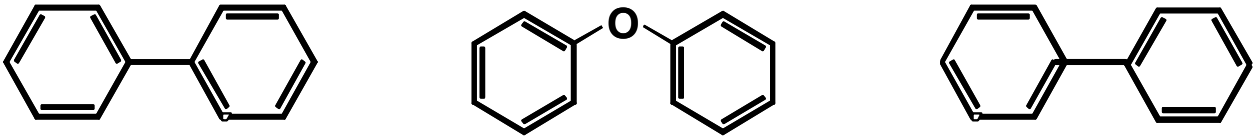
United States Environmental Protection Agency

EPA Region 2

Bioaccumulative Contaminants in Lake Ontario Surface Water, 1999



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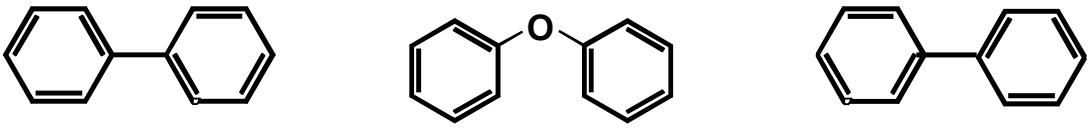

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Executive Summary

Concentrations of PCBs, pesticides and other bioaccumulative contaminants were measured in Lake Ontario surface water in October 1999 to help the U.S. - Canada Lake Ontario Lakewide Management Plan develop better information on contaminants of concern. Most surface water bioaccumulative contaminants have been reduced to extremely low, parts per trillion levels, due to controls on their use, improvements in wastewater treatment plants and the general de-industrialization of the Buffalo-Niagara area. Reliable quantification of such low contaminant concentrations is a significant technical challenge. This study used large volume sampling methods coupled with state-of-the-art analytical techniques to achieve low parts per quadrillion detection limits.

Surface water samples were collected in the eastern, central and western basins in waters greater than 100 m deep with the assistance of U.S. Environmental Protection Agency's Great Lakes Research Vessel the *Lake Guardian*. Water was drawn from 1 m below the surface and pumped through large volume samplers as the vessel criss-crossed an area ~50 sq km over a 24 hour period at an average speed of 5 knots. These spatially and temporally integrated samples are representative of average contaminant concentrations for each basin. Contaminants were field concentrated by processing hundreds of liters of surface water through glass fiber filters to capture suspended solid contaminants and then through XAD-2 resin columns to capture dissolved contaminants.

All contaminant levels were well below New York State's Department of Health's maximum contaminant levels that apply to public drinking water supplies. PCBs and dieldrin did exceed more stringent New York State Department of Environmental Conservation ambient water quality values. Dioxins, furans and dissolved mercury could not be fully evaluated due to detection limit issues and suspected data quality problems. All other contaminants including DDT and mirex were below their respective NYSDEC ambient water quality values.

PCBs, PBDEs and pesticides were found almost entirely in the dissolved phase (~90%). The one notable exception was mirex with more than 80% of its total found on suspended solids. Surface water total PCB concentrations averaged 38 pg/L. The types of dominant PCB congeners and their relative contributions to total PCB concentrations were remarkably similar across the three basins in the dissolved and suspended solid phases. Trichlorobiphenyls and tetrachlorobiphenyls were the dominant PCB homolog groups.

Dieldrin, heptachlor epoxide, endosulfan sulfate and hexachlorocyclohexanes were the pesticides found at the highest concentrations in the range of 10 to 100 pg/L. Concentrations of other pesticides were ~1 pg/L or less. Octochlorodibenzodioxin (OCDD) was the dominant dioxin congener detected on suspended solids (0.034 to 0.064 pg/L) followed by 1,2,3,4,6,7,8 heptachlorinated dibenzodioxin (1,2,3,4,6,7,8-HpDD) (0.003 to 0.006 pg/L). Dissolved phase dioxin and furan results were judged to be unreliable.

Total concentrations of polybrominated diphenyl ethers (PBDEs) were ~ 4 pg/L. 2',4,4',5-penta- bromodiphenyl ether (BDE-99) was the most abundant PBDE congener making up more than 50% of the total. Next in relative abundance were 2,2',4,4',5,5'-hexabromodiphenyl ether (BDE-153) and 2,2',4,4',5,6'-hexabromodiphenyl ether (BDE-154) each contributing ~10% of total PBDEs.

Table ES-1. Surface water concentrations of bioaccumulative contaminants in Lake Ontario's eastern, western and central basins (October 1999) compared with NYSDEC's ambient water quality values.

	Units =pg/L				NYSDEC Ambient Water Quality Value & Basis Code	
	Central	Eastern	Western-1	Western-2		
PCB	46	26	40	37	1	H (FC)
Dioxin + Furan TEQs	?[1]	?[1]	?[1]	?[1]	0.0006	H (FC)
4,4-DDD	3	2	2	1	80	H (FC)
4,4-DDE	2	1	0	1	7	H (FC)
4,4-DDT	0.95	0.81	0.64	0.54	10	H (FC)
Total DDT	6	4	3	3	11	W
HCH, alpha	237	204	133	165	2000	H (FC)
HCH, beta	52	55	32	44	7000	H (FC)
HCH, gamma	210	199	125	167	8000	H (FC)
Total Chlordane	3	4	2	3	20	H (FC)
Aldrin	0.23	0.43	0.03	0.02	1000	H (FC)
Dieldrin	62	53	29	44	0.6	H (FC)
Aldrin + Dieldrin	62	53	29	44	1000	H (FC)
Total Endosulfan	161	162	96	124	9000	A(C)
Endrin	4	3	3	3	2000	H (FC)
Endrin aldehyde	0.55	0.50	0.10	0.23	5,000,000	H (WS)[2]
Endrin ketone	2	2	1	1	5,000,000	H (WS)[2]
Heptachlor	<0.03	<0.06	<0.04	<0.07	200	H (FC)
Heptachlor epoxide	27	25	11	17	300	H (FC)
Hexachlorobenzene	6	4 R	5 R	5 R	30	H (FC)
Methoxychlor	2	2	0	1	30,000	A(C)
Mirex	0.26	0.18	0.30	0.15	1	H(FC)
Photomirex	0.03	<0.03	<0.02	0.02	None	None
PBDE	14.96 R	4	4	19.50 R	None	None
Methyl-mercury	<18	<18	<18	NS	None	None
Total Dissoved Mercury	1040 R	400 R	410 R	NS	700	H (FC)
Total Mercury	510 R	1340 R	1200 R	NS	None	None

