EVALUATION OF THE NEED FOR REMEDIATION OF MERCURY-CONTAMINATED SEDIMENTS IN PENINSULA HARBOUR, LAKE SUPERIOR

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ABSTRACT
Peninsula Harbour was designated as an Area of Concern due to residual mercury contamination. As part of the Stage 2 RAP, two overlapping studies have been completed: The evaluation of the feasibility of combining sediment remediation with the completion of the Town of Marathon's waterfront development by incorporating a confined disposal facility into the marina design, and: The delineation of the extent and depth of Hg-contaminated sediments and assessment of their biological impact. Total and methyl Hg in surficial sediments range from<0.015 to 68 μg/g, and from <0.5 to 24 ng/g, respectively. Lead-210 dating of sediment cores indicates there is considerable mixing of surficial sediments in the Harbour. The benthic community shows enrichment, and there is no laboratory toxicity due to Hg. Mercury levels in invertebrates are above background levels and there are significant relationships between Hg in sediment and biota. The potential risk to trophically linked receptor species is currently being examined.

RÉSUMÉ
En raison de la contamination résiduelle par le mercure, Peninsula Harbour a été reconnu Zone Préoccupante. Comme partie de la phase 2 RAP, deux études concomitantes ont été complétées: L'Évaluation de la faisabilité d'harmoniser une correction sédimentaire à la réalisation du développement portuaire de la ville de Marathon en incorporant au plan de la marina un traitement par confinement, et: La délimitation de l'étendue et de la profondeur des sédiments contaminés au mercure et l'estimation de leur impact biologique. Le mercure total et le méthyle de mercure dans les sédiments de surface varient de <0.015 à 68 µg/g, et de <0.5 à 24 ng/g respectivement. La datation au plomb-210 de carottes sédimentaires révèle un brassage important des sédiments de surface dans le port. La communauté benthique montre un enrichissement et il n'y a pas de toxicité due au mercure en laboratoire. Les niveaux de mercure présents chez les invertébrés sont au dessus des niveaux moyens et il y a un rapport significatif entre le mercure dans les sédiments et la biocénose. Une étude est présentement en cours afin d'examiner le risque potentiel pour les espèces réceptrices ayant un lien trophique.

1. INTRODUCTION

Peninsula Harbour is located on the Northeastern shore of Lake Superior, Marathon, Ontario, Canada. From 1952 to 1977, a chlor-alkali plant used mercury in its production of caustic soda and chlorine, which resulted in discharge of mercury into the Harbour. Subsequently, mercury contamination exists in the sediment in portions of the Harbour, with the highest levels observed in Jellicoe Cove, located adjacent to the pulp mill and former alkali plant. Mercury contamination, as well as the presence of bark and woody fibres, has designated Peninsula Harbour as a Canadian area of concern (Peninsula Harbour RAP team 1998). To determine whether there is a need for remediation due to mercury contamination, several studies were performed in Jellicoe Cove by the National Water Research Institute (NWRI) of Environment Canada and Beak-Stantec Consultants. Data were collected on sediment physical and chemical characteristics, sediment Pb-210 dating, benthic community structure, and laboratory toxicity testing. To confirm possible ongoing mercury bioaccumulation in the food chain and to evaluate the potential risk to higher trophic levels, sediments and benthic macroinvertebrates were also collected. These data are to provide the technical rationale for sediment remediation.

2. METHODS

2.1 Sample Collection

In August-September of 2000, surficial sediment samples (0 – 10 cm), overlying water samples, benthic community samples, and sediment for use in laboratory toxicity testing were collected at 21 sites in Jellicoe Cove. In addition, sediment core samples were collected at 61 locations (Fig. 1).

In May 2002, sediments and resident benthic macroinvertebrates (amphipods and midges) were collected at sampling locations in Jellicoe Cove with known high (e.g., within a hotspot), intermediate, and low contamination (based on results from the 2001 survey). Twenty-four sites were sampled in Jellicoe Cove (Fig. 2), and 13 reference sites were sampled (outside of Jellicoe Cove) to provide background comparison.

