

Sediment Quality in Canadian
Lake Ontario Tributaries: Part Two
(Bay of Quinte and St. Lawrence River)

A Screening-Level Survey

Environmental Conservation
Branch

Ontario
Region

EHD

Environment Canada



Ecosystem Health Division Report No. ECB/EHD-OR/04-01/1

**Sediment Quality in Canadian Lake Ontario Tributaries:
Part Two (Bay of Quinte and St. Lawrence River)**

A Screening-Level Survey

A. Dove, S. Painter and J. Kraft

**Ecosystem Health Division, Ontario Region
Environmental Conservation Branch
Environment Canada**

**March 2004
Report No. ECB/EHD-OR/04-01/I**

Executive Summary

A screening-level survey of recently deposited sediment quality was undertaken in the summer of 2003 near the mouths of tributaries draining to the Lake Ontario and the St. Lawrence River. The geographical scope of the program was from the Trent River in the west to the Quebec provincial border in the east. A total of 97 samples were obtained, representing 87 sites from 80 tributaries, plus 10 field duplicate samples.

The sampling program was based on the Guidelines for Collecting and Processing Samples of Stream Bed Sediment for Analysis of Trace Elements and Organic Contaminants, developed by the United States Geological Survey (USGS) for the U.S. National Water-Quality Assessment Program (NAWQA; Shelton and Capel, 1994). A number of sub-samples were combined at each site so that one sample is obtained that is representative of the overall conditions in that tributary.

The samples were analysed for 26 organochlorine compounds plus nine (9) PCB Aroclors and Total PCBs. Sixteen (16) PAH compounds and 27 metals were analysed, and the inorganic and organic carbon content as well as grain size distribution of each sample was determined. For many of the tributaries, this study represents the first information related to organic compounds in sediments.

A total of eighteen (18) organochlorine parameters were not detected in any sample. The DDT metabolite DDE was the most commonly detected organochlorine, with a detection frequency of 24%. Concentrations were, in general, lower than those observed in a 2001 survey of Lake Erie tributaries and a 2002 survey of western Lake Ontario tributaries. The parent product DDT was only detected at one site.

One or more PCB Aroclors was detected in 43 tributaries (49% of all sites). Total PCB concentrations exceeded federal TEL guidelines at 19 sites and the federal PEL was exceeded at a further two (2) sites.

Polycyclic aromatic hydrocarbons (PAHs) were found to be widespread, with one or more of the 16 PAH compounds detected in 60 tributaries (68% of sites). The frequency of detection was somewhat lower than that observed in 2001 in Lake Erie tributaries and in 2002 in western Lake Ontario tributaries. However, some of the tributaries examined contained the highest total PAH concentrations observed to date.

At many sites, the detection of metals is likely related to their background concentrations stream sediments. For some metals, however, concentrations at some sites exceeded federal PEL (probable effect level) sediment quality guidelines as well as background levels as determined using Ontario Geological Survey stream sediment data, and may, therefore, be toxic to aquatic biota. These metals included: arsenic, chromium, copper, iron, manganese, mercury, lead, and zinc. Elevated silver and tin concentrations were observed at one and two sites, respectively.

This work is a continuation of the screening-level survey conducted in Canadian tributaries to Lake Erie in 2001 (Dove et al., 2002) and western Lake Ontario tributaries in 2002 (Dove et al., 2003), and concludes the sampling of approximately 320 sites in tributaries to the lower Great Lakes. Plans are being made to sample upper Great Lakes tributaries, including selected sites in the Lake Huron watershed in 2004. The sediment surveys will collectively provide an indication of the contaminant status of Canadian tributaries to the Great Lakes and their connecting channels, as well as indicate possible sources of contaminants from Ontario watersheds to the Great Lakes.

1.0 Introduction and Purpose

The Ecosystem Health Division (EHD) of Environment Canada (EC), Ontario Region, conducted a screening-level survey of sediment quality in Canadian tributaries to Lake Ontario from the Bay of Quinte and east and to the St. Lawrence River as far east as the Quebec provincial border during the summer of 2003. The results of the sampling program are used to identify potential sources of contaminants to the lower Great Lakes that are not being addressed by other Great Lakes programs. These screening level surveys are a part of Environment Canada's commitment toward the virtual elimination of the discharges of persistent toxic substances as required under the Great Lakes Water Quality Agreement (GLWQA) and the Canadian Environmental Protection Act (CEPA).

The purpose of the sampling was to assess sediment quality in deposition zones in each tributary prior to discharge to Lake Ontario or the St. Lawrence River. One sediment sample, consisting of many subsamples, was taken from each tributary in a manner that is representative of the overall sediment quality in that tributary.

The study was designed to maximize the probability of detecting persistent toxic substances entering the lake. The intent of the program is to identify sources of contamination for subsequent follow-up work. It is not the intent to quantify the loadings of contaminants entering the Great Lakes. Instead, the results from this program will be combined with existing water quality, fisheries, benthic and sediment contaminant information, using a weight-of-evidence approach, to prioritize subsequent track-down efforts.

Targeted parameters for the sediment screening were those identified in the Lake Ontario Lakewide Management Plan (Lake Ontario LaMP) as impairing lake-wide beneficial uses. In addition, a suite of contaminants targeted for virtual elimination in the Canada-U.S. Binational Toxics Strategy (BTS) was measured as part of Canada's commitments toward that Strategy. Additional parameters were included for contextual information (such as particle size and total organic carbon) and to improve our understanding of the contaminant status of Lake Ontario tributaries (e.g., metals, pesticides, contaminants of emerging concern).

Sampling these tributaries in 2003 represented the third year of investigations conducted by Environment Canada. In 2001, approximately 100 tributaries to Lake Erie, including the upstream connecting channels (St. Clair River and Detroit River) and Lake St. Clair were sampled. In 2002, approximately 130 tributaries to the Niagara River and Lake Ontario, as far east as the Bay of Quinte, were sampled. The results of these investigations are available as Ecosystem Health Division, Environment Canada, reports (Dove et al., 2002 and 2003).

2.0 Methodology

The sampling program consisted of a survey-level, screening assessment of recently deposited sediment quality near the mouths of tributaries entering Lake Ontario. The targeted substances are relatively insoluble in water (i.e., hydrophobic) and are therefore typically found at higher concentrations in sediments. In addition, bed sediments in depositional environments provide a time-integrated sample of particulate matter transported by a stream. Analysis of bed sediments alleviated problems associated with detecting trace levels of substances in water samples. Bed sediment sampling can overcome problems detecting periodic or intermittent sources of contaminants in water from pollution sources.