Table Notes

[1] - Could not be fully evaluated
[2] - Guidance Value
ND - Not Dectected
R - Rejected (<3X Blank Concentration)
NS - Not sampled

Value Basis Codes:

H (FC) - Human Health Fish Consumption
H (WS) - Source of Drinking Water
A(C) - Aquatic Propoagation
W - Wildlife Protection

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Acronyms & Abbreviations

BDE - brominated diphenyl ether

C - centigrade

CDD - chlorinated dibenzodioxin

CDF - chlorinated dibenzofuran

cm - centimeter

DOC - dissolved organic carbon

EPA - U.S. Environmental Protection Agency

gms - grams

fg/l - femptograms per liter = parts per quintillion = 0.001 pg/L.

HCH - hexachlorocyclohexane

HRGC - high resolution gas chromatography

HRMS - high resolution mass spectrometer

IUPAC - International Union of Pure and Applied Chemists

LaMP - Lake Ontario Lakewide Management Plan

LDPE - low density polyethylene

mL - milliliter

m/z - mass to charge ratio

ng/L - nanograms/Liter = parts per trillion = 1000 pg/L

pg/L - picograms/Liter = parts per quadrillion = .001 ng/L

NYSDEC - New York State Department of Environmental Conservation

PBDE - polybrominated diphenyl ether

PCB - polychlorinated biphenyls

RRF - relative response factor

RRT - relative response time

R/V - research vessel

TEQ - 2,3,7,8-dioxin toxicity equivalency factor

TOPS - Total Organics Platform Sampler

TSS - total suspended solids

uM - micromoles

XAD - divinylbenzene-styrene copolymer resin

Homolog and Congener Terminology

Polychlorinated biphenyls (PCBs), dioxins, furans and polybrominated diphenyl ethers (PBDE) occur as a variety of chemical structures known as congeners. Congeners are defined by the number and specific locations of chlorines (PCBs, furans and dioxins) or bromines (PBDE) on a pair of benzene rings. There are 209 possible molecular congeners for both PCB and PBDE. Congeners with the same molecular weight, having the same number of chlorines or bromines, are said to belong to the same homolog group. Careful analysis of specific congeners detected and the relative abundance of homolog groups in environmental samples can provide clues as to the nature of contaminant sources.

The formal names for specific congeners can be lengthy so this report utilizes the International Union of Pure and Applied Chemists' (IUPAC's) congener numbering system as a shorthand system to identify specific PCB and PBDE congeners. For example, using the IUPAC system the PCB congener 2,2',3,4,5,5',6-heptachlorobiphenyl is simply referred to as PCB-185. The raw data summary available upon request uses an abbreviated form of the congener name, in addition to the IUPAC identification number. With this system 2,2',3,4,5,5',6-heptachlorobiphenyl is shortened to 2,2,'3,4,5,5',6-HpCB. The table below summarizes the abbreviations used in this report to refer to the PCB homolog groups. The same terminology is used to describe PBDE homologs with the term "bromo" replacing "chloro" and "PBDE" replacing "PCB".

PCB Homolog Groups & Related Abbreviations

1 chlorine:	Monochlorobiphenyl	"Mono"	"MoCB"	includes PCB-1 to PCB-3
2 chlorines:	Dichlorobiphenyl	"Di"	"DiCB"	includes PCB-4 to PCB-15
3 chlorines:	Trichlorobiphenyl	"Tri"	"TriCB"	includes PCB-16 - PCB-39
4 chlorines:	Tetrachlorobiphenyl	"Tetra"	"TeCB-	includes PCB-40 to PCB-81
5 chlorines:	Pentachlorobiphenyl	"Penta"	"PeCB-	includes PCB-82 to PCB-127
6 chlorines:	Hexachlorobiphenyl	"Hexa"	"HxCB-	includes PCB-128 to PCB 169
7 chlorines:	Heptachlorobiphenyl	"Hepta"	"HpCB"	includes PCB-170 to PCB-193
8 chlorines:	Octachlorobiphenyl	"Octa"	"OcCB-	includes PCB-194 to PCB-205
9 chlorines:	Nonachlorobiphenyl	"Nona"	"NoCB"	includes PCB-206 to PCB-208
10 chlorines:	Decachlorobiphenyl	"Deca"	"DeCB"	includes PCB-209

This report only addresses those 17 dioxin and furan congeners that have been identified as having relatively high toxicity. Full congener and homolog names are used in the discussions but abbreviations are used on tables and figures. The abbreviations begin with a set of numbers that define the specific locations of chlorines on the benzene rings followed by the homolog abbreviation. For example 2,3,7,8-tetradibenzodioxin is shortened to 2,3,7,8-TCDD. The abbreviations for the dioxin and furan homolog groups are provided below:

Dioxin Homologs

4 chlorines: Tetrachlorodibenzodioxin	TCDD
5 chlorines: Pentachlorodibenzodioxin	PeCDD
6 chlorines: Hexachlorodibenzodioxin	HxCDD
7 chlorines: Heptachlorodibenzodioxin	HpCDD
8 chlorines: Octachlorodibenzodioxin	OCDD

Furan Homologs

4 chlorines: Tetrachlorodibenzofuran	TCDF
5 chlorines: Pentachlorodibenzofuran	PeCDF
6 chlorines: Hexachlorodibenzofuran	HxCDF
7 chlorines: Heptachlorodibenzofuran	HpCDF
8 chlorines: Octachlorodibenzofuran	OCDF

Introduction

Concentrations of PCBs and other bioaccumulative contaminants were measured in Lake Ontario surface water in October 1999 to help the U.S. - Canada Lake Ontario Lakewide Management Plan evaluate and prioritize bioaccumulative contaminants of concern. Concentrations of most Lake Ontario surface water bioaccumulative contaminants have been reduced to parts per trillion levels, or less, thanks to improvements in wastewater treatment plants and controls on the use of bioaccumulative chemicals implemented over the last three decades. Reliable quantification of such low concentrations is a significant technical challenge. This study used large volume sampling methods coupled with state-of-the-art analytical techniques to achieve low parts per quadrillion detection limits.

