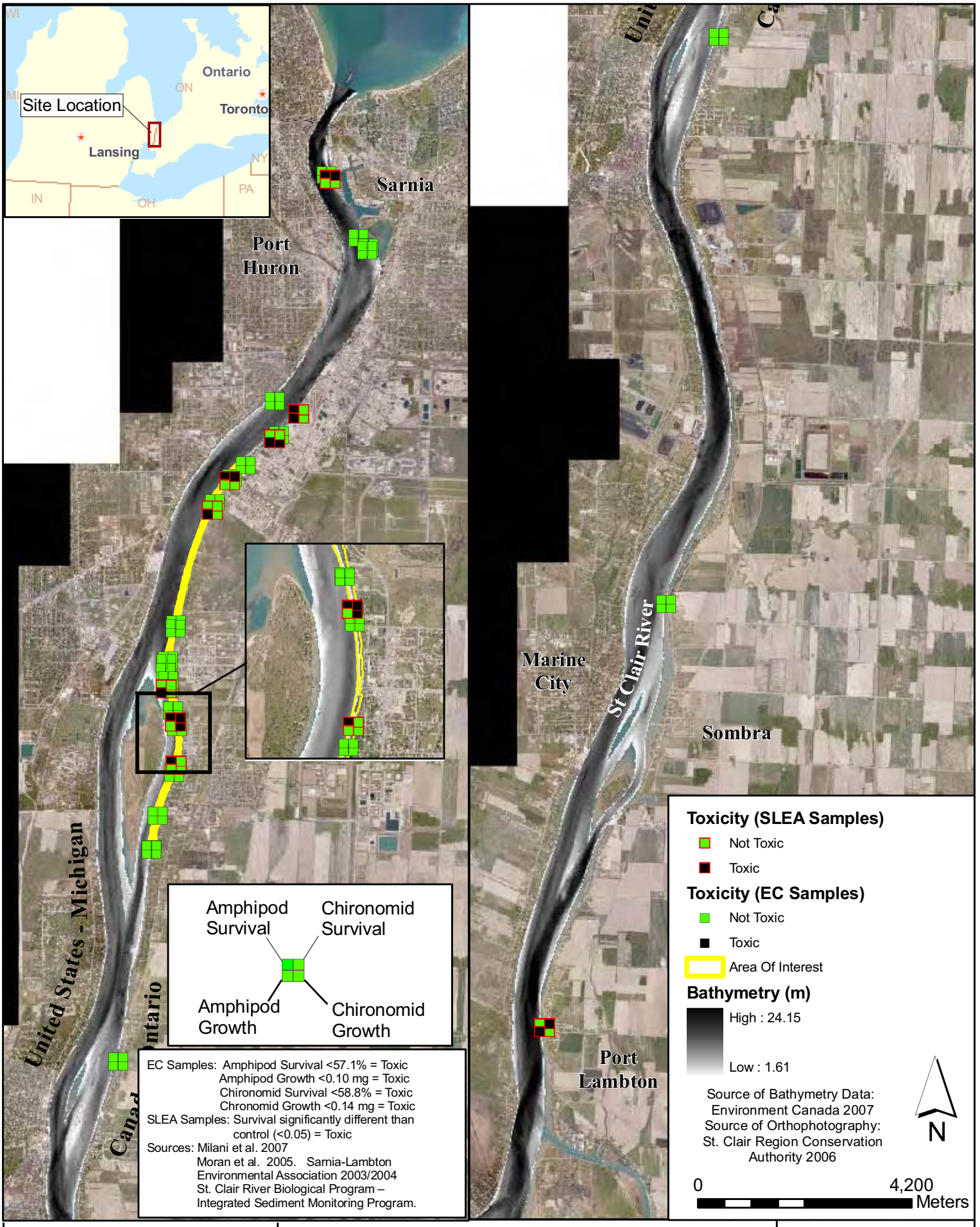

ENVIRON

Spatial Trends in Amphipod and Chironomid Toxicity

Figure 5-2

Tuesday, March 10, 2009 10:55:16 AM
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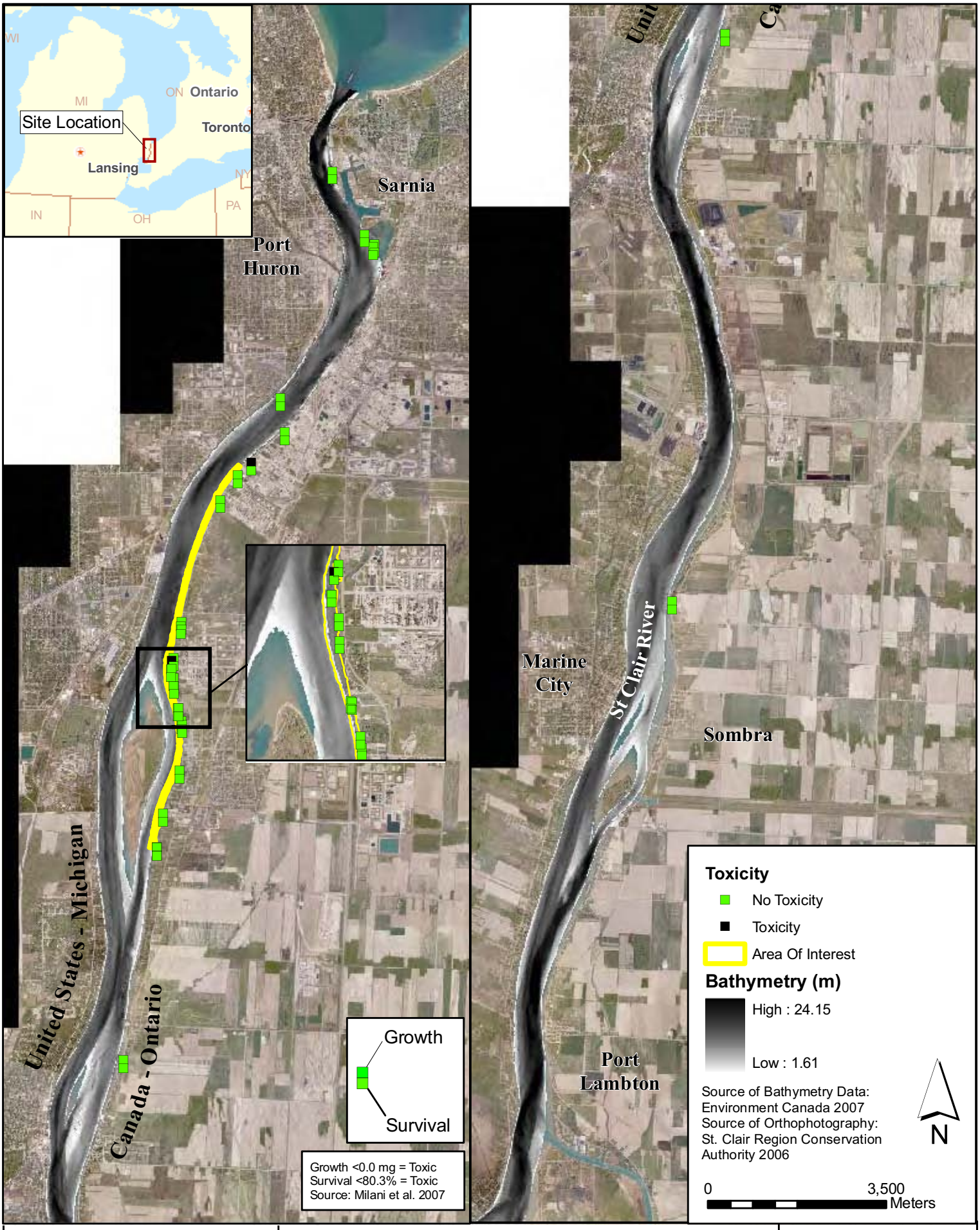