2.1 Field Program

Tributary Selection

A reconnaissance survey was conducted in the autumn of 2002 to identify tributaries and select the sampling sites. Sediment deposition zones were selected near the mouths of the tributaries so that they were likely downstream from potential contaminant sources yet sufficiently far upstream not to be influenced by the water body into which the tributary drains. In other words, sites were selected to be outside of the zone of lake influence, to the extent possible.

During the reconnaissance survey, the method of access was also identified. Most sites were accessed by wading, or were sampled from a bridge crossing. In certain, larger tributaries, sampling sites were accessed by boat. In the majority of cases, the sample site coincided with the most downstream road crossing of the tributary.

Number of Sites

Virtually every tributary draining the Canadian side of Lake Ontario and the St. Lawrence River was sampled in this program. For many sites, this program has provided the first information about organic contaminants in sediments. The geographic extent of the program was from the Trent River in the west to the Quebec provincial border in the east. The tributaries sampled during the project are shown in Figure 1 and with the tributary names in Appendix B.

A total of 97 samples were obtained, representing 87 sites from 80 tributaries, plus 10 field duplicate samples. The field duplicates were blind duplicate samples; that is, they were split samples that were assigned a fictitious name in the field (usually a name of a rodent). The blind duplicates were used to assess variability due to sample handling and laboratory precision. A list of blind duplicates and the corresponding tributary is provided in Table 1.

Table 1. Blind Duplicate Sample Listing

Tributary	Blind Duplicate Sample
Consecon Creek	Gerbil Creek
Marshy Creek Picton	Vole Creek
Millhaven Creek	Mole Creek
Glen Miller Creek	Doormouse Creek
Canoe, Gananoque River	Rat Creek
Jones Creek	Pica Creek
Bradleys Creek	Lemming Creek
Flagg Creek	Marmot Creek
Raisin River	Bunny Run
Buells Creek	Groundhog Creek

In several of the larger rivers, more than one sample was collected. In the Trent River, three samples were taken; one at Glen Miller along the west shore of the river, one further downstream near Trenton, plus a third in the river at the mouth of Mayhew Creek, a tributary to the river.

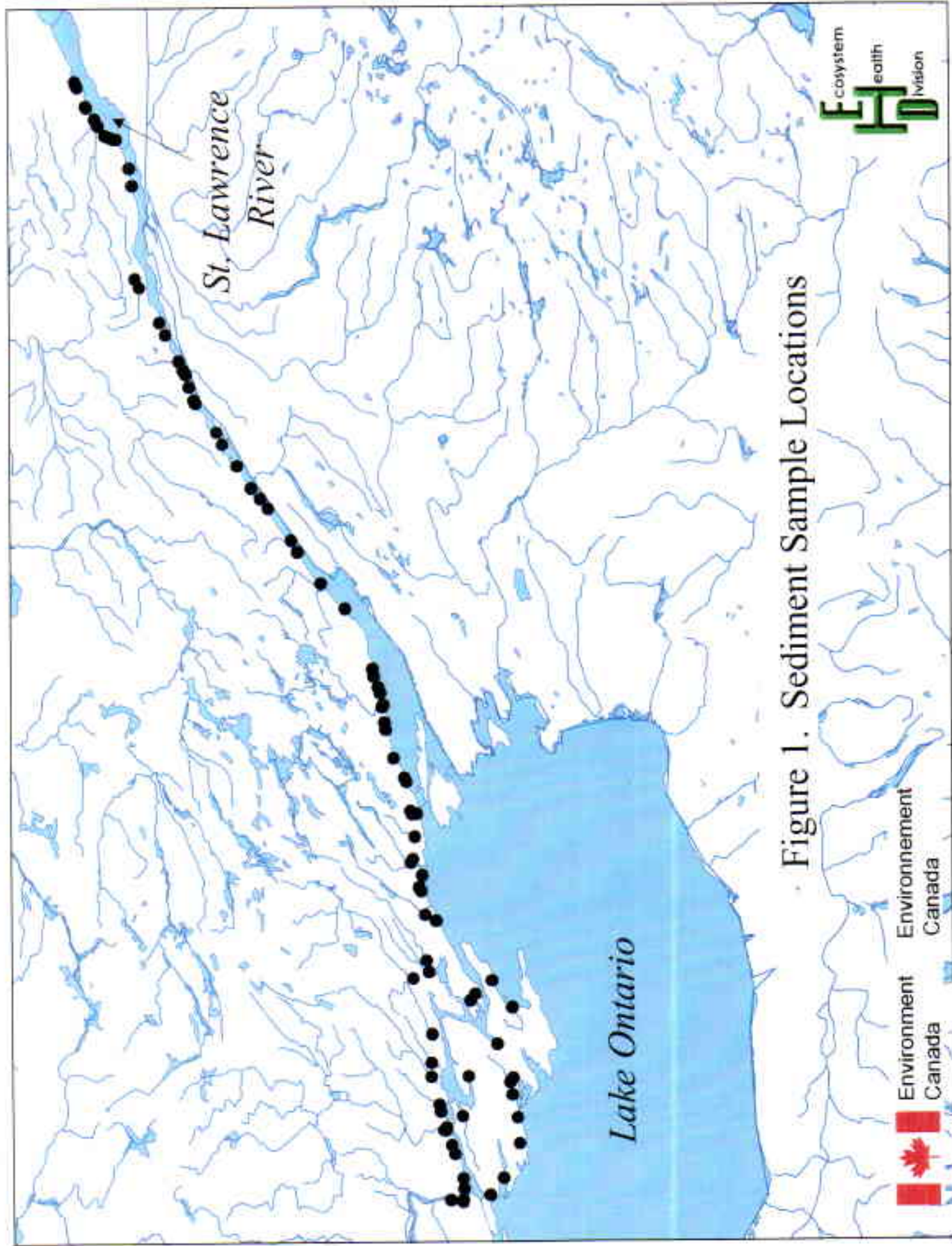


Figure 1. Sediment Sample Locations

In the Moira River, three samples were taken; one upstream of Highway 2 plus two further downstream (one from the western portion of the river and one from near Meyer's Pier). In the Gananoque River, two samples were taken. At the primary, downstream location, sediments were relatively coarse, therefore another site ("Canoe") was sampled upstream of the dam, along the eastern shore, where the sediments were much finer. In the Cataraqui River, three samples were taken; one each from the eastern and western portions of the river and one offshore from Fort Frontenac. At other sites, a single composite sample was taken, as described below.