Geographic Setting

Lake Ontario is the last in the Great Lakes chain (Fig. 1). It receives the majority of its inflow from Lake Erie via the Niagara River and is approximately 160 miles long, 40 miles wide with a maximum depth of 802 feet. It is among the fifteen largest lakes in the world. Bordered on the north by the Province of Ontario and the State of New York to the south, Lake Ontario is a major transportation route to the industrial heartland of Canada and northeastern United States. It supports a multi-million dollar commercial and recreational fishing industry and is the primary source of drinking water for metropolitan and rural communities around the basin.

Figure 1. Great Lakes Basin.

Sample Collection Methods

Sampling Approach

Samples were collected aboard the *R/V Lake Guardian*, a research vessel operated by the U.S. EPA Great Lakes National Program Office. Bioaccumulative contaminants were field concentrated by pumping hundreds of liters of lake water through NYSDEC's Trace Organic Platform Sampler (TOPS). TOPS pushes water through glass fiber filters to collect suspended sediment and then draws clarified water through XAD-2 resin columns to sequester dissolved phase contaminants. Water was pumped from a depth of ~1 m through a 48 lb, P-72 Point Integrating suspended sediment sampler, designed to orient itself facing into the current, modified to hold a horizontally placed intake coupled to a 1/2 inch diameter LDPE intake line connected to the TOPS sampling units (Figs 2 & 3). This assembly, referred to as a "fish" was suspended by a cable from a boom off the side of the vessel as it traversed a grid pattern covering ~50 sq km over a 24 hours period at a speed of ~ 5 knots. Sampling grids were located in the eastern, central and western basins of the lake in waters greater than 100 m in depth (Fig. 3). This allowed for the collection of spatially and temporally integrated samples.

Temperature-depth profiles showed the thermocline in the open lake to be ~20 m deep. Epilimnetic surface waters were ~21 C. Sample collection was halted periodically to allow the collection of water and biological samples as part of long-term GLNPO monitoring activities.

Figure 2. Surface water intake.

A P-72 point integrating suspended sediment sampler modified to sample surface water through a ½ inch diameter LPDE intake line. The aluminum torpedo shaped body maintains the intake opening facing in the "upstream" direction as it is towed off the side of the vessel.

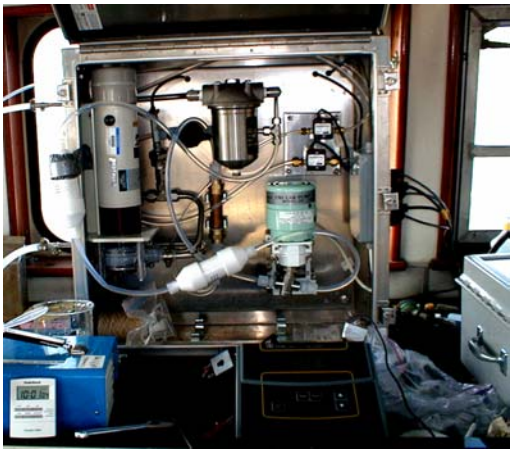

Figure 3. Total Organic Platform Sampler (TOPS).

Water is pumped through a glass fiber cartridge filter to collect suspended solids and then through two XAD resin cartridges arranged in series to capture dissolved hydrophobic contaminants.

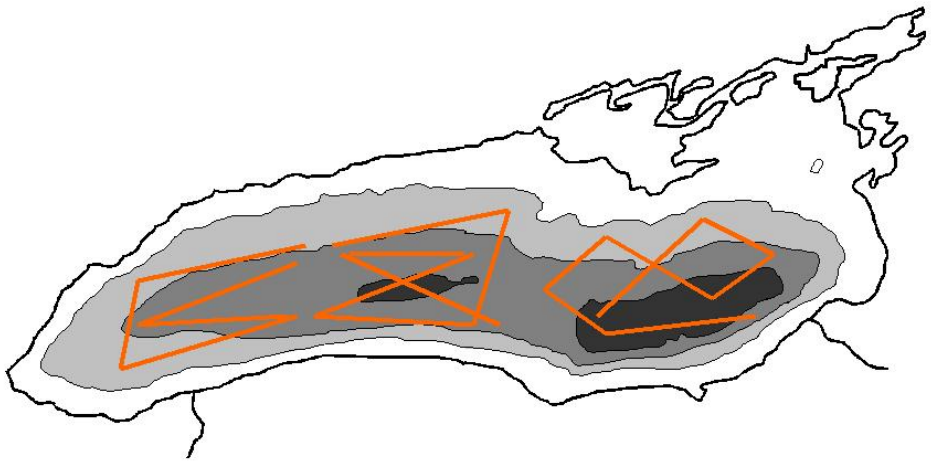

Figure 4. Surface water sampling locations.

Lines indicate the track of the *R/V Lake Guardian* in the western, eastern and central basins of Lake Ontario as surface water was processed through the TOPS units over a 24-hour period.

Experience gained from a 1997 NYSDEC- EPA Lake Ontario large volume sampling effort (Litten 1998) was used to improve this 1999 sampling design. The "fish" was damaged during the 1997 effort when it hit the side of the ship during rough weather. The *R/V Lake Guardian*'s captain designed a boom for this 1999 effort that hung closer to the water thereby shortening the length of the tow line. This greatly increased the stability of the "fish" as it was towed through the water and kept it safely away from vessel's hull.