ENVIRON

Spatial Trends in Mayfly Toxicity

Figure 5-3

Friday, January 16, 2009 11:35:47 AM
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ENVIRON

Spatial Trends in Methylmercury Concentrations in Oligochaete Tissue

Figure 6-1

Friday, March 6, 2009 4:47:50 PM
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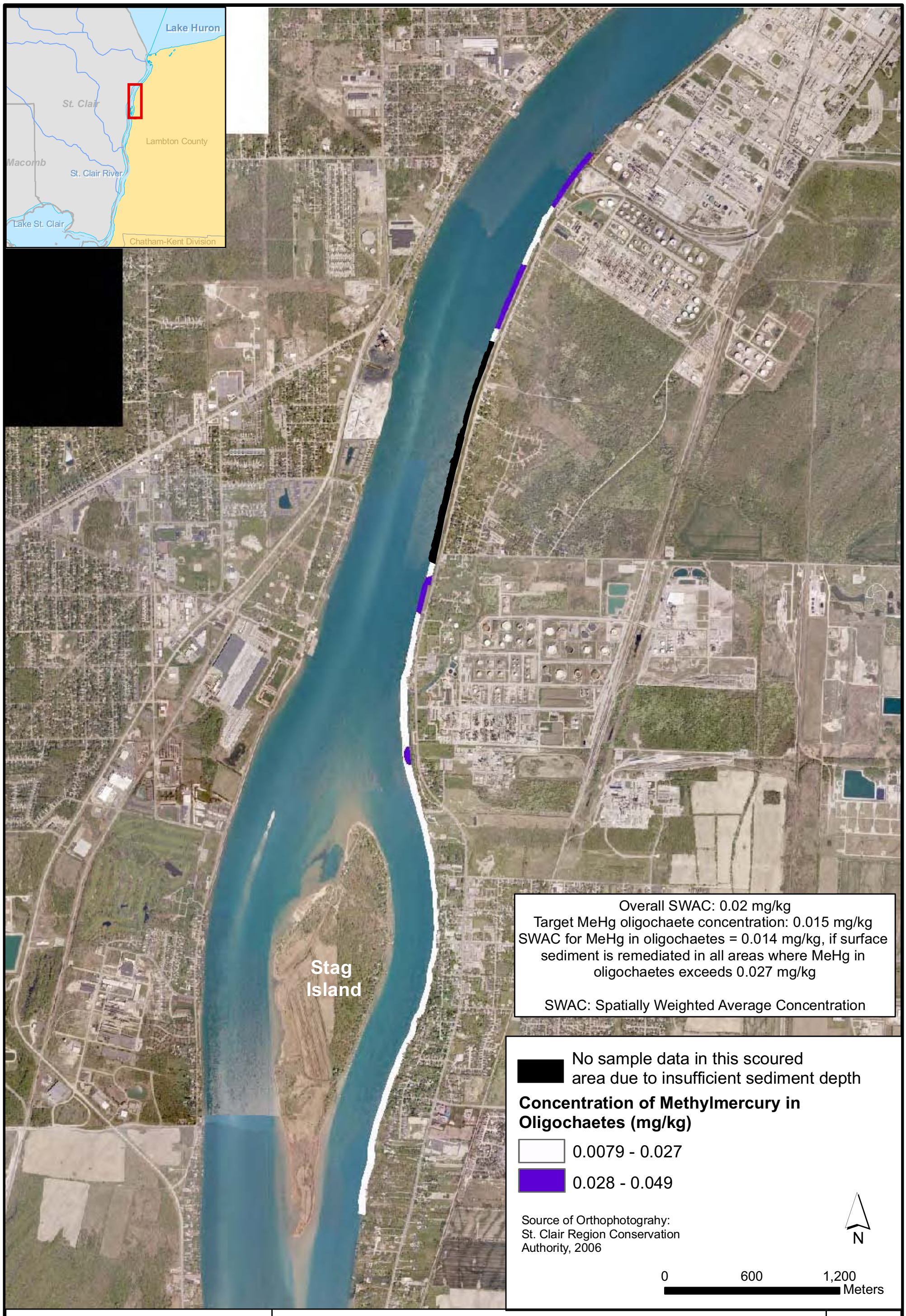