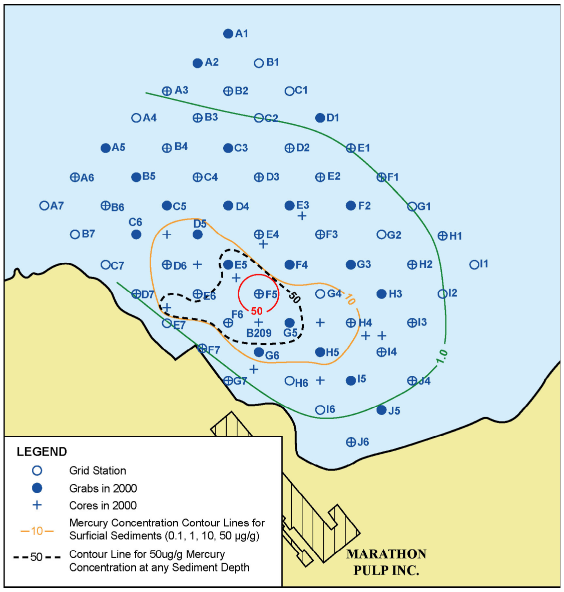

Figure 1. 2001 Sediment sampling locations.

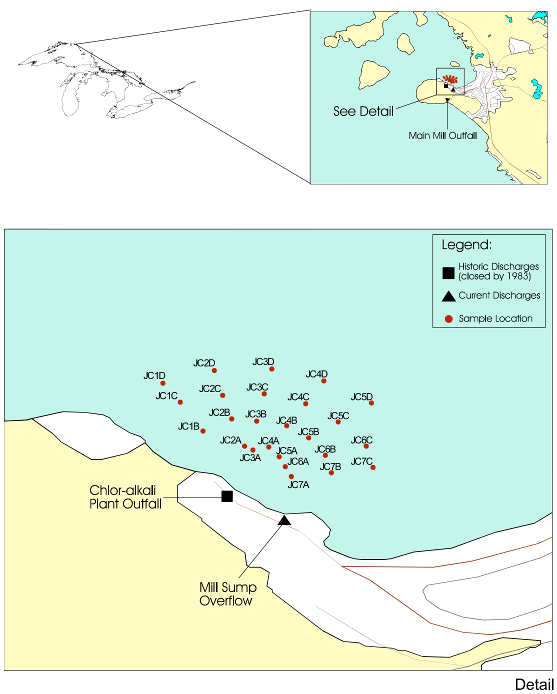

Figure 2. May 2002 sediment and tissue sampling locations.

2.2 Analysis of Sediment and Water

Sediment was collected using either a mini-box core or a ponar sampler. Sediments were analyzed for total and methyl mercury (Flett Laboratory, Winnipeg, Mn), particle size (percents gravel sand, silt, and clay) (Sedimentology Laboratory, NWRI), trace metals, and sediment nutrients (total phosphorus (TP), total nitrogen (TKN), and total organic carbon (TOC)) (Caduceon Enterprises, Ottawa, On). Water samples were collected with a van Dorn sampler 0.5 m from the bottom, and measured for pH, dissolved oxygen, and conductivity, and analyzed for TKN, TP, and alkalinity (National Laboratory for Environmental Testing, NWRI). Sediment core samples (analyzed for total Hg) were sectioned at 0- to 5-cm and 5- to 10-cm intervals, with deeper intervals sectioned by sediment type.

2.3 Benthic Community Structure

Benthic community samples were collected using either a mini-box core (1 box core - 5 core tubes per site) or a ponar sampler (3 grabs per site). Sediment was sieved through a 250 µm sieve and residue was preserved in 4% formalin. Organisms were identified to the lowest level possible.