Sampling Methodology

The sampling program design was based on the Guidelines for Collecting and Processing Samples of Stream Bed Sediment for Analysis of Trace Elements and Organic Contaminants, developed by the United States Geological Survey (USGS) for the U.S. National Water-Quality Assessment Program (NAWQA; Shelton and Capel, 1994). In the NAWQA program, downstream locations in watersheds are selected to provide a coarse-scale network of sites. At these "integrator" sites, problems that may not be detected in smaller basins have a reasonable chance of being detected. A number of sub-samples are combined so that one sample is obtained that is representative of the overall conditions in that tributary.

Field Campaign

Sampling was conducted between July 22 and November 19, 2003. One or more depositional zones were sampled in each tributary. Only the very fine-grained surface deposits, to a maximum depth of approximately 1 or 2 cm, depending on the site, were collected. These surface sediments better represent relatively recent rather than historic deposition. Depositional zones were chosen to be representative of the variety of locations (i.e., mid-channel, left bank, right bank) and habitat types (pools, different depths of water, behind obstacles such as boulders or sand bars) present at each site. Only wetted depositional zones were sampled.

Where water depths permitted wading and water velocities were slow enough to permit sample retrieval, samples were obtained using a stainless steel spoon and collected in a glass bowl. At sites where the water depth was too great for wading, or water velocities were swift enough to wash the fine particles from the spoons during sample retrieval, an all-stainless steel Wildco Petite Ponar sampler was used.

Upon arrival at each site, the sampling equipment was thoroughly rinsed in the ambient river water. The surface sediments were collected (either by spoon or Ponar, as described above) and combined in a glass bowl. The sediments were sieved through a 2-mm stainless steel sieve to remove the larger size fractions and to assist with homogenization of the sample. The sample was further homogenized by mixing with a spoon for approximately two minutes.

Several sample jars were filled at each site. In general, four jars were used:

- one 125-mL polyethylene container filled with approximately 2 cm of sediment for metals analysis;
- one 125-mL polyethylene container filled approximately ½ full for total organic carbon and grain size analysis;
- one 250-mL amber glass container with Teflon-lined screw cap filled approximately ¾ full for organochlorine (OC) and polyaromatic hydrocarbon (PAH) analysis, and;
- one 250-mL amber glass container filled approximately ¾ full for archiving purposes.

Sample jars were labeled with permanent marker on both the lids and on laboratory tape affixed to the side of the jars. The recorded information included the site name, date, organization (EHD/OR), and parameters for analysis (e.g. OCs and PAHs, metals, TOC and grain size, Archive). After the appropriate sample jars were filled, the sampling equipment was thoroughly rinsed in the ambient river water.

A field drawing was made and digital photos were taken at each site. A sketch of each tributary reach was made to include its major features, habitat types, approximate dimensions, surrounding land uses, major road crossings, etc. The locations and number of sampling sites were identified on each sketch, and the method of sediment retrieval was noted. A Lowrance Global Map 100 geographic positioning system (GPS) device was used to obtain the coordinates for each location using the position averaging function. The GPS location within the site was included on the sketch.

Samples were kept on ice in portable coolers while in the field. Upon return to the Canada Centre for Inland Waters in Burlington, the samples were decanted then frozen at -10°C . Samples in glass bottles were frozen on their sides to prevent bottle breakage.

2.2 Laboratory Methods

The samples in polyethylene containers (i.e., those for metals, TOC and grain size analysis) were freeze-dried prior to analysis. Freeze drying, and grain size distribution and organic carbon content analyses were conducted by Natural Resources Canada (NRCAN) in Ottawa, Ontario. Once freeze-dried, TOC was analyzed by Leco Cr-412 and grain size fractions were determined using a Lecotrac Particle Size Analyzer LT100.

A suite of 28 metals was analyzed by Caduceon Enterprises Inc. using aqua regia digestion methods.

Analysis of organochlorines (OCs) (including PCBs) and polycyclic aromatic hydrocarbons (PAHs) was done by Maxxam Analytics Inc. in Mississauga. Frozen, wet sediment samples were sent to Maxxam in the autumn of 2002. Samples were thawed and OCs analyzed by gas chromatography/dual column electron capture detector (GC/ECD) after accelerated solvent extraction following the EPA protocol SW846 EPA 3545. Samples for PAH analysis were extracted using a sonication method. The extracts were then concentrated and analyzed by gas chromatography/mass spectrometry (GC/MS). Sample results were reported on a dry weight basis.

The archived sediments are stored frozen at -20°C at the Canada Centre for Inland Waters in Burlington, Ontario. The Ontario Ministry of the Environment is analyzing portions of selected samples for dioxins, furans, dioxin-like PCBs, and selected compounds of emerging concern (e.g., in-use pesticides, polychlorinated naphthalenes). The results of these analyses will be reported under separate cover as they become available.

2.3 Data Analysis

The laboratory results were analyzed in a spreadsheet program. Results were compared with the federal and provincial sediment quality objectives, other sites sampled in this program in the approximately 230 tributaries to Lakes Erie and Ontario sampled in 2001 and 2002 (Dove et al., 2002, 2003). The frequency of detection and frequency of exceedence of the sediment quality objectives were computed. Mapping of selected compounds was performed on 1:250,000 basemaps of the Lake Ontario basin using ArcView 8.1.

3.0 Results

Throughout this report, references and comparisons are made to the federal and provincial sediment quality guidelines. For clarity and consistency, each guideline is assigned a unique colour. The graphics presented in this report use these colours to indicate exceedences of the guidelines. The following colour coding is also referenced in Appendix B:

Guideline	Colour Code
Federal Sediment Quality Guidelines	
Below Threshold Effect Level (TEL)	Green
Above Federal TEL but below PEL	Yellow
Above Probable Effect Level (PEL)	Orange
Provincial Sediment Quality Guidelines	
Below Lowest Effect Level (LEL)	Green
Above LEL but below SEL	Blue
Above Severe Effect Level (SEL)	Red

In this report, concentrations of organochlorine compounds and PCBs are provided in parts-per-million (ppm or $\mu\text{g/g}$). Concentrations of metals are also reported in parts-per-million (ppm or $\mu\text{g/g}$), with the exception of mercury which is reported in ppb (ng/g). Polycyclic aromatic hydrocarbons (PAHs) are reported in parts-per billion (ppb or ng/g).

3.1 Quality Assurance/Quality Control

All laboratories used for the project were Canadian Association for Environmental Analytical Laboratories (CAEAL) accredited for their respective analytical parameters. As cited above, Maxxam Analytical Inc. performed the organochlorine and PAH analyses. The Maxxam laboratory QA/QC program consisted of blanks, spiked blanks and duplicate samples (i.e., laboratory replicate runs).