ENVIRON

Areas of Risk to Fish Based on Low End Biomagnification Factor of 13

Figure 6-2

Wednesday, March 25, 2009 10:41:53 AM
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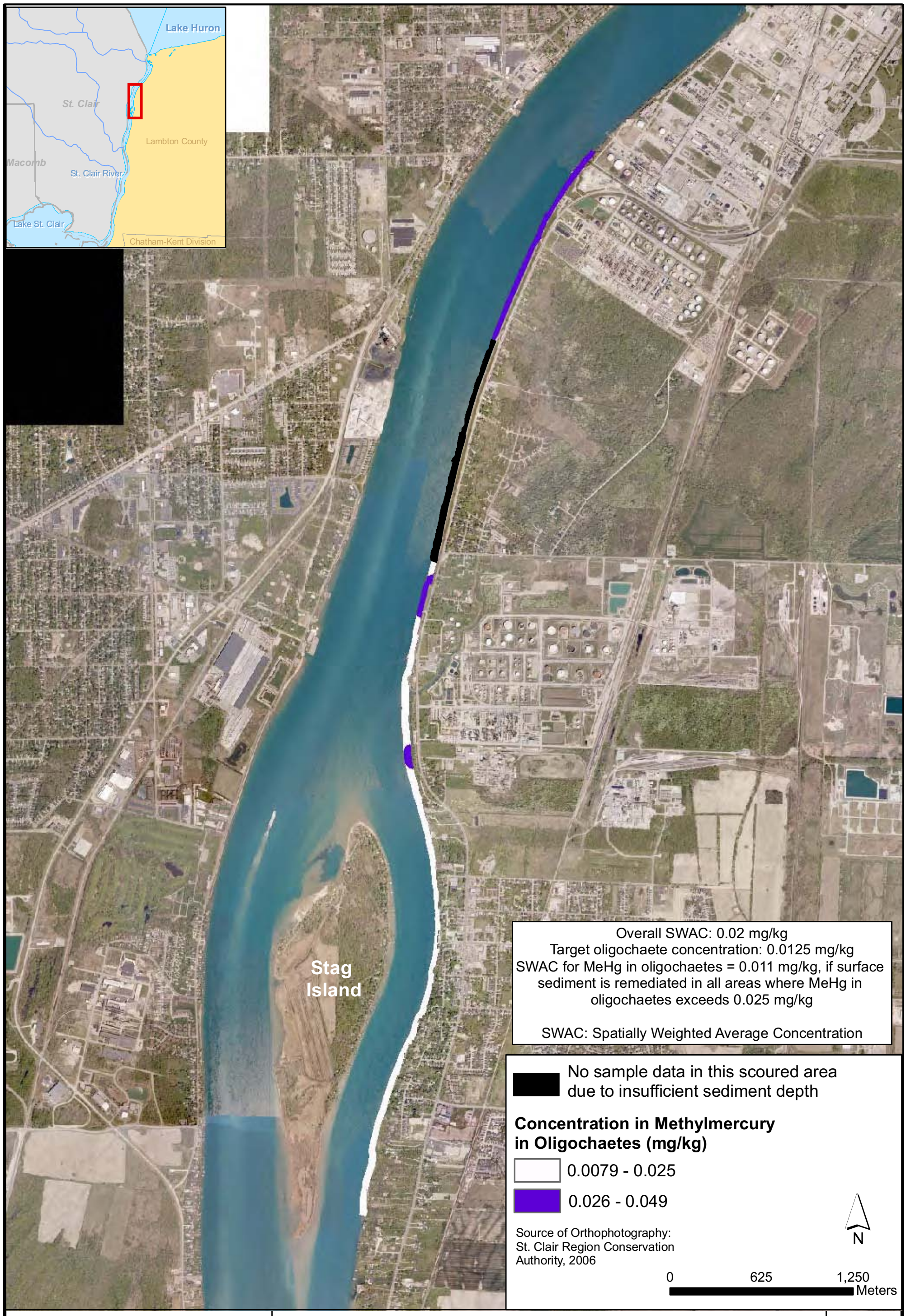


ENVIRON

Areas of Risk to Fish Based on High End Biomagnification Factor of 16

Figure 6-3

Wednesday, March 25, 2009 10:51:23 AM
\\mesrv02\Client_Files\St Clair\GIS\MXD\Figure6-4_BMF_16.mxd

A

0 200 Meters

B

0 100 Meters

C

0 100 Meters

Lake Huron

STAG ISLAND

St. Clair

Lambton County

Macomb

St. Clair River

Lake St. Clair

Chatham-Kent Division

Priority Areas

High : 0.049 mg/kg MeHg

Low : 0.0079 mg/kg MeHg

No sample data in this scoured area due to insufficient sediment depth

Source of Orthophotography:
St. Clair Region Conservation Authority, 2006

0 0.6 Miles

N

ENVIRON

Prioritized Zones for Sediment Management

Figure 6-4

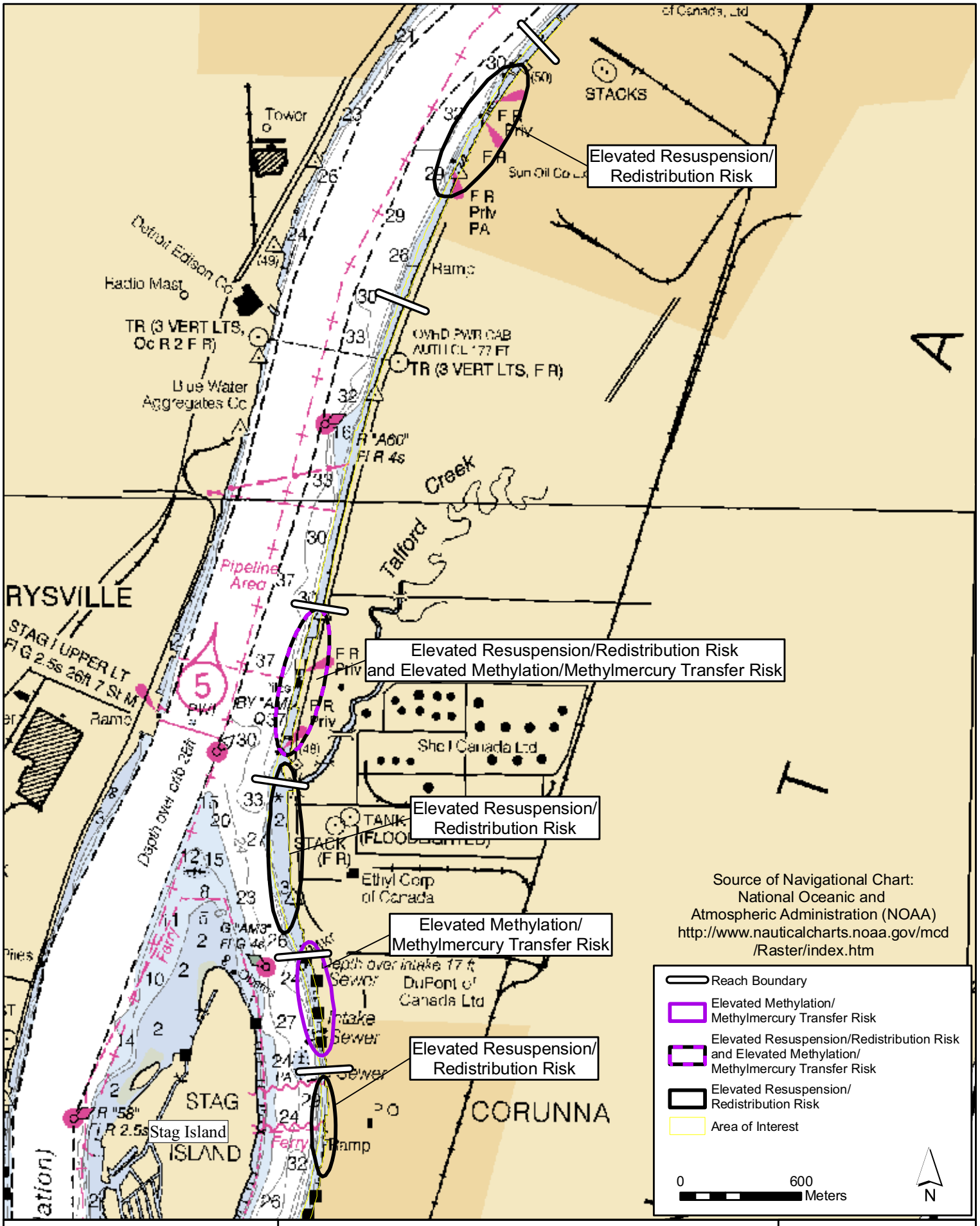
Monday, February 23, 2009 10:53:42 AM
\\mesrv02\Client_Files\St Clair\GIS\MXD\Figure6-5_PriorityZones_WithInsets.mxd