2.4 Sediment Toxicity Tests

Sediment was collected using a mini-ponar sampler (5 grabs per site). Four sediment toxicity tests were performed using the amphipod, *Hyalella azteca*; the midge, *Chironomus riparius*; the mayfly, *Hexagenia* spp.; and the oligochaete worm, *Tubifex tubifex*. Tests ranged from 10 to 28 days in duration and measured survival, growth, and/or reproduction.

2.5 Lead-210 Dating

A core collected at B209 was sectioned at 1 cm intervals to produce 20 sections. The top 10 sections were dated by the Pb-210 method (Robbins 1978). Below this level there was not enough Pb-210 to permit dating. A second core was collected for dating at H4 but had no excess Pb-210 in the top part of the core and therefore could not be dated, likely due to sediment mixing. The dating was performed by MYCORE Scientific located in Dunrobin, Ontario.

2.6 Tissue Analysis

Sediment was collected using a ponar sampler. Tissue was removed from the sediment by wet sieving through a 500 µm mesh screen. Organisms were sorted into two major taxa – amphipods and midges. Organisms were weighed and frozen on site (organisms were not gut cleared).

2.7 Data Analysis

Data on benthic community structure, the functional responses of laboratory organisms in toxicity tests, and the physical and chemical attributes of the sediment and overlying water were analyzed using multivariate methods (non-hybrid multidimensional scaling). For community structure analysis, a multiple discriminant model was used to assign test sites to 1 of 5 possible reference community types using habitat predictors. Data from test sites were compared to biological criteria developed for the Laurentian Great Lakes (Reynoldson et al. 1995, 2000). Results are depicted in ordination plots (e.g. Fig. 3). Confidence ellipses (90, 99, and 99.9%) are drawn around the reference sites, and test sites fall into 1 of 4 possible bands. The departure of test sites from reference (the centroid) depicts the degree of community stress or toxicity.

Sites in which Hg concentrations in sediments and in invertebrates were significantly elevated above background levels for the study area were identified by comparing Hg in the sediment and in invertebrates for Jellicoe Cove sites to the upper 99th percentile for the reference sites. This was done separately for methyl Hg and total Hg and for each invertebrate taxon.

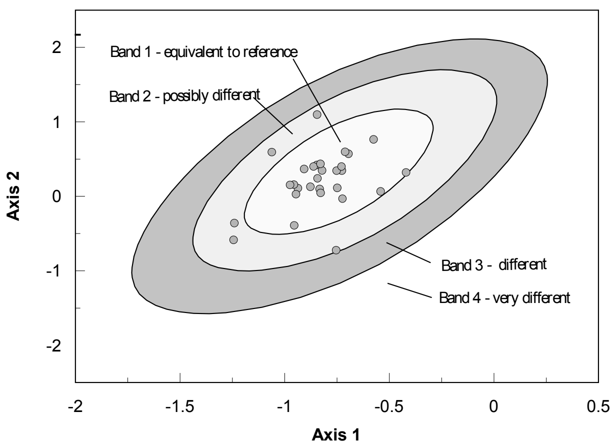

Figure 3. Use of 90, 99 and 99.9% probability bands in determining departure from reference conditions.

Relationships between concentrations of sediment total Hg and methyl Hg, and between Hg concentrations in sediment and invertebrates were examined using regression analysis. For invertebrates, this was done separately for total and methyl Hg and for each invertebrate taxon.

3. RESULTS

3.1 Sediment Total and Methyl Mercury Concentrations

Total mercury concentrations range from <0.015 to 68 µg/g in the surficial sediments, and methyl mercury concentrations range from <0.5 to 24 ng/g, based on all available data.

In the May 2002 samples, on a dry weight basis, the lowest total mercury levels were found in the reference sediments (range 8 - 169, mean 53 ng/g). Total mercury levels at test sites range from 114 to 32160 ng/g (mean 12455 ng/g). All test sites are above the upper 99th percentile for the reference sites, with the exception of sites 1B and 3A (Fig. 4).

Methyl mercury levels were lowest at reference sites, ranging from 0.013 to 0.602 ng/g dry wt (mean 0.182). Methyl mercury levels at test sites range from 0.09 to 23.7 ng/g (mean 8.4). All test sites except two (sites 2A, 3A) are above the upper 99th percentile for the reference sites (Fig. 5).