Lake water was first pumped through Nytex netting with a nominal porosity of 100 µm to remove large zooplankton and debris. At this point the intake line was split to direct water into 2 sampling units to provide duplicate samples. The TOPS units pump sample water through glass fiber filters with 1 um nominal porosity at ~3 L/minute to remove suspended solids. For the purposes of this study the dissolved phase was operationally defined as water that passed through the 1µm glass fiber filter.

A portion of the filtered water was then pumped through two XAD-2 (divinylbenzene-styrene copolymer resin) columns holding 35 g each, at 250 to 600 ml/minute to capture dissolved hydrophobic contaminants. The XAD-2 columns were connected in series to increase the total volume of resin available to capture dissolved contaminants thereby improving extraction efficiency. Flow rates typically used by NYSDEC have been about 600 mL/min. XAD columns deployed in series provided a bed volume per minute rate of 3. XAD resin has been used to concentrate dissolved hydrophobic contaminants in water for over 25 years (Junk et al. 1974, Rees and Au 1979, Swackhammer and Armstrong 1987).

Given the lower flow capacity of the XAD columns compared to the filter cartridges, only 300 to 800 L of water was pumped through the XAD columns as opposed to the ~4000 to 5000 L of water that could be pumped through the cartridge filters over the same period of time (Table 1). Flow meter measurements recorded the sample volume processed by the filters and XAD columns. Periodic manual flow calibration measurements were also made as a check on the flow meters' accuracy. Manually calculated sample volumes were within 5% of metered sampled volumes indicating that the meters were performing well (Table 2).

		Sample Volume (Liters)	
Location	TOPS Unit	Dissolved Phase (XAD Cartridges)	Suspended Solids (Glass Fiber Cartridge Filters)
Western Basin	W1	404	4271
	W2	868	5037
Central Basin	C1	349	4337
	C2	729	4781
Eastern Basin	E1	431	4563
	E2	845	5522

Table 1. Volumes of surface water processed through TOPS samplers.

Total volume (Liters) processed through XAD resin columns (dissolved phase) and glass fiber cartridge filters (suspended solids phase).

		Flow Volumes (Liters)								
		XAD			XAD Overflow			Filter = (XAD + Overflow)		
Location	TOPS Unit	Meter	Calculated	RPD	Meter	Calculated	RPD	Meter	Calculated	RPD
Western Basin	W1	NA	404	NA	3943	3867	2	NA	4271	NA
	W2	868	816	6	4169	3987	4	5037	4803	5
Central Basin	C1	NA	431	NA	4226	4131	2	NA	4563	NA
	C2	845	843	0	4676	4675	0	5522	5519	0
Eastern Basin	E1	NA	349	NA	3837	3988	4	NA	4337	NA
	E2	729	717	2	4052	4066	0	4781	4783	0

NA = Not Available
RPD = Relative Percent Difference

Table 2. Comparison of metered versus calculated TOPS sample volumes. Sample volume was measured at two points after the water had passed through the cartridge filter: after the water passed thru the XAD resin columns and at the overflow point for water that could not flow through the XAD-2 columns. Filter flow is the sum of these two measurements. TOPS Unit #1, an earlier model, was not equipped with a meter for XAD-2 flow and relied on calculated flows.

XAD-2 Column & Filter Preparation

AXYS Analytical Services at Sydney, British Columbia, Canada, prepared the XAD-2 columns. Prior to sample collection the glass fiber filters were baked at 450 degrees C for 4 hours, wrapped in baked aluminum foil, double bagged in Ziplock bags and stored frozen. Prior to use the XAD-2 resin was cleaned by a modified version of EPA method 0010A. Raw XAD-2 resin was sifted through a 297 mm sieve to remove fines and then rinsed with Type II water, and allowed to soak over-night in fresh type II water. The resin was then flushed for 8 hours with Type II water before being placed in a 2 L Soxhlet and extracted for 22 hours with fresh methylene chloride. The cleaned XAD-2 was dried on a fluidized bed of purified nitrogen. The dried XAD-2 was then made into a slurry with methanol and poured into Teflon columns. Teflon columns contained 35 g of oven-dried (50 g air-dried; 65-70 g wet weight) XAD-2 with a total bed volume of 100 ml. XAD-2 columns were spiked in the lab with C^{13} labelled PCB congeners (PCB-31, PCB-95 and PCB-153). These "wash-out" surrogates provide information about the permanence of PCBs attached to XAD and they provide a check on the recovery of analytes from the beginning to the end of sampling and analysis.

Analytical Methods

XAD-2 Resin & Filter Extract Preparation

XAD resin column and cartridge filters were spiked with suite of C^{13}- labelled internal standards, de-watered with acetone and methanol respectively and then soxhlet extracted for 18 hours with a 80:20 toluene/acetone solvent mixture. Each extract was split into five equal fractions for PCB, pesticide, dioxin/furan, PBDE analysis and one for backup.

PCB Analytical Methods

Samples extracts were analyzed using USEPA Method 1668A developed by for congener-specific determination of all 209 PCB congeners. Some congeners within the same homolog group do coelute. PCB congeners and the beginning and ending level-of-chlorination PCBs are determined by isotope dilution high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). The remaining PCB congeners were determined by internal standard HRGC/HRMS. The make-up of all Method 1668A solutions 1668 was expanded to allow quantification of individual congeners in each chlorination group.

The extract obtained from soxhlet extraction was concentrated and the solvent exchanged to hexane. Extract clean up included Florisil, activated copper, acid/base silica and alumina columns. Final sample extract volumes were 20 µL from which 1 µL was injected onto the HRGC column. PCB analyses were conducted by HRGC/HRMS on a VG magnetic sector high resolution MS equipped with an HP 5890 gas chromatograph, a CTC autosampler, and a VG data system running MicroMass software. An SPB-Octyl (30m, 0.25 mm i.d., 0.25 um film thickness) chromatography column was coupled directly to the MS source. The MS was operated at a mass resolution of 10,000 (static) in the EI mode using multiple ion detection, acquiring at least two ions for each target and surrogate compound.