ENVIRON

Spatial Trends in Maximum Total Mercury Concentrations in Subsurface Sediment (2000-2008)

Figure 6-5

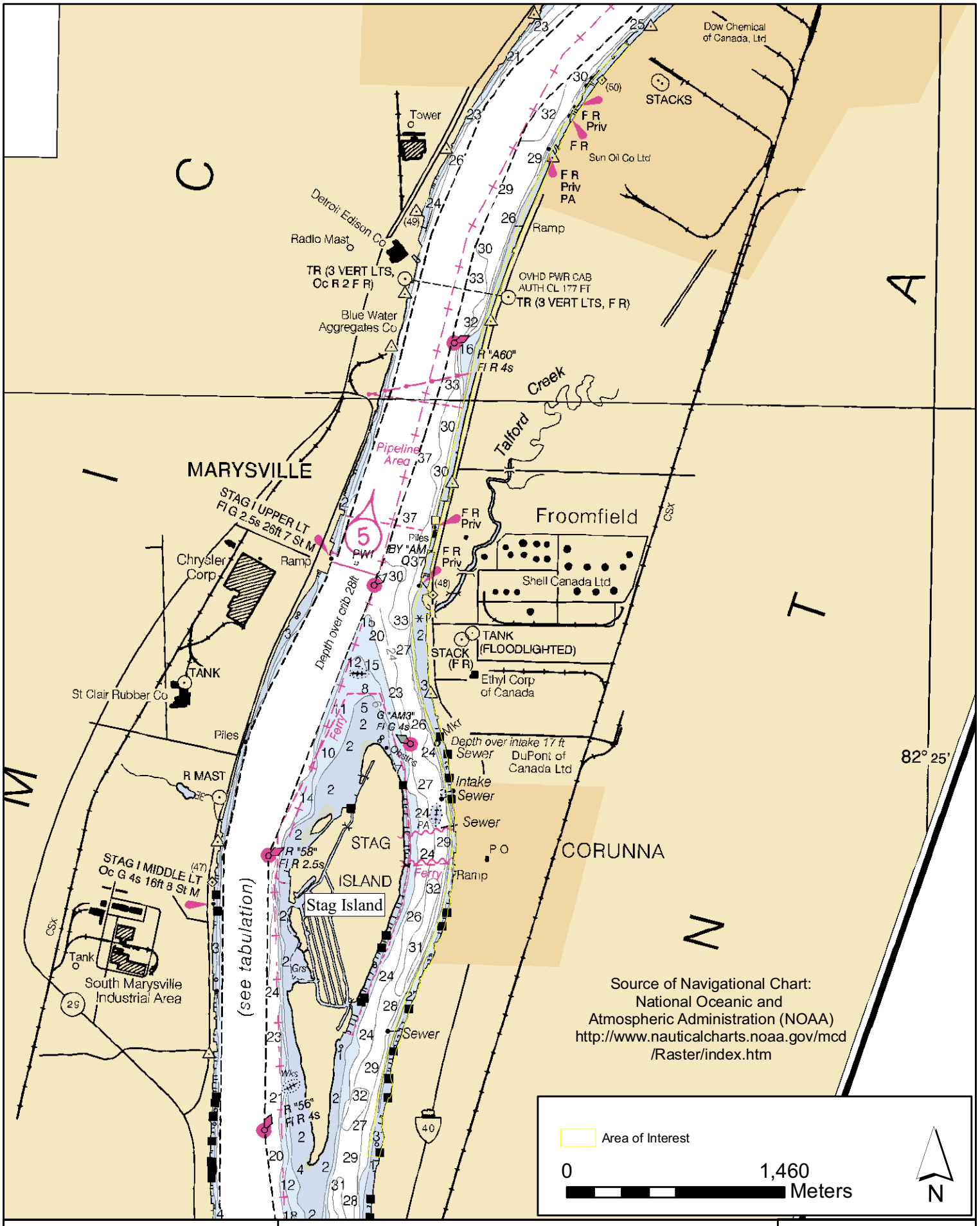
Wednesday, January 21, 2009 2:48:01 PM
\\mesrv02\Client_Files\St Clair\GIS\MXD\TotalHg_SubsurfaceSed_IDW_11x17.mxd



ENVIRON

Areas of Elevated Sediment Redistribution
and/or Methylation Risk
St. Clair River Area of Interest