Based on core samples both total mercury and methyl mercury concentrations were generally lower in the surface sediment (0 to 5 cm) with higher concentrations at greater depths. A significant "hotspot" was identified with total mercury greater than 50 µg/g in deeper sediments (Fig. 1). The highest concentrations of total mercury and methyl mercury, respectively, were 250 µg/g (F6, 10 to 21 cm interval) and 203 ng/g (B209, 13 to 28 cm interval).

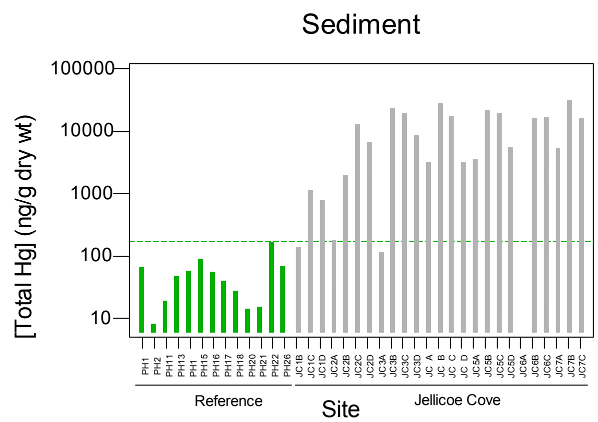

Figure 4. Total Hg in sediment. Dotted line indicates the 99th percentile for reference sites.

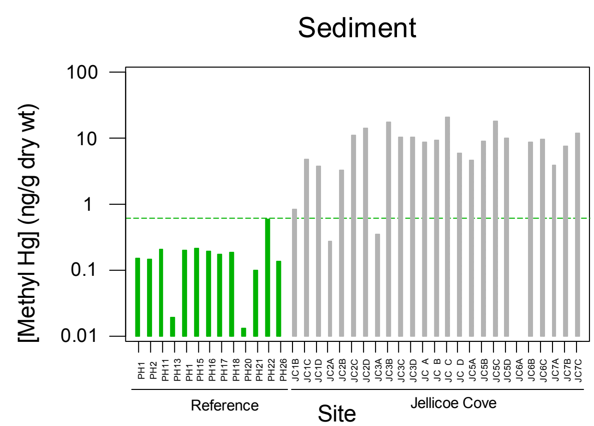

Figure 5. Methyl Hg in sediment Dotted line indicates the 99th percentile for reference sites.

Regression analyses on log transformed data show the relationship between methyl mercury and total mercury in the sediment. A significant positive correlation ($P < 0.001$) was found between the total and methyl mercury concentrations in the sediment (Fig. 6).

3.2 Benthic Community Structure

From the multiple discriminant model, all Jellicoe Cove sites were predicted to the same Great Lakes faunal group (Reference Group 5) based on four habitat attributes: alkalinity, sample depth, latitude, and longitude. Test sites are dominated primarily by chironomids, tubificids, and pisiidids and show greater abundance compared to the reference mean, indicating enrichment. Other families showing overall enriched numbers compared to the reference mean include Naididae, Valvatidae, and Asellidae, while Haustoriidae (amphipod family) numbers are low compared to the reference. Test sites show overall greater family diversity compared to reference.

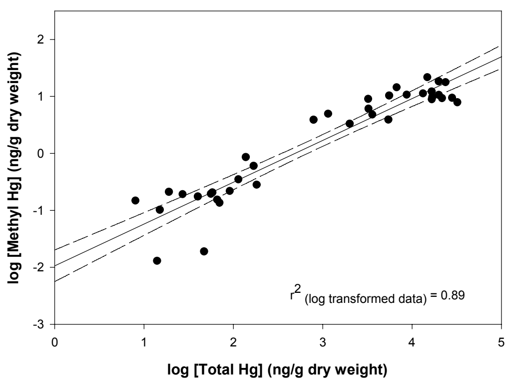

Figure 6. Methyl Hg versus total Mercury in sediments with the 95% confidence interval indicated (dashed lines).