All method blanks were below method detection limits and spike recoveries were within acceptable limits (40-130%) for all parameters with the exception of endrin aldehyde, which had a spike recovery of between 8 and 91%.

Paired student t-tests were performed to assess differences between blind duplicate samples submitted to the laboratory. The majority of parameters could be assessed this way, with the exception of parameters that were detected in fewer than three samples. There were no significant differences observed between the blind duplicate samples at the 95% confidence level for any parameter tested.

3.2 Method Detection Limits

Many of the analytical parameters reported in the study are hydrophobic (i.e., they have a propensity for solid surfaces such as sediments as opposed to the dissolved phase). Sampling very fine, flocculent surface deposits, as was done here, serves to maximize the probability of encountering these parameters, if they are present in the environment. Typical laboratory detection limits are, therefore, sufficient to detect these parameters at ambient concentrations. The laboratory method detection limits for both laboratories used in this study are provided in Table 2. This Table also summarizes the parameters measured in the study.

**Table 2. Analytical Parameters and Laboratory Method Detection Limits
a. Maxxam Analytics Inc. (Organics)**

<u>Polychlorinated Biphenyls (PCBs)</u>		<u>Polycyclic Aromatic Hydrocarbons (PAHs)</u>		<u>Organochlorine Pesticides (OCs)</u>	
Parameter	MDL	Parameter	MDL	Parameter	MDL
Aroclor 1016	0.01 ug/g	Naphthalene	25 ng/g	Hexachlorobenzene	0.002 ug/g
Aroclor 1221	0.02 ug/g	Acenaphthylene	25 ng/g	o,p'-DDD	0.002 ug/g
Aroclor 1232	0.01 ug/g	Acenaphthene	50 ng/g	Endrin aldehyde	0.002 ug/g
Aroclor 1242	0.02 ug/g	Fluorene	25 ng/g	o,p'-DDT	0.002 ug/g
Aroclor 1248	0.01 ug/g	Phenanthrene	25 ng/g	Toxaphene	0.08 ug/g
Aroclor 1254	0.01 ug/g	Anthracene	25 ng/g	o,p'-DDE	0.002 ug/g
Aroclor 1260	0.01 ug/g	Fluoranthene	25 ng/g	Aldrin	0.002 ug/g
Aroclor 1262	0.01 ug/g	Pyrene	25 ng/g	a-BHC	0.002 ug/g
Total PCB	0.01 ug/g	Benz(a)anthracene	50 ng/g	b-BHC	0.002 ug/g
		Chrysene	50 ng/g	d-BHC	0.002 ug/g
		Benzo(b)fluoranthene	50 ng/g	g Lindane	0.002 ug/g
		Benzo(k)fluoranthene	50 ng/g	a-Chlordane	0.002 ug/g
		Benzo(a)pyrene	25 ng/g	g-Chlordane	0.002 ug/g
		Indeno(1,2,3-cd)pyrene	100 ng/g	p,p'-DDD	0.002 ug/g
		Dibenzo(a,h)anthracene	100 ng/g	p,p'-DDE	0.002 ug/g
		Benzo(ghi)perylene	100 ng/g	p,p'-DDT	0.002 ug/g
				Dieldrin	0.002 ug/g
				Endosulfan I	0.002 ug/g
				Endosulfan II	0.002 ug/g
				Endosulfan sulfate	0.002 ug/g
				Endrin	0.002 ug/g
				Heptachlor	0.002 ug/g
				Heptachlor epoxide	0.002 ug/g
				Methoxychlor	0.008 ug/g
				Mirex	0.002 ug/g
				Octachlorostyrene	0.002 ug/g

**Table 2 cont. Analytical Parameters and Laboratory Method Detection Limits
b. Caduceon Enterprises (Metals)**

Parameters	Units	MDL
Aluminum	%	0.03
Arsenic	µg/g	5
Barium	µg/g	1
Beryllium	µg/g	0.2
Bismuth	µg/g	5
Cadmium	µg/g	0.5
Calcium	%	0.01
Chromium	µg/g	1
Colbalt	µg/g	1
Copper	µg/g	1
Iron	%	0.03
Lead	µg/g	5
Magnesium	%	0.01
Manganese	µg/g	1
Molybdenum	µg/g	1
Nickel	µg/g	1
Potassium	%	0.03
Silver	µg/g	0.5
Sodium	%	0.02
Strontium	µg/g	1
Thallium	µg/g	0.02
Tin	µg/g	10
Titanium	µg/g	1
Vanadium	µg/g	1
Yttrium	µg/g	0.5
Zinc	µg/g	1
Mercury	ng/g	5

All laboratory method detection limits were below sediment quality guidelines, with the exception of five of the individual PAH compounds (acenaphthylene TEL = 5.9 ng/g; acenaphthene TEL = 6.7 ng/g; fluorine TEL = 21.2 ng/g; benz(a)anthracene TEL = 31.7 ng/g; dibenzo(a,h)anthracene TEL = 6.22 ng/g).

3.3 Laboratory Results

This section reviews the detection frequency and exceedences of sediment quality guidelines for the measured parameters. A discussion of the highest observed levels for selected parameters is presented in Section 4. A full listing of the laboratory data for the 87 unique sites is provided in Appendix A. The blind duplicate sample data are not provided, but may be obtained from Environment Canada upon request.

3.3.1 Frequency of Detection

In general, organochlorine parameters were not detected, with some notable exceptions. A total of 18 organochlorine pesticide parameters were not detected in any sample. In addition, six (6) of the nine (9) PCB Aroclors analyzed were not detected. Each of the PAHs was detected in at least

one sample. One metal was not detected in any sample. The parameters that were not detected are listed in Table 4.

Table 4. Parameters Not Detected

Organochlorines
<ul style="list-style-type: none"> • Hexachlorobenzene • Octachlorostyrene • Endrin aldehyde • Toxaphene • Aldrin • a-BHC • b- BHC • d-BHC • o,p'-DDD • o,p'-DDE • o,p'-DDT • Dieldrin • Endosulfan I • Endosulfan II • Endrin • Heptachlor • Heptachlor epoxide • Mirex
PCB Aroclors
<ul style="list-style-type: none"> • Aroclor 1262 • Aroclor 1016 • Aroclor 1221 • Aroclor 1232 • Aroclor 1248 • Aroclor 1268
Metals
<ul style="list-style-type: none"> • Bismuth

The frequency of detection of the remaining parameters is provided in Table 5. Metals were commonly detected due to their natural presence in most sediment. Polycyclic aromatic hydrocarbons were also commonly detected, likely due to inputs from anthropogenic sources. Of the organochlorines, the DDT metabolite p,p'-DDE was the most frequently detected parameter.