Figure
6-6

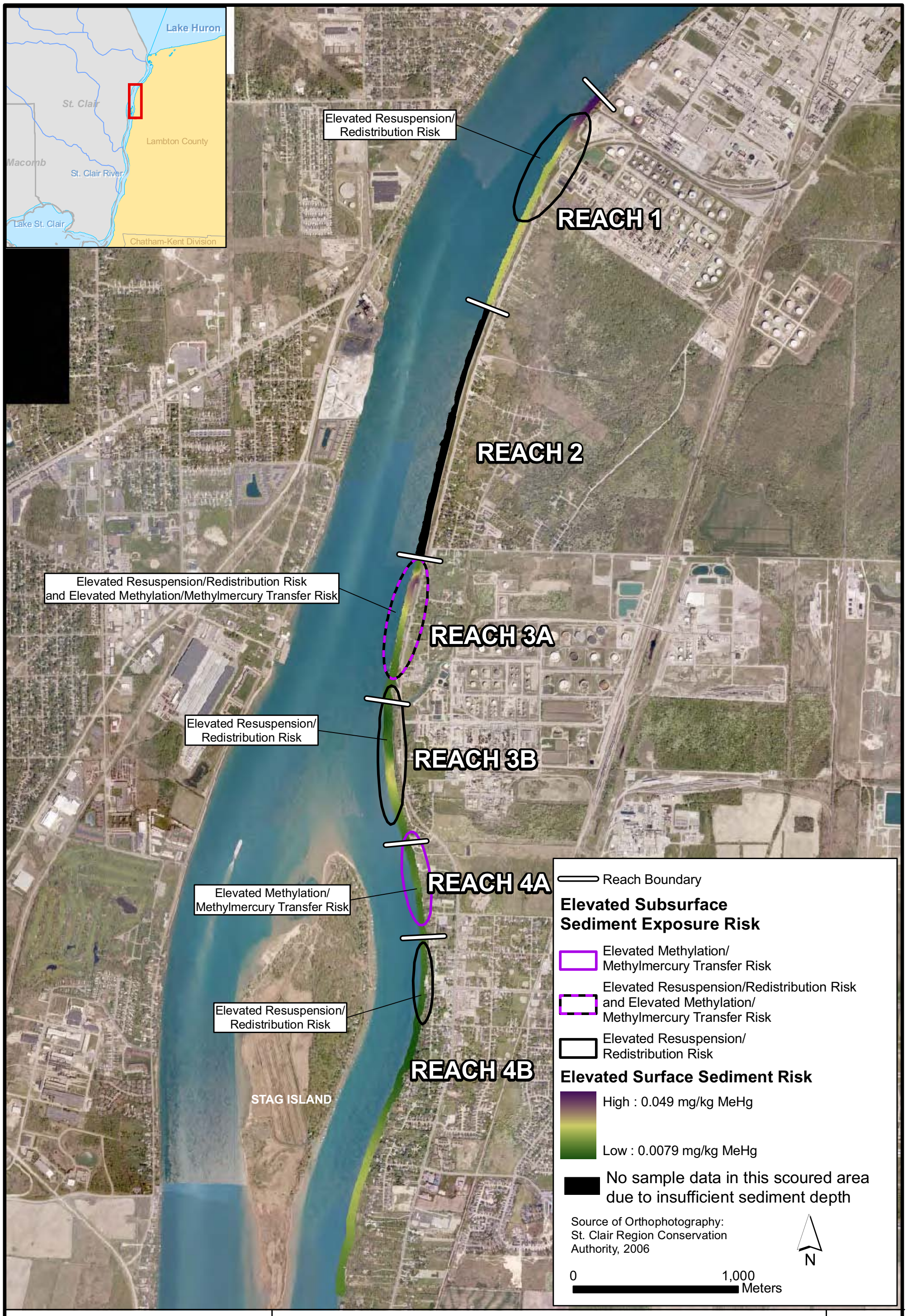


ENVIRON

NOAA Navigational Chart
St. Clair River Area of Interest

Figure
6-7

Friday, February 20, 2009 12:07:14 PM
\\mesrv02\Client_Files\St Clair\GIS\MXD\Figure6-8_NOAA_Nav.mxd



ENVIRON

Zones of Comparable Risk in Surface and Subsurface Sediment
St. Clair River Area of Interest

Figure 6-8

Friday, March 6, 2009 10:18:05 AM
\\mesrv02\Client_Files\St Clair\GIS\MXD\Figure6-9a_PriorityZones_surfaceandsubsurface.mxd

Appendix A

Project Database

Appendix B

Derivation of Target Tissue Concentration Equation

Appendix B
Detailed Derivation of Equation for Calculating Target Prey Tissue Concentrations for Protection of Wildlife

1. To calculate the aquatic prey concentration that will NOT result in a HQ above 1, start with the equation for HQ: HQ = Dose/TRV and set HQ = 1, so that
    a. 1 = Dose/TRV, which is the same as Dose = TRV
    b. The left side of this equation must then be expanded to allow isolation of the term for the aquatic prey concentration (Caq)

2. Figure 4-2 of EPA's Wildlife Exposure Factors Handbook (p. 4-6 of Volume I) gives the equation for dose (or ADD) as:
    a. Dose = Σ (C_k x FR_k x NIR_k) where
        i. C_k = average chemical concentration in the kth type of food (mg/kg), which effectively weights the concentration by the proportion of that food in its diet. Thus C_k can also be expressed as Ca x Pa, where P is the proportion of food type a in the diet
        ii. FR_k = fraction of intake of the kth food type that is contaminated (unitless) (we call this the AUF)
        iii. NIR_k = normalized food ingestion rate of the kth food type (g/g-day). By definition, NIR_k = FIR_k/BW where
            1. FIR_k = food ingestion rate for the kth food type (g/day)
            2. BW = body weight (g)
    b. If a receptor's diet incudes aquatic and terrestrial prey, this dose equation can also be expressed as:
    Dose = (AUF x Caq x FIRaq/BW) + (AUF x Cterr x FIRterr/BW) = TRV
    c. If the receptor's home range area is smaller than the length of the AOI and the terrestrial portion of the diet is not contaminated, then AUF = 1 and Cterr = 0, leading to:
    d. Dose = Caq x FIRaq x 1/BW = TRV
    e. Because FIRaq = FIR x Paq, this is equivalent to

Dose = Caq x FIR x Paq x 1/BW = TRV

3. Now that the Caq term has been isolated, the overall Dose = TRV equation can be solved for the C_{aq} term:
    a. C_{aq} = [TRV x BW] / [FIR x AUF x P_{aq}]

Appendix C

Methodology Used in the Anisotropic Interpolation of St. Clair River Surface Sediment

Appendix C
Methodology Used in the Anisotropic Interpolation of St. Clair River Surface Sediment

Spatial interpolation is commonly used to predict concentrations in unsampled locations based on known concentrations. Kriging, inverse distance weighting (IDW), spline, and natural neighbour are all frequently employed interpolation methods. Ordinary interpolation methods assume equal variation in site conditions in all directions from the known sampled location. However, in some settings directional variation does exist, and may influence concentrations of unsampled locations. Accounting for this variability is important to accurately predict unknown concentrations.