Calibration of the mass spectrometer is a two-step process. The initial set of instrument calibration solutions contains five sets of 19 unlabelled PCB congeners, covering the full range of calibration levels (2.5 to 2000 ng/mL) used to establish linearity of the mass spectrometer's response, relative to increasing congener mass, and RRFs. These RRFs are used to quantify the calibration verification and the OPR sample. The additional calibration solution containing all 209 congeners was analyzed immediately after the initial calibration to establish RRFs for all congeners not present in the initial calibration solution

Calibration verification samples are run between sample batches to verify that the mass spectrometer RRFs and RRT remain in control using one of the five initial calibration standard solutions (CS3) specified in Method 1668A. Acceptable criteria for sample RRFs was set as ±25% of the expected value based on the initial calibration run results. The calibration process was repeated if this calibration verification failed.

Field and lab blank sample extracts are spiked with known concentrations of 21 C^{13} -labelled PCB congeners covering the full range of chlorination levels. The percent recoveries of these C^{13} -labelled congeners were used to correct reported native PCB congener concentrations.

Pesticides

The extract obtained from soxhlet extraction was concentrated and the solvent exchanged to hexane. The extracts were treated with activated copper prior to chromatographic clean up. The extracts were spiked with a suite of isotopically labeled surrogate standards and cleaned up on a Biobead column. The extract was then separated into two fractions using Florisil. The first fraction is eluted with hexane followed by a 15:85 dichloromethane. The second fraction containing the more polar pesticides, is eluted with 1:1 Dichloromethane:hexane followed by dichoromethane. The fractions were concentrated to a final volume of 200 µL and transferred to autosampler viles and recovery (internal) standards added. HRGC/HRMS analyses were preformed on a VG high resolution MS equipped with an HP 5890 gas chromatograph, a CTC autosampler, and a data system running VG software. A DB-5 (60 m, 0.25 mm i.d., 0.1 um film thickness) chromatography column is directly coupled to the MS source. The MS is operated at 10,000 (static) mass resolution in the electron ionization (EI) mode using multiple ion detection (MID). A spitless/split injection sequence was used.

Dioxins & Furans

Dioxins and furans were analyzed using EPA Method 1613. C^{13}-labelled 2,3,7,8-TCDD was added to each extract to measure the efficiency of the cleanup process. The extract obtained from soxhlet extraction was concentrated and the solvent exchanged to hexane. Chromatographic clean up of extracts included silica gel, alumina and carbon. Final sample extract volume was 20 µL. Immediately prior to injection, internal standards were added to each extract, and a 1 uL aliquot of the extract was injected into the gas chromatograph. The analytes were separated on a HP 5890 gas chromatograph using a DB-5 capillary column (60m, 0.25 mm i.d., 0.1um film thickness) with a CTC autosampler and a VAX 4000 data system. The gas chromatograph was coupled to a VG Ultima high-resolution mass spectrometer operated at 10,000 (static) mass resolution in the electron ionization (EI) mode using multiple ion detection (MID). Two exact m/z's are monitored for each analyte. An individual CDD/CDF is identified by comparing the GC retention time and ion-abundance ratio of two exact m/z's with the corresponding retention time of an authentic standard and the theoretical or acquired ion-abundance ratio of the two exact m/z's. The non-2,3,7,8 substituted isomers and congeners are identified when retention times and ion-abundance ratios agree within predefined limits. Isomer specificity for 2,3,7,8-TCDD and 2,3,7,8-TCDF is achieved using GC columns that resolve these isomers from the other tetra-isomers.

Quantitative analysis was performed using selected ion current profile (SICP) areas, in one of three ways. For the 15 2,3,7,8-substituted CDDs/CDFs with labelled analogs, the GC/MS system is calibrated, and the concentration of each compound is determined using the isotope dilution technique. For 1,2,3,7,8,9-HxCDD, OCDF, and the labelled compounds, the GC/MS system is calibrated and the concentration of each compound is determined using the internal standard technique. For non-2,3,7,8-substituted isomers and for all isomers at a given level of chlorination (i.e., total TCDD), concentrations are determined using response factors from calibration of the CDDs/CDFs at the same level of chlorination.

PBDE

There are no EPA approved analytical methods for PBDEs. The analytical method used was essentially the same as EPA Method 1668A used for PCB congeners. The extract obtained from soxhlet extraction was concentrated and the solvent exchanged to hexane. Chromatographic clean up of extracts included silica gel, alumina and carbon. The final volume of the sample extracts was 100 µL; 1 µL was injected onto the HRGC column. Mono to deca bromo PBDE congeners were separated by gas chromatography using a 30m 0.25 mm i.d. 0.1µm DB-5HT column (J&W Scientific) in a single run using a temperature and pressure programmed mode. The final volume of the extracts was 100 µL; 1µLwas injected onto the column. PBDEs were detected using a high resolution Micromass Autospec Ultima mass spectrometer, EI positive ion mode at 10,000 mass resolution, in selected ion mode, monitoring two peaks in the molecular ion cluster for each homologue group. The method was calibrated with a set of 41 PBDE congeners (mono to deca), based on Cambridge Isotope Labs (CIL) analytical standard #EO-4980.

Mercury

Mercury samples were collected directly from the intake line after the auxiliary pump but before the water entered the stainless steel and the TOPS sampling unit using "clean hands – dirty hands" methods process in accordance with EPA Method 1669 as designed to minimize the likelihood of field contamination during the sample collection. One unfiltered and two filtered samples were collected at each location. Filtered samples were filtered in the field using polysulfone metals cartridge filters (pre-cleaned and supplied by Frontier Geoscience).