Table 5. Frequency of Parameter Detection

Organochlorines	# Detections	Frequency
p,p'-DDE	21	24%
p,p'-DDD	11	13%
γ-Chlordane	1	1%
p,p'-DDT	1	1%
Endosulfan sulfate	1	1%
Methoxychlor	1	1%

PAH	# Detections	Frequency
Total PAH	60	68%
Fluoranthene	60	68%
Pyrene	52	59%
Phenanthrene	39	44%
Chrysene	31	35%
Benzo(a)pyrene	28	32%
Benzo(b)fluoranthene	27	31%
Benzo(a)anthracene	20	23%
Benzo(k)fluoranthene	20	23%
Anthracene	19	22%
Indeno(1,2,3-cd)pyrene	15	17%
Benzo(ghi)perylene	14	16%
Acenaphthylene	10	11%
Fluorene	8	9%
Naphthalene	6	7%
Acenaphthene	6	7%

PCB	# Detections	Frequency
Total PCB	43	49%
Aroclor 1254	40	45%
Aroclor 1260	38	43%
Aroclor 1242	4	5%

Metal	# Detections	Frequency
Silver	1	1%
Aluminum	87	100%
Antimony	0	0%
Arsenic	5	6%
Barium	87	100%
Beryllium	83	94%
Bismuth	0	0%
Cadmium	64	73%
Calcium	87	100%
Chromium	87	100%
Cobalt	87	100%
Copper	87	100%
Iron	87	100%
Lead	87	100%
Lithium	63	72%
Magnesium	87	100%
Manganese	87	100%
Molybdenum	5	6%
Nickel	87	100%
Potassium	87	100%
Sodium	87	100%
Titanium	87	100%
Thallium	4	5%
Tin	6	7%
Strontium	87	100%
Vanadium	87	99%
Yttrium	87	100%
Zinc	87	100%
Mercury	87	100%

3.3.2 Comparison of Results with Sediment Quality Guidelines

The sediment quality results were compared to the Canadian Environmental Quality Guidelines (Canadian Council of Ministers of the Environment (CCME), 2002). The CCME sediment quality guidelines provide scientific benchmarks, or reference points, for determining the potential for adverse biological effects in aquatic systems. The guidelines are derived from

available toxicological information. The lower value, referred to as the Threshold Effect Level (TEL), represents the concentration below which adverse biological effects are expected to occur rarely. The higher value, referred to as the Probable Effect Level (PEL), represents the level above which adverse effects are expected to occur frequently. Fewer than 25% of adverse effects (in the Biological Effects Database for Sediments, CCME 2002) occur below the TEL, and more than 50% of adverse effects occur above the PEL.

Where no federal guidelines were available, the provincial guidelines were used for comparison (Persaud et al., 1993). The provincial sediment quality guidelines are based on the long-term ecotoxic effects of contaminants to benthic organisms. The Lowest Effect Level (LEL) is considered to be the level of contamination that can be tolerated by the majority of benthic organisms, and is lower than the federal TEL for many parameters. The Severe Effect Level (SEL) would be detrimental to the majority of benthic species, and is higher than the federal PEL for most parameters. Severe Effect Levels for organochlorine compounds and PAHs were calculated individually for each site using the organic carbon concentration in that particular sediment sample.

Table 6 provides a summary of the numbers of exceedences of the federal and provincial sediment quality guidelines. A complete list of the sediment quality guidelines themselves is provided in Appendix B.

Table 6. Number of Sites Exceeding Sediment Quality Guidelines

A. Metals	Federal Guidelines		Provincial Guidelines	
	Exceeds TEL ¹	Exceeds PEL ²	Exceeds LEL ³	Exceeds SEL ⁴
Arsenic	2	2	1	1
Cadmium	44	0	44	0
Chromium	21	0	23	2
Copper	14	2	43	1
Iron			49	1
Lead	17	6	4	0
Manganese			44	12
Nickel			47	0
Zinc	38	6	2	0
Mercury	0	2	4	0
B. Organochlorines				
Chlordane	0	0	0	0
p,p'-DDD	-	-	0	0
p,p'-DDE	-	-	9	0
Total DDD (o,p' + p,p')	2	0	-	-
Total DDE (o,p' + p,p')	12	9	-	-
Total DDT (o,p' + p,p')	1	0	-	-
Total DDT (DDD+DDE+DDT)	-	-	9	0
PCB Aroclor 1254	6	0	6	-
PCB Aroclor 1260	-	-	37	-
Total PCB	11	2	8	-

Table 6 cont. Number of Sites Exceeding Sediment Quality Guidelines

C. Polycyclic Aromatic Hydrocarbons	Exceeds TEL¹ Below PEL	Exceeds PEL²	Exceeds LEL³ Below PEL
Naphthalene	5	1	-
Acenaphthylene	4	6	-
Acenaphthene	1	5	-
Fluorene	5	3	2
Phenanthrene	34	1	11
Anthracene	12	5	2
Fluoranthene	25	5	9
Pyrene	34	8	5
Benzo(a)anthracene	10	10	0
Chrysene	19	5	7
Benzo(k)fluoranthene	-	-	8
Benzo(a)pyrene	18	6	4
Indeno(1,2,3-cd)pyrene	-	-	12
Dibenzo(a,h)anthracene	0	1	0
Benzo(ghi)perylene	-	-	12

- Notes:
- 1 Federal Threshold Effect Level (CCME, 2002)
 - 2 Federal Probable Effect Level (CCME, 2002)
 - 3 Provincial Lowest Effect Level (Persaud et al., 1992)

4.0 Discussion

4.1 DDT and Metabolites

DDT (dichlorodiphenyltrichloroethane) is a chlorinated hydrocarbon that has broad-spectrum pesticide properties. It was used in large quantities in the 1950s and 1960s on crops. The U.S. banned the use of DDT in 1973. The use of DDT in Canada was severely restricted in the early 1970s and discontinued in 1985, with the sale and use of existing stocks permitted until the end of 1990 (CCME, 2002). DDT is still used as an insecticide in other countries.

DDT has two metabolites: DDE (dichlorodiphenyldichloroethylene) and DDD (dichlorodiphenyldichloroethane). Each DDT molecule has several isomeric forms, depending on the configurations of the chlorine atoms on the molecule. For comparison with sediment quality guidelines, the laboratory results were analysed according to the following:

$$\begin{aligned} \text{Total DDT} &= o,p' \text{- plus } p,p' \text{-DDT} \\ \text{Total DDE} &= o,p' \text{- plus } p,p' \text{-DDE} \\ \text{Total DDD} &= o,p' \text{- plus } p,p' \text{-DDD} \\ \text{Total DDT and metabolites} &= \text{Total DDT} + \text{Total DDE} + \text{Total DDD} \end{aligned}$$

DDT, including its metabolites, was the most commonly detected organochlorine compound in the current study. Of the 87 tributaries sampled, 24 (27% of sites) had detectable quantities of one or more isomer of DDT or its metabolites. The most commonly detected isomer was *p,p'*-DDE, with a detection frequency of 24%.