Rivers typically exhibit greater variability in sediment characteristics transverse to river flow as opposed to along the flow direction. In addition, the direction of this variability is not constant over the entire river, but rather changes with flow direction. In order to account for the changing anisotropy of the St. Clair River bed, ENVIRON International Corporation (ENVIRON) employed anisotropic interpolation in a flow-oriented coordinate system. Following the methods detailed in Merwade (2006), ENVIRON utilized an elliptical inverse distance weighting interpolation method in s,n coordinate space. This method assigns weights to known concentrations based on the anisotropic nature of the river channel. In other words, a sample located along river flow will have greater influence on an unsampled location than a sample located transverse to river flow. The process used to interpolate surface sediments in the St. Clair River is outlined below. The following methodology was employed using ArcGIS 9.3 with the Geostatistical Analyst, 3D Analyst, and Spatial Analyst Extensions.

C-1 Coordinate Transformation

Step 1: Create a centerline.

The centerline is used to develop the s,n coordinate space. In the case of the St. Clair River, the Area of Interest (AOI) is only a small portion of the river. Thus, the centerline, as shown in Figure C-1, divides the AOI in half.

Step 2: Create regularly spaced points along the centerline.

The station points along the centerline serve as the s coordinate in the new s,n coordinate system. The points can be spaced at any interval, but the closer the points are together the more precise the coordinate system will be. ENVIRON chose a spacing of 0.5 metres, which creates a fairly precise location along the horizontal axis. Included in the attribute table of the station

Figure C-1

points is a field showing the distance the point is along the centerline. As previously noted, this field serves as the s coordinate in the new flow-oriented coordinate system.

Step 3: Create a regularly spaced point grid within the Area of Interest.

A point grid is spaced at the same interval as the centerline station points. Thus, ENVIRON created a regularly spaced point grid of 0.5 metres, as shown in Figure C-2 (referred to as AOI-point grid) This spacing balances efficiency and speed in calculations with precision in the final raster surface. The point grid serves as the s,n coordinate grid after joining to the centerline station points and is used to transform the interpolated surface back to x,y coordinate space after the interpolation.

Figure C-2

Step 4: Conduct a spatial join of the point grid to the centerline station points.

In the spatial join, each point in the grid is joined to the nearest centerline station point and is assigned all the attributes of the station point. Thus, each point in the resulting grid is assigned a distance downstream (s) and a distance from the centerline (n).

Step 5: Assign positive and negative n values.

In order to produce the final flow-oriented coordinate system, all points to the left of the centerline are assigned a negative value and all points to the right of the centerline remain positive. This prevents any points from having the same s,n value and produces the final flow-oriented coordinate system.

Step 6: Conduct a spatial join of the sample data to the point grid with the s,n coordinates.

By conducting a spatial join of the sample data to the point grid, each sample point is assigned s,n coordinates. In the spatial join, all attributes of the joined table are merged with the original table. Thus, the final attribute table describes each known sample location with x,y coordinates and s,n coordinates.

C-2 Plotting Data in s,n Coordinate Space

Step 7: Export the attribute table created during Step 6 and bring it into the Geographic Information System (GIS) project. Create an event class using the n field in the attribute table as the x-coordinate and the s field as the y-coordinate.

This step yields the sample data plotted in s,n coordinate space, as seen in Figure C-3. The flow-oriented coordinate system accounts for the variable-direction anisotropy of the river channel (Merwade 2006). Thus, variation is constrained to the horizontal (s) axis.

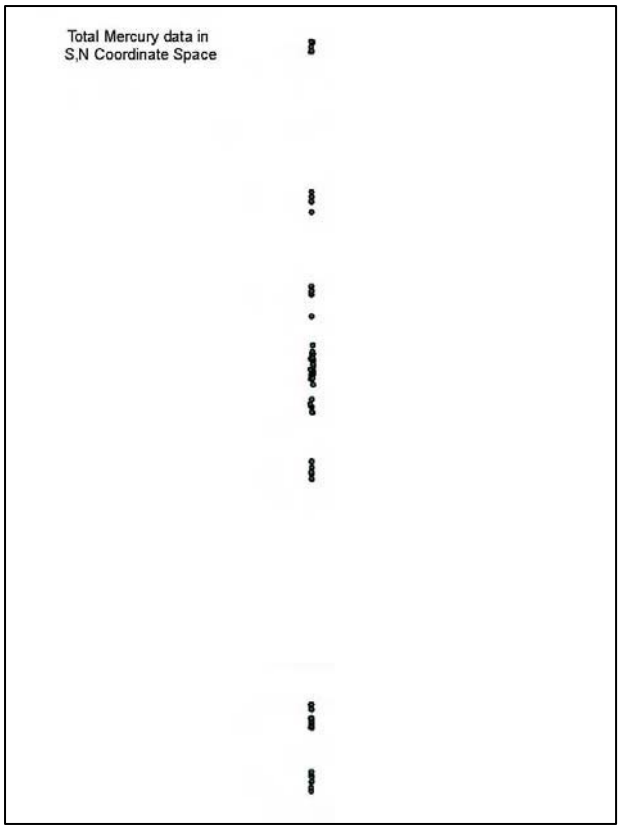


Figure C-3

C-3 Elliptical Inverse Distance Weighting

Step 8: Using the geostatistical wizard in Geostatistical Analyst, select the event class and the results you want to interpolate

Elliptical Inverse Distance Weighting (EIDW) was chosen as the interpolation method for the St. Clair River because it is a relatively simple deterministic interpolation technique that is directly based on the surrounding measured values to produce the interpolated surface. Unlike IDW, EIDW takes into account greater variability in one direction by including more sample points lying along the flow direction and assigning these sample points greater weight compared to samples transverse to river flow. In a study by Merwade (2006), EIDW in a flow-oriented coordinate system significantly reduced the root mean square error (RMSE).

The geostatistical wizard progresses through the interpolation decision points and creates the interpolated surface. Figure C-4 illustrates the first screen of the geostatistical wizard.