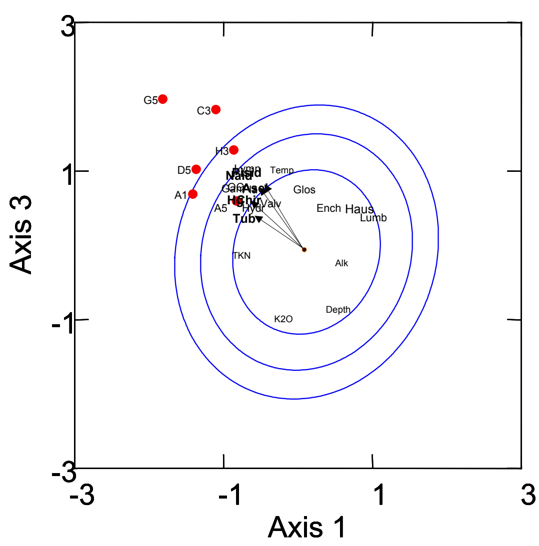

Figure 7. Assessment of a subset of Jellicoe Cove sites using ordination at the family level.

Figure 7 shows the multivariate assessment of a subset of Jellicoe Cove sites summarized on two of three axes. The movement of sites outside of reference is associated with increased abundance of several families. Environmental variables that appear associated with the test sites are elevated levels of Hg and TOC.

3.3 Laboratory Toxicity Tests

Toxicity was evident at only one location (site A1, Fig.1). Mercury levels at this site were low (0.041 µg/g). Mercury concentrations do not appear to elicit acute or sublethal toxicity to laboratory benthic organisms.

3.4 Lead-210 Dating

Lead-210 dating of core sections at one location (B209) indicated an average sediment accumulation rate of 0.17 cm per year over the past 60 years. If this rate is considered typical, most of the surficial sediment layer has been deposited after cessation of operations at the chlor-alkali plant. However, there has been some mixing of sediments due to wave action and boat traffic.

3.5 Invertebrate Total and Methyl Mercury Concentrations

On a whole-body, uncleared-gut basis, midges (chironomids) show a greater range of total Hg accumulation (42 – 5457 ng/g) compared to the amphipods (36 – 2075 ng/g). The midges accumulated more total Hg than amphipods at 89% of the sites.

The midges also show a greater range of methyl Hg accumulation (12.6 – 533 ng/g) compared to the amphipods (19.0 – 359 ng/g). The amphipods, however, accumulated more methyl Hg than the midges at 66% of the sites.

Figures 8 and 9 show total Hg and methyl Hg levels for the amphipods, respectively. For total Hg, all test sites, with the exception of JC2A and JC3A, exceed the upper 99th percentile for the reference sites. Thirteen test sites exceed the upper 99th percentile for the reference sites for methyl Hg. For midges (not shown), 15 test sites exceed the upper 99th percentile for total Hg, and 4 sites exceed the upper 99th percentile of the reference sites for methyl Hg.

3.6 Relationships Between Mercury Concentrations in Biota and Sediment

For both taxa, tissue total Hg is related to sediment total Hg ($P \leq 0.0001$). The adjusted r^2 values are 0.716 (midges) and 0.858 (amphipods) (Fig. 10). The relationships between methyl Hg in biota and methyl Hg in sediment are weaker than those for total Hg (Fig. 11). With [Methyl Hg]$_{sed}$ alone as the predictor, regressions are significant for both taxa ($p=0.026$ and $p<0.0001$ for the midges and amphipods respectively). The r^2_{adj} values are 0.109 and 0.526 for the midges and amphipods, respectively.