The concentrations of DDT observed in 2003 were lower than those measured in 2001 in Lake Erie tributaries and in 2002 in western Lake Ontario tributaries. The frequency of sediment

Technical grade endosulfan is a mixture of two stereoisomers (endosulfan I and endosulfan II) which are present in approximately a 7:3 ratio, respectively (NRCC, 1975). Both were measured in the current study, as well as the primary break-down product of both isomers, endosulfan-sulfate.

No technical grade endosulfan (i.e., the parent products endosulfan I or endosulfan II) was detected in this study. The breakdown product, endosulfan-sulfate, was detected at one site, Marshy Creek in Picton.

Similar to other organochlorines, the frequency of detection of endosulfan was low compared to other lower Great Lakes tributaries. In Lake Erie tributaries sampled in 2001, one or more forms of endosulfan were detected in 15 tributaries (15% of sites; Dove et al., 2002) and in the Lake Ontario tributaries sampled in 2002, 26 tributaries (20% of sites) had detectable concentrations of technical grade endosulfan (Dove et al., 2003).

4.3 PCBs

Polychlorinated biphenyls, or PCBs, were commonly used in electrical equipment such as transformers and capacitors due to their dielectric and flame retardant properties, and their chemical stability. The manufacture of PCBs was halted in 1977 in the United States. PCBs were not produced in Canada but approximately 40 000 tonnes of PCBs were imported and used commercially prior to the 1980s. Like many other organochlorine compounds, PCBs are persistent, bioaccumulative and toxic. They are the cause of the majority of the fish consumption advisories in each of the Great Lakes and they are considered a priority pollutant by many authorities. The Great Lakes Water Quality Agreement calls for the virtual elimination of discharges of PCBs.

In the current study, PCBs were analysed in the laboratory as Aroclors, the trade name that describes the complex mixture of PCB congeners under which some PCBs were manufactured. This method is much less expensive than the more elaborate congener analyses although it is also less precise and less accurate. The detection limit for Aroclor analysis was 10 ng/g, which is below the sediment quality guidelines and sufficient for the purposes of detecting PCBs in sediments.

Only three of the nine PCB Aroclors were detected in this study. Aroclors 1254, 1260 and 1242 were detected at 40, 38 and 4 sites, respectively. One or more Aroclors were detected in 43 tributaries, representing about 49% of all sites sampled. The composition of the PCBs and the frequency of detection was similar to the other surveys of lower Great Lakes tributaries (Dove et al., 2002, 2003).

In about one-half of the cases where PCBs were detected, the concentration was below the Federal TEL of 0.0341 ug/g. The TEL was exceeded at 19 sites, and the PEL (0.277 ug/g) was exceeded at a further two (2) sites. As shown in Figure 3, the highest concentrations of PCBs were found in the western portion of the Cataraqui River in Kingston, and in Wells Creek, which flows into the St. Lawrence River east of Maitland, Ontario. Sites with total PCB concentrations above 0.070 ug/g (the provincial LEL) are listed below, and a map of total PCB concentrations is provided in Figure 3.

Tributary	Total PCB concentration (ug/g)
Cataraqui West	0.42
Wells Creek	0.3
Consecon Creek	0.19
Cataraqui Fort Frontenac	0.14
Marshy Creek, Picton	0.11
Moira River	0.11
Salmon River	0.11
Moira West	0.09
Napanee River	0.08
Buells Creek	0.078

At the sites showing PEL exceedences, confirmatory sampling will be initiated. The federal and provincial environmental agencies in Ontario (Environment Canada and the Ontario Ministry of the Environment) have partnered to conduct source track-down work at locations in the Great Lakes basin where ambient data indicate potentially significant sources of PCBs may exist. This track-down program is part of the partners' commitment to achieve the virtual elimination of discharges of PCBs in the Great Lakes basin. A source track-down project is already underway in the Cataraqui River in Kingston. Environment Canada plans to conduct confirmatory sampling in Wells Creek in 2004.

4.4 PAHs

Polycyclic aromatic hydrocarbons are produced during the incomplete combustion of organic substances, most commonly the combustion of fossil fuels. As an indicator of human industrial activities, PAH contamination is relatively widespread.

PAHs were commonly detected in the current survey, and in the 2001 and 2002 surveys of other lower Great Lakes tributaries (Dove et al., 2002, 2003). In 2003, one or more of the 16 PAH compounds measured were detected in 60 tributaries (68% of sites). The frequency of detection was somewhat lower than that observed in 2001 in Lake Erie tributaries (95% of sites; Dove et al., 2002) and in 2002 in Lake Ontario tributaries (98%; Dove et al., 2003). However, selected tributaries sampled in 2003 contained some of the highest PAH concentrations observed to date. Four of the ten tributaries with the highest PAH concentrations were found in the 2003 survey.