Samples were analyzed for total mercury and methyl mercury using EPA Method 1638. For total mercury analyses samples are first solubilized by gentle refluxing with nitric and hydrochloric acids. After cooling, the sample is made to volume, mixed, and centrifuged or allowed to settle overnight prior to analysis. For the determination of dissolved mercury in a filtered aqueous sample aliquot, the sample is made ready for analysis by the appropriate addition of nitric acid, and then diluted to a predetermined volume and mixed before analysis. The digested sample is introduced into a radio frequency plasma where energy transfer processes cause desolvation, atomization, and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio (m/z) by a mass spectrometer having a minimum resolution capability of 1 amu peak width at 5% peak height at m/z 300. An electron multiplier or Faraday detector detects ions transmitted through the mass analyzer and the resulting current is processed by a data handling system.

Data Quality Review

Several field sampling and laboratory data quality procedures were considered to ensure that reported contaminant concentrations are representative of environmental concentrations. Data quality issues included checking the accuracy of flow measurements, filter extraction efficiency, XAD resin capture efficiency, field contamination, laboratory contamination and other factors discussed below. The major data quality issues identified were: 1) elevated levels of certain PCB and PBDE congeners in some lab and field blanks; 2) relatively high mercury field blanks and; 3) questionable dissolved phase dioxin results.

Flow Meter Accuracy

Accurate measurements of the total sample volume processed through the XAD resin columns and glass fiber cartridge filters are essential to calculate quantitative chemical concentrations. Flow meters measured the volume of water at two points after the water passed through the cartridge filters: after water passed through the XAD columns and the overflow volume, water that could not be processed through the XAD column due to its lower flow rate. Cartridge filter sample volume is the sum of these two measurements. Manual flow measurements were periodically collected as a check on the accuracy of flow meter measurements. The time needed to fill large plastic containers with processed water from the XAD overflow and outflow was recorded to the nearest second. These containers were weighed later on shore. The flow rate for specific times periods was calculated by converting the weight of the water, minus the container weight, to liters and dividing this by the time needed to fill the container. These manual measurements were used to calculate a total sample volume for each sampling event. These estimates agreed well with the flow meter results (0 – 6 relative percent difference) indicating that the flow meters were functioning reasonably well (Table 2).

Suspended solids capture efficiency of glass fiber cartridge filters

Suspended solids (SS) samples were collected before and after lake water passed through the glass fiber cartridge filters providing a qualitative check on how well they were removing suspended solids. SS samples were collected by filtering water through a Whatman glass fiber cartridge filter until the rate of water passing through the filter began to visibly slow. Pre-filter SS concentrations were approximately 2 mg/l ranging from 1.8 to 2.28 mg/L. Post-filter SS were non detectable, < 1 mg/L. (Table 3). Approximately five times more post-filter water could be filtered through the filter before it began to clog than pre-filter water (~25 L vs.~5 L) indicating that the filters had removed a significant amount of solids from the sample.

Location	TOPS Unit	Stage	Volume Filtered (Liters)	Conc. (mg/L)	PQL (mg/L)
Western Basin	**W1**	pre-filter	5.4	2.01	1
	W1	post-filter	21.8	ND	1
Central Basin	**C1**	pre-filter	5.6	2.28	1
	C1	post-filter	26.0	ND	1
Eastern Basin	**E1**	pre-filter	5.6	1.8	1
	E1	post-filter	28.0	ND	1
	E1	post-filter (Dup.)	38.0	ND	1
	Blank	NA	NA	ND	1

NA - Not Applicable.
ND - Not Dectected.
PQL - Practical Quantitation Limit of the analytical method

Table 3. Comparison of pre- and post filter suspended solids concentrations (mg/L).

Capture efficiency of XAD resin

XAD resin columns were placed in series to increase the total volume of resin available to capture dissolved phase contaminants and to allow a check on the extraction efficiency of the resin. Ideally all of the dissolved contaminants should be detected on the first resin column. Equal or higher contaminant masses found on the second column might suggest that the resin was not effectively capturing dissolved phase contaminants. In this situation sample results may underestimate contaminant concentrations. One set of XAD columns collected in the western basin was analyzed separately in order to perform this check. Extracts from the two XAD columns were combined and analyzed together for all of the other samples .

Extraction efficiency based on detected concentrations was very good for PCBs. 85 to 100% of PCB congener mass was captured on the first column (Fig. 5). Only two congeners had lower extraction efficiencies with ~75% of their masses detected on the first column. Extraction efficiencies were more variable for pesticides ranging from 60 to 100% (Fig. 5). Extraction efficiencies for DDT & metabolites and photomirex were 100%. Mirex was much lower at ~ 60%.

Non-detections on the second XAD column do not necessarily mean that 100% of the contaminant mass was actually captured on the first XAD column. In some cases the analytical detection limit can be very close to ambient concentrations. Therefore it is possible that the actual extraction efficiencies could be lower. However, a comparison of the duplicate sample results, where the XAD extracts from the first and second columns were combined and analyzed as one sample showed very similar concentrations to the summed concentrations of the two XAD columns analyzed separately. This suggests that the non-detections encountered on the second XAD column did not result in a gross overestimation of dissolved phase extraction efficiency.

Detected levels of several dioxins and furans on XAD resins columns were so close to the sample specific detection limit (within 1 to 3 pg) that a reliable comparison of first and second XAD columns cannot be made. Sample specific detection limits differed from column to column which further complicates such a comparison.

A comparison of first and second column PBDE results could not be interpreted because the sample batch that included this pair of XAD columns extracts was severely impacted by lab contamination related to a newly installed lab ventilation system constructed with materials containing PBDE.