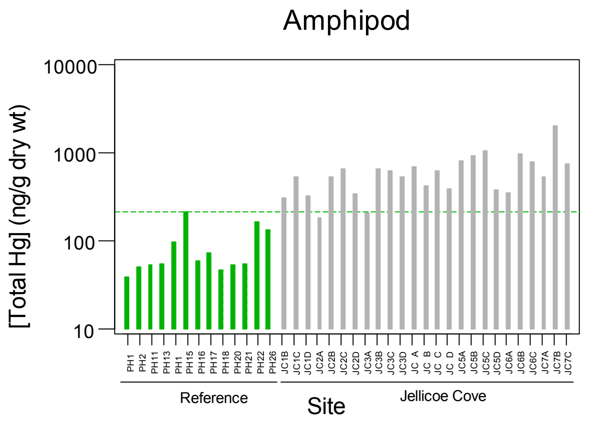

Figure 8. Total [Hg] in amphipods (ng/g). Dotted line indicates the 99th percentile for reference sites.

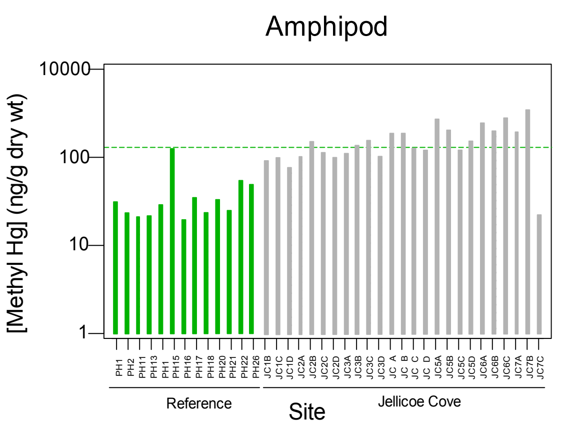

Figure 9. Methyl [Hg] in amphipods (ng/g). Dotted line indicates the 99th percentile for reference sites.

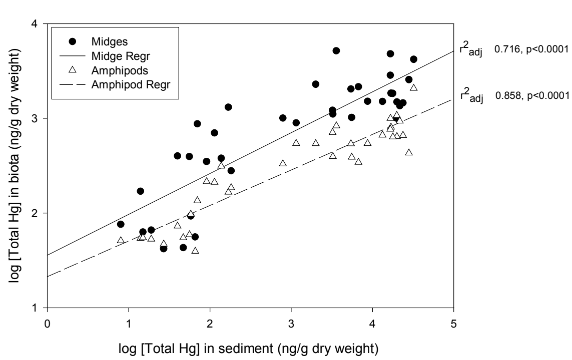

Figure 10. Relationship between total Hg in midges and amphipods and total Hg in sediment.

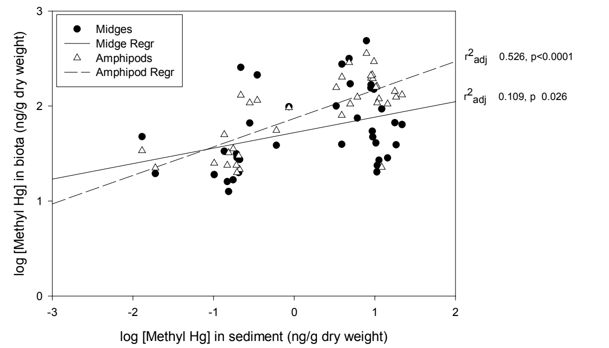

Figure 11. Relationship between methyl Hg in midges and amphipods and methyl Hg in sediment

4. DISCUSSION

Concentrations of total Hg in the upper 10 cm layer of sediment sampled in 2002 from most sites in Jellicoe Cove are substantially greater than total Hg in sediment from references sites. On average, there is less contamination closest to shore (in each respective arm), the most contaminated area in the encompasses the "B" and/or "C" series sites in arms 2 – 7 (Fig. 2), and total Hg decreases at the "D" series sites farthest from shore (but not less than that seen closest to shore). For MeHg, the same general pattern was observed as for total Hg. Differences in total and methyl Hg between Jellicoe Cove sites and the reference sites are up to three orders of magnitude.