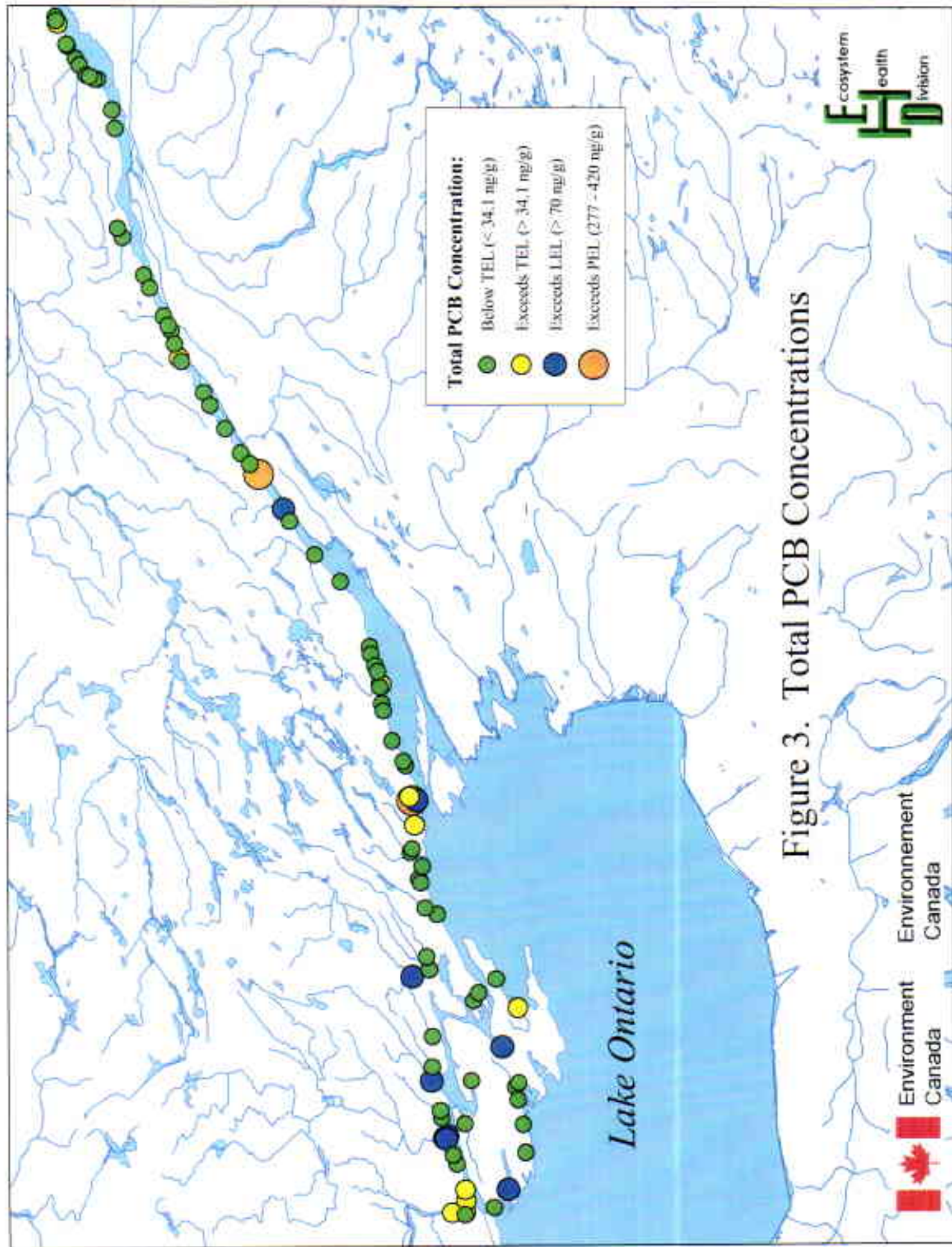


Figure 3. Total PCB Concentrations

A listing is provided below of the ten tributaries with concentrations of total PAH greater than 10,000 ng/g. Sites with the highest total PAH concentrations tended to be located in urban areas, such as Kingston (Catarqui River and Lakeview Creek), Gananoque (Gananoque River) and Brockville (Buell's Creek). A map of the PAH concentrations in 2003 is provided in Figure 4.

Tributary	Total PAH concentration (ng/g)
Catarqui Fort Frontenac	120,895
Lakeview Creek	22,471
Gananoque River	19,686
Warnica Creek	15,547
Buell's Creek	11,878
Wells Creek	10,882

4.5 Metals

4.5.1 Arsenic

Arsenic is a metalloid and a nonessential trace element. Its release from anthropogenic sources is mainly from gold and base metal production facilities, with smaller releases from the use of arsenical pesticides, wood preservatives, coal-fired power generation and disposal of domestic and industrial wastes (Environment Canada, 1993).

In the past surveys, arsenic has been found to exceed sediment quality criteria relatively frequently. At approximately 50% of the sites sampled in 2001 and 2002, concentrations were above the federal TEL of 5.9 µg/g, and the PEL of 17 µg/g was exceeded at 4% of sites. Exceedences of the TEL may be due to naturally elevated arsenic levels. In the National Geochemical Reconnaissance (NGR) program of the Geological Survey of Canada, the mean concentration of arsenic in stream sediments (from selected areas of Canada) was determined to be 10.7 µg/g (P.W.B. Friske, 1996 in CCME 2002), which is greater than the federal TEL of 5.9 µg/g.

In the current survey, only three (3) samples were found to have concentrations of arsenic exceeding the federal PEL. These three samples were all collected from different areas of the Moira River. The Moira River is known to have arsenic contamination originating from the Deloro gold mine within its watershed. Only two other sites contained concentrations of arsenic exceeding the threshold effect level, and these are more likely to be due to natural sources. The lower levels of arsenic in stream sediments in eastern Ontario likely indicate that natural arsenic levels are lower here than they are in other areas of the country.

4.5.2 Cadmium

Cadmium is a non-essential trace element that is produced commercially from base-metal smelters and refineries, especially zinc refining. It is used in batteries, coatings, pigments, stabilizers and alloys (Hoskin, 1991 in Environment Canada, 1994a). Natural, background levels of cadmium may be equivalent or greater than the TEL, as the NGR program determined the mean concentration of cadmium in Canadian stream sediments to be 0.63 µg/g (P.W.B. Friske,