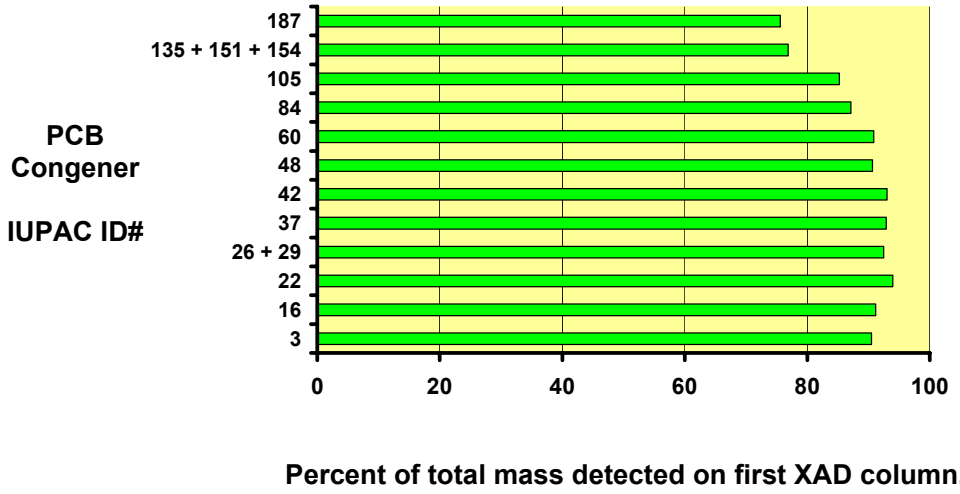

Figure 5. Percent of individual PCB congeners detected on first XAD column.

All of the detectable PCB mass of individual congeners were detected on the first column except for the congeners shown on this figure. This suggests that the XAD resin captured PCBs reasonably well under the specific conditions found in Lake Ontario, relatively low levels of suspended solids and contaminants.

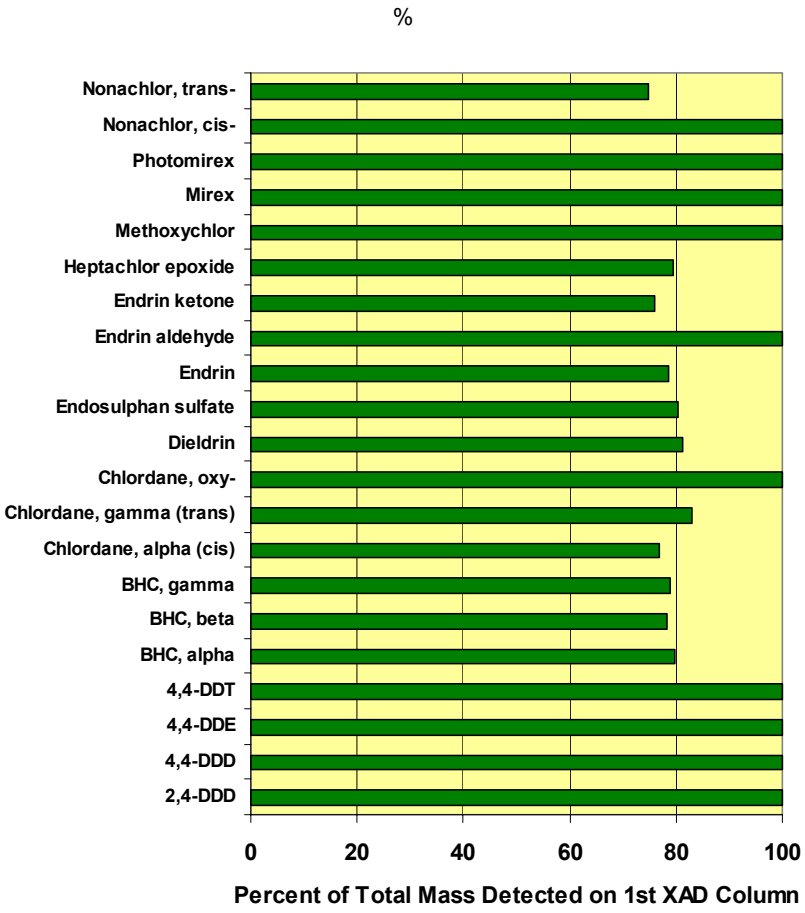

Figure 6. Percent of total pesticide mass detected on the first XAD column. Pesticides not included on this figure did not pass QA review for one or both columns.

Checking for possible XAD resin "wash-out"

It has been suggested that under certain circumstances dissolved organic carbon (DOC), along with any bound contaminants captured from the lake water, might be lost from the XAD resin beads due to "wash-out" on particles of resin as sample water is pumped through the cartridge. This could result in an underestimation of actual contaminant concentrations. Surface water dissolved organic carbon (DOC) samples were collected before and after water flowed through the XAD resin columns to see if DOC "wash-out" was a concern for these particular sampling conditions. The results of the twelve pairs of samples collected suggest that this is not a concern. Outflow DOC values were lower than inflow concentrations for 8 of the 12 samples (Table 4). The relative percent difference between those pairs where the outflow DOC concentrations were higher than inflow concentrations was less than 6% for 2 of the 4 samples with higher outflow DOC values. The other two had relative percent differences of 24 and 36 percent.

Location	TOPS Unit	Timing	Inflow DOC Units = uM	Outflow DOC Units = uM	RPD
Central Basin	C1	Final	387.99	291.48	28
	C1	Mid	291.68	272.24	7
	C1	Early	300.72	282.76	6
	C2	Final	337.82	276.41	20
	C2	Mid	410.96	286.50	36
Eastern Basin	E1	Mid	294.27	291.00	1
	E2	Mid	270.15	284.82	-5
Western Basin	W1	Final	293.39	423.27	-36
	W1	Mid	289.76	296.62	-2
	W1	Early	269.95	344.07	-24
	W2	Final	367.41	335.87	9
	W2	Early	1093.76	365.90	100

RPD - Relative Percent Difference.
uM = micromoles
Sample volume = 0.06 L each
"Early", "mid" & "final" refer to approximately when during the 24 hour sampling period the DOC samples were collected.

Table 4. Comparison of DOC concentrations in sample water before and after passing through XAD columns.