While benthic communities at test sites are *different* or *very different* than at reference sites, data show a general trend towards greater diversity and abundance of taxa at test sites in Jellicoe Cove. Community enrichment is likely due to the high organic matter present in the sediment. While there are high levels of mercury at some sites, the high TOC levels may affect mercury availability to the benthos.

Toxicity, observed mainly in *Hyalella* at one site, is not related to sediment Hg levels ([Hg] = 0.01 µg/g). Toxicity may be substrate related, as mercury concentrations are low at this site (site A1 consists of a high proportion of compact clay).

The provincial sediment quality guideline (PSQG) "lowest effect level" (LEL) of 0.2 µg/g total mercury (Persaud *et al.*, 1993) is exceeded over most of Jellicoe Cove. The "severe effect level" (SEL) of 2 µg/g is exceeded over most of the 2002 sampling area (Fig. 1). The lack of sediment toxicity or benthic community impairment within this area suggests that the provincial criteria do not represent effect levels for the Jellicoe Cove benthic community. Nevertheless, bioaccumulation of mercury from sediments into benthic

invertebrate tissues is occurring and may be of significance to organisms at higher trophic levels.
Both total and methyl mercury bioacummulate in the tissues of amphipods and midges and to levels higher than that seen in background conditions. There are significant relationships between total Hg in the sediment and total Hg in invertebrates, and methyl Hg in sediment and methyl Hg in invertebrates (stronger for total Hg). Differences in observed [Hg] in biota between Jellicoe Cove sites and reference sites are similar for total Hg and methyl Hg. Sites located in arms 5, 6, and 7 are consistently highest in [total Hg] and [methyl Hg] for both taxa.

<u>The Prediction of Mercury Concentrations in Receptor Species</u>

An ongoing component of this study is the prediction of total and methyl mercury concentrations in receptor species (this will be examined at each sampling site). The concentration in each receptor species will be calculated by multiplying observed mercury concentrations in invertebrates by appropriate literature derived biomagnification factors (BMFs), and considering likely foraging areas.

Receptor total Hg and methyl Hg concentration will be presented as a mean and as a range. The low values in the range will be derived from the minimum $[Hg]_{inv}$ of the invertebrate taxa collected at a site and the minimum of the screened BMFs obtained from the review of available studies. The high values are derived from the maximum $[Hg]_{inv}$ for a site and the maximum of the screened BMFs. The predictions of interest – those for the receptor species at the Jellicoe Cove sites – will be compared to two criteria: (1) the upper 99^{th} percentile for the predicted $[Hg]_{inv}$ for the reference sites, and (2) tissue residue guidelines (TRGs). For the first comparison, this will be done separately for the mean, and the low and high predictions.

The TRG for total Hg is the IJC's GLWQA specific objective for the "protection of aquatic life and fish-consuming birds" (500 ng/g ww). The TRG used for methyl Hg will be the lowest of the reference concentrations derived by the CCME (2000) for the protection of wildlife receptors in the AOC that consume aquatic biota.

This use of a minimum, maximum and intermediate (mean) value will aid in determining the severity of contamination between sites. For example, if there is an exceedance of the TRG using the low invertebrate tissue value and the low BMF at a site, then this would be the greatest risk. If there is exceedance of the TRG using the mean values, then there is likely risk. If predictions are below the TRG using the maximum values, then there is no risk.

Five receptor species, representing different trophic levels, will be examined for the Peninsula Harbour area. Fish species will include the Lake trout and longnose sucker. Longnose suckers in Peninsula Harbour are strict benthivores and have Hg in tissue concentrations twice as high as lake trout (mean 0.66 vs. 0.32 µg/g in 2002, MOE/MNR data). The Hg levels in suckers exceed the MOE (1994) guideline of 0.5 µg/g and have not declined over the past five years. Also being examined will be the yellow perch, as well as the great blue heron and mink.
This assessment of the potential for Hg biomagnification will aid in determining whether areas in Jellicoe Cove require remediation.

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