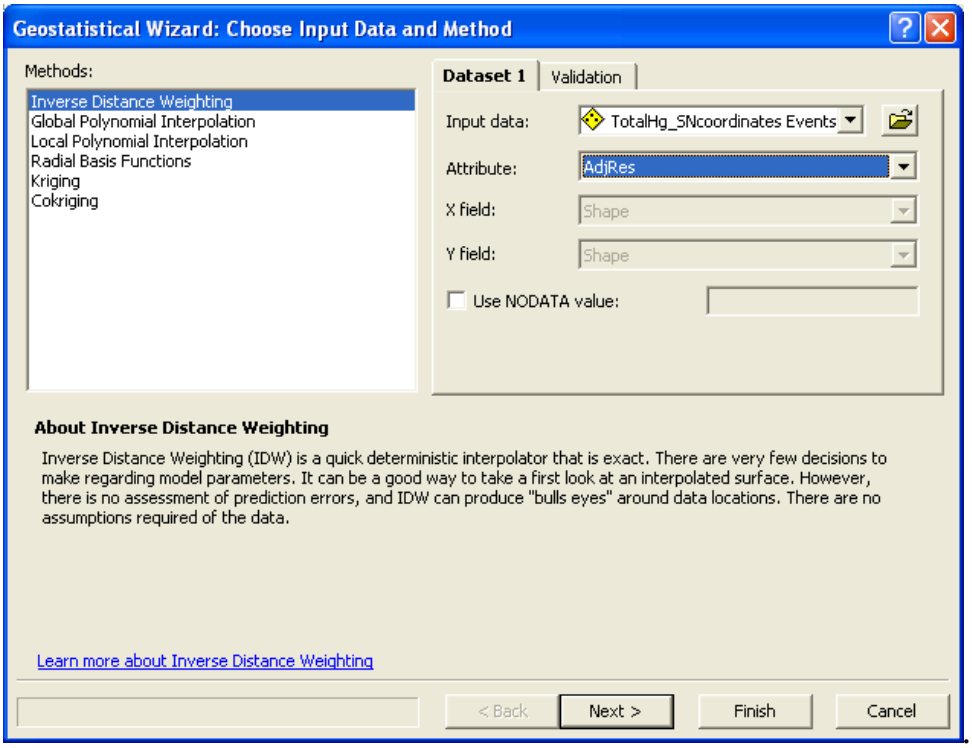


Figure C-4

Step 9: Proceed through the geostatistical wizard.

The following parameters were used in all interpolations for the St. Clair River:

- Maximum of coincident points used in the interpolations
- Maximum of 15 neighbours used in the interpolation, minimum of 10
- Standard search neighbourhood
- Major semi axis = 2000
- Minor semi axis = 500
- Anisotropic ratio = 4
- Power = 2

With the exception of the anisotropic ratio, the default parameters were used in all interpolations. The anisotropic ratio was determined by adjusting the major semi axis and minor semi axis to minimize the RMSE. The power variable influences whether points closest to the unknown location will receive higher weight than points farther away; a higher power indicates that samples closest to the unknown location receive the highest weight. By using a power of 2, nearby samples are given higher weight, which results in more localized hot spots rather than a smoothing of the data. Figure C-5 illustrates the parameters used in the interpolations.

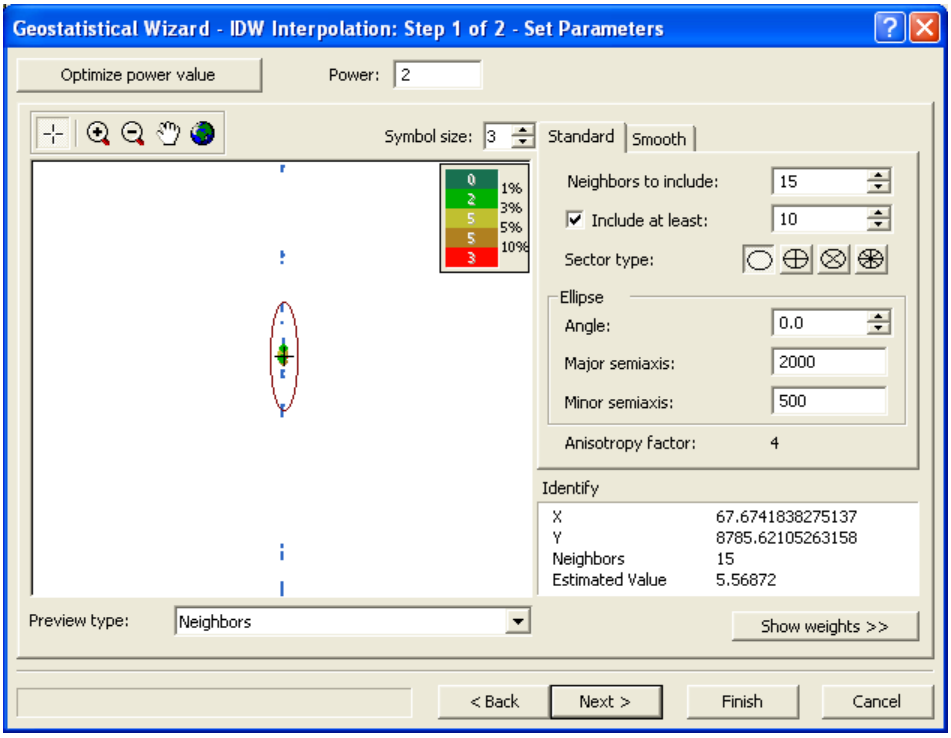


Figure C-5

Step 10: After completing the interpolation, export the interpolated surface to a raster

The resulting interpolated surface is not permanent until it is exported as a raster.