XAD Surrogate Spike Recoveries

XAD columns were spiked in the lab with C^{13} labelled PCB congeners (PCB-31L, PCB-95L and PCB-153L) before they were used in the field. After the columns are used in the field and analyzed these "wash-out" surrogates can provide qualitative information about the permanence of PCBs attached to XAD and provide a check on the recovery of analytes from the beginning to the end of sampling and analysis. Results show some loss of the lighter molecular weight PCB-31L, 5 to 25 percent less than spike concentrations, averaging 9% less (Table 5). All of the reported PCB-95L values were greater than spike values averaging 35% higher with a range of 12 to 58%. The C^{13} labelled congener PCB-153L ranged from 14% less than, to 9% greater than the spike values with an average of 2% greater than spike values.

Field and Lab Blank Contamination Issues

Blank concentrations were the single most important factor considered in determining the validity of field sample results. Each batch of samples included one lab blank sample to identify contamination associated with sample extraction and preparation. An unused XAD resin column and glass fiber cartridge filter, prepared at the same time as the other XAD columns and filters, were brought along on the cruise and then analyzed to provide an indication of any contaminants that may have been introduced during the preparation of these supplies or in the field. Field results were rejected if they were less than three times their respective lab or field blank.

Blank contamination resulting in the rejection of certain field sampling results can be broken into three general categories: 1) high levels (>1000 pg/sample) of some PCB and PBDE congeners; 2) low levels (~1 pg/sample) pesticide and dioxin/furans blank levels only slightly lower than field samples and; 3) dissolved and total mercury levels approximately the same as field samples. The following discussion describes these results in terms of raw contaminant mass detected (mass/sample) and should not be confused with environmental concentrations (sample mass/sample volume).

Sampling Location	TOPS Unit - XAD Column	Isotopically Labelled PCB Congener	pg / sample		% Recovery
			Spike	Measured	
Western Basin	W2 - 1	PCB-31 L	85000	71500	84
Western Basin	W2 - 2	PCB-31 L	85000	63700	75
Western Basin	W1 - 1 & 2	PCB-31 L	170000	151000	89
Central Basin	C2 - 1 & 2	PCB-31 L	170000	152000	89
Eastern Basin	E2 - 1 & 2	PCB-31 L	170000	161000	95
	Field Blank	PCB-31 L	85000	77900	92
Western Basin	W2 - 1	PCB-95 L	52000	62600	120
Western Basin	W2 - 2	PCB-95 L	52000	58700	113
Western Basin	W1 - 1 & 2	PCB-95 L	104000	138000	133
Central Basin	C2 - 1 & 2	PCB-95 L	104000	135000	130
Eastern Basin	E2 - 1 & 2	PCB-95 L	104000	162000	156
	Field Blank	PCB-95 L	52000	82300	158
Western Basin	W2 - 1	PCB-153 L	76000	74000	97
Western Basin	W2 - 2	PCB-153 L	76000	65100	86
Western Basin	W1 - 1 & 2	PCB-153 L	152000	165000	109
Central Basin	C2 - 1 & 2	PCB-153 L	152000	152000	100
Eastern Basin	E2 - 1 & 2	PCB-153 L	152000	171000	113
	Field Blank	PCB-153 L	76000	82900	109

Table 5. Percent recoveries of C^{13} labelled PCB congener spike concentrations placed on XAD resin columns before they were used in the field.

XAD field blank results showed concentrations of two PCB congeners, PCB-44 and PCB-55 (9030 pg & 1170 pg), to be three to five times higher than those found in either field samples or the XAD lab blanks. The XAD field blank extract was re-analyzed and the presence of these anomalously high congener levels was confirmed. A likely source of this field blank contamination could not be identified. Fortunately these three congeners did not make up a significant amount of the total PCB found in the field samples. Levels of individual PCB congener contamination in filter field blanks were relatively low, ~500 pg/sample, compared to ~10,000 to 20,000 pg/sample in filter field samples.

One batch of PBDE sample results was completely rejected due to high lab blank contamination. Follow-up investigations determined that ventilation ducts recently installed in the lab contained significant concentrations of PBDE for flame retardant purposes. Although some of the PBDE congener results from these affected samples were not impacted by the lab contamination, the most environmentally significant congeners,BDE-47 & BDE-99 (>3000 pg/sample) were.

Some pesticide, dioxin and furan results were rejected due to blank contamination although this was not due so much to the presence of "high" blank concentrations but more to the fact that environmental concentrations are so low. For some of the rejected pesticide field results, which included hexachlorobenzene, aldrin, mirex, methoxychlor and endosulphan results, the lab blank concentrations were < 1 ng/sample. The rejected pesticide field results were in the range of 0.01 to 2 ng/sample. These masses translate to environmental concentrations in the extremely low parts per quintillion range when sample volume is considered.

With certain exceptions, rejected dioxin and furan field results were in the same general range of their respective field and lab blank concentrations (1 to 10 pg/sample). The dissolved phase dioxin/furan results were rejected given some serious inconsistencies with this data set. The one reportable dissolved phase dioxin congener was detected in the central basin sample and that was 2,3,7,8-TCDD. Typically dioxins and furans are most easily detected on suspended solids.

However, 2,3,7,8-TCDD was not detected on the suspended solids even though the sample specific detection limits for the suspended solids were an order of magnitude lower than the dissolved phase. In addition, with one exception, 2,3,7,8-TCDF, none of the dioxin/furan congeners detected consistently in the suspended solids were found in the dissolved phase. Given these inconsistencies, together with an improved understanding of additional QA measures needed to measure low levels of dissolved phase dioxins, the dissolved phase results are considered to be unreliable.

All total mercury and dissolved mercury field sample results were rejected because they were less than three times the field blank concentration of 0.75 ng/L. There were no blank issues with the methyl-mercury samples.

Duplicate Sample Results

The data quality objective for duplicate results was set at 50% relative percent difference (RPD) between pairs. Additional screening factors were added to account for data interpretation problems associated with the extremely low detection limits and detections achieved by large volume samplers combined with HRMS analyses. Relatively minor, <1 pg/L differences between duplicate pair concentrations can in some cases result in RPDs greater than 50% when for all practical purposes the pair concentrations are essentially the same given analytical variability. In other cases a parameter was detected in one