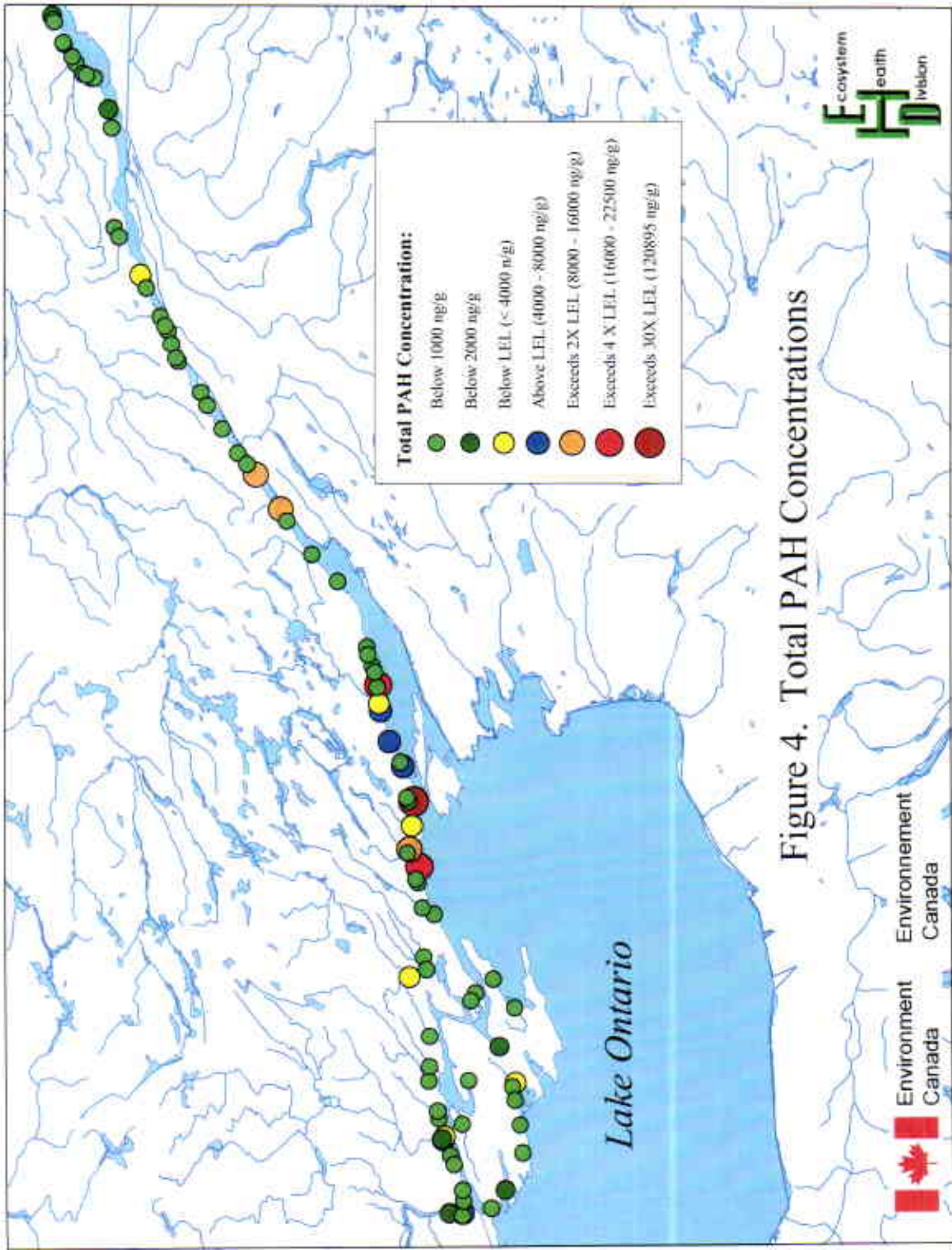


Figure 4. Total PAH Concentrations

1996 in CCME 2002). In an assessment of the NGR data, Painter et al. (1994) found that 95% of the data were below 1.3 µg/g.

Cadmium was detected at 63 sites in the current study. The federal PEL of 3.5 µg/g was not exceeded at any site. The federal TEL (0.6 µg/g and equivalent to the provincial LEL) was exceeded at 44 sites.

4.5.3 Chromium

Chromium is a biologically essential trace element that can be toxic to organisms at elevated levels (CCME 2002). It is not mined in Canada, but its import contributes to the production of pigments, metal finishing, leather tanning and wood preservatives (Nriagu 1988 cited in Environment Canada 1994b).

Chromium was found at concentrations exceeding the TEL of 37.3 µg/g at 21 sites, and two sites were found to exceed the PEL of 90 µg/g and the SEL of 110 µg/g. These highest concentrations of chromium were observed in the western portion of the Cataraqui River, Kingston. For comparison, the chromium concentration in the eastern portion of the Cataraqui River ("Cataraqui East") was 60 µg/g.

Tributary	Chromium (µg/g)
Cataraqui West	1270
Cataraqui Fort Frontenac	157

4.5.4 Copper

Copper is a biologically essential trace element whose anthropogenic sources are mainly from mining and smelting operations. Naturally elevated copper concentrations may contribute to the copper content in streambed sediments. In an analysis of the NGR sediment database, Painter et al. (1994) found that 95% of Cu concentrations were below 76 µg/g. In the current study, three sites exceeded this level. Two sites exceed the federal PEL of 197 µg/g, and one additional site exceeded the provincial SEL of 110 µg/g.

Tributary	Copper (µg/g)
Buells Creek	1080
Marshy Creek	215
Gananoque River	126

4.5.5 Mercury

Mercury is a nonessential trace element that is toxic, persistent and, when methylated, bioaccumulative. Fish consumption advisories are in effect for mercury in much of the Great Lakes ecosystem. Current uses of mercury include some batteries, dental fillings, thermometers and switches, cathode tubes and household cleaners. Sources of mercury to the environment include mining and smelting, wastewater, fossil fuel combustion and waste incineration.

Sediment from most tributaries contained relatively low concentrations of mercury. Six sites exceeded the federal TEL of 170 ng/g, including two sites which exceeded the PEL of 486 ng/g. Local, natural mercury deposits can impact environmental concentrations. The 95th percentile for

mercury in the NGR database was determined to be 190 ng/g (Painter et al., 1994). Levels above this are therefore unlikely to be of natural origin.

The two tributaries with mercury concentrations in exceedence of the federal PEL were also found to have elevated levels of other parameters. Confirmatory sampling is planned prior to additional, targeted sampling. Mercury is considered to be a lakewide critical pollutant in the Lake Ontario LaMP, therefore, targeted actions will be required to address any significant ongoing source of this metal to the lake.

Tributary	Mercury (ng/g)
Marshy Creek	647
Buells Creek	575
Cataraqui West	312
Gananoque River	265
Moir River, Meyers Pier	230
Cataraqui Fort Frontenac	204

4.5.6 Lead

Lead is a nonessential trace element. Its past use as an additive in gasoline has resulted in its widespread distribution in the environment above background levels. Currently, sources of lead to the environment include lead processing activities, batteries, and industrial and municipal effluents. Lead concentrations exceeded the PEL of 91.3 µg/g at six (6) sites and the federal TEL of 35 µg/g at a further 17 sites. The concentrations of lead found in the survey are shown in Figure 6, and sites showing PEL exceedences are listed below.

The 95th percentile of stream and lake sediment lead concentration in the NGR database was 25 µg/g (Painter et al., 1994). Even TEL exceedences are, therefore, likely due to anthropogenic sources. The high number of TEL exceedences may be due to the widespread use of lead in the past as a fuel additive. At the six sites showing PEL exceedences, local sources may also be contributing to elevated levels in the stream sediments.

Tributary	Lead (µg/g)
Cataraqui West	151
Buells Creek	145
Trent River	142
Gananoque River	100
Moir River, Meyers Pier	97
Cataraqui Fort Frontenac	92

4.5.7 Zinc

Zinc is an essential trace element that is considered toxic to aquatic biota at elevated concentrations (CCME, 2002). Anthropogenic zinc sources are primarily related to metals processing, with smaller releases from fossil fuel burning and ancillary sources such as fertilizers, rubber goods and pharmaceuticals.