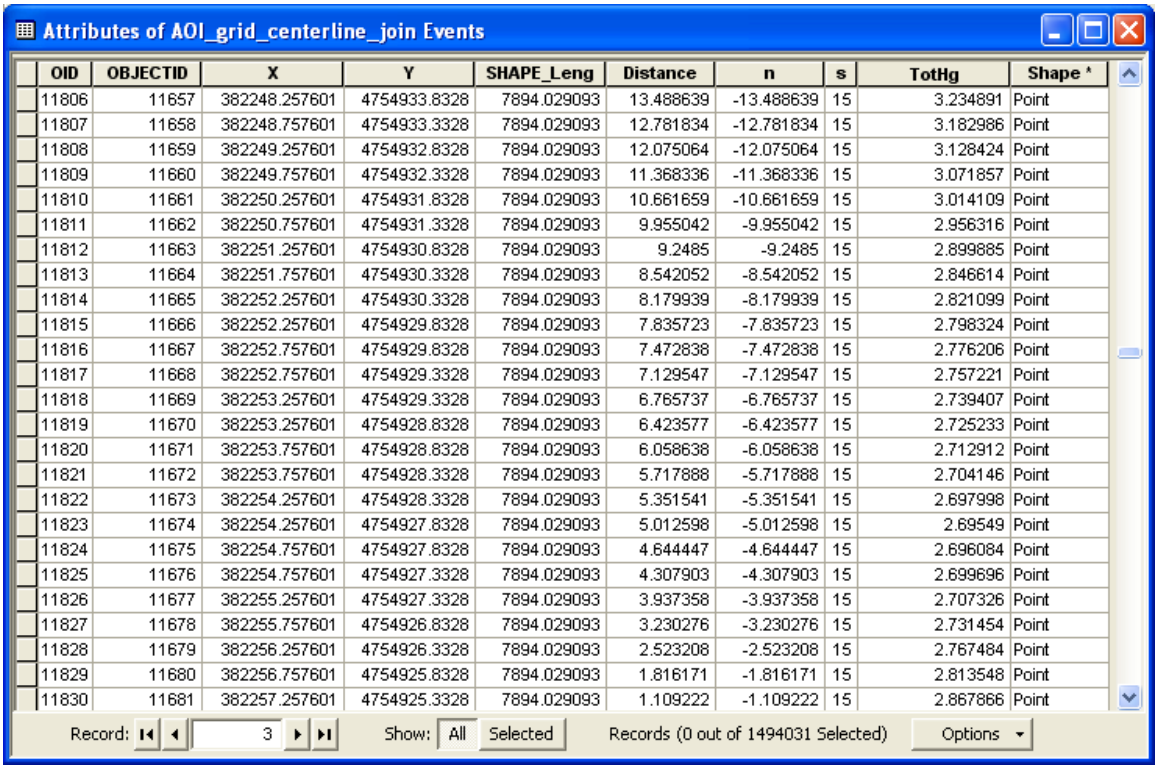
C-4 Transforming the Interpolated Surface Back into x,y Coordinate Space

Step 11: Bring the original point grid into s,n coordinate space

In the same way that the sample data were brought into s,n coordinate space (Step 7), the point grid (AOI-point grid) is also plotted in the flow-oriented coordinate system. The attribute table of the point grid has both x,y and s,n coordinates. Use the n coordinates in the point grid attribute table as the x values and the s coordinates as the y values. This step enables the interpolated raster to be brought back into x,y coordinate space.

Step 12: Using 3D Analyst, conduct a Surface Spot to assign the interpolated raster value to each point in the point grid.

The Surface Spot tool assigns the value of the pixel that corresponds to each point in the point grid. The end result is an attribute table with x,y coordinates, s,n coordinates, and the raster value for each point in the grid. Figure C-6 provides an example of the attribute table.



Attributes of AOI_grid_centerline_join Events

OID	OBJECTID	X	Y	SHAPE_Leng	Distance	n	s	TotHg	Shape *
11806	11657	382248.257601	4754933.8328	7894.029093	13.488639	-13.488639	15	3.234891	Point
11807	11658	382248.757601	4754933.3328	7894.029093	12.781834	-12.781834	15	3.182986	Point
11808	11659	382249.257601	4754932.8328	7894.029093	12.075064	-12.075064	15	3.128424	Point
11809	11660	382249.757601	4754932.3328	7894.029093	11.368336	-11.368336	15	3.071857	Point
11810	11661	382250.257601	4754931.8328	7894.029093	10.661659	-10.661659	15	3.014109	Point
11811	11662	382250.757601	4754931.3328	7894.029093	9.955042	-9.955042	15	2.956316	Point
11812	11663	382251.257601	4754930.8328	7894.029093	9.2485	-9.2485	15	2.899885	Point
11813	11664	382251.757601	4754930.3328	7894.029093	8.542052	-8.542052	15	2.846614	Point
11814	11665	382252.257601	4754930.3328	7894.029093	8.179939	-8.179939	15	2.821099	Point
11815	11666	382252.257601	4754929.8328	7894.029093	7.835723	-7.835723	15	2.798324	Point
11816	11667	382252.757601	4754929.8328	7894.029093	7.472838	-7.472838	15	2.776206	Point
11817	11668	382252.757601	4754929.3328	7894.029093	7.129547	-7.129547	15	2.757221	Point
11818	11669	382253.257601	4754929.3328	7894.029093	6.765737	-6.765737	15	2.739407	Point
11819	11670	382253.257601	4754928.8328	7894.029093	6.423577	-6.423577	15	2.725233	Point
11820	11671	382253.757601	4754928.8328	7894.029093	6.058638	-6.058638	15	2.712912	Point
11821	11672	382253.757601	4754928.3328	7894.029093	5.717888	-5.717888	15	2.704146	Point
11822	11673	382254.257601	4754928.3328	7894.029093	5.351541	-5.351541	15	2.697998	Point
11823	11674	382254.257601	4754927.8328	7894.029093	5.012598	-5.012598	15	2.69549	Point
11824	11675	382254.757601	4754927.8328	7894.029093	4.644447	-4.644447	15	2.696084	Point
11825	11676	382254.757601	4754927.3328	7894.029093	4.307903	-4.307903	15	2.699696	Point
11826	11677	382255.257601	4754927.3328	7894.029093	3.937358	-3.937358	15	2.707326	Point
11827	11678	382255.757601	4754926.8328	7894.029093	3.230276	-3.230276	15	2.731454	Point
11828	11679	382256.257601	4754926.3328	7894.029093	2.523208	-2.523208	15	2.767484	Point
11829	11680	382256.757601	4754925.8328	7894.029093	1.816171	-1.816171	15	2.813548	Point
11830	11681	382257.257601	4754925.3328	7894.029093	1.109222	-1.109222	15	2.867866	Point

Record: 3 Show: All Selected Records (0 out of 1494031 Selected) Options

Figure C-6

Step 13: Export the attribute table created in Step 12 and bring it into the GIS project. Create an event class using the x,y coordinates.

The point grid is now returned to x,y coordinate space. Since each point is assigned a total mercury value from the interpolation, it is now possible to create a surface in x,y space.

Step 14: Using Spatial Analyst, convert the point grid into a raster.

The pixel size of the output raster should be the size of the original grid (in this example, 0.5 metres). The final result is an interpolated surface of the chemical of interest created by assigning higher weights to known samples located in the direction of river flow. Since the original point grid was confined to the AOI, the final interpolated surface covers the same spatial extent and does not need to be clipped to the AOI.

References

Merwade, V.M., D.R. Maidment, and J.A. Goff. 2006. Anisotropic considerations while interpolating river channel bathymetry. Journal of Hydrology 331:731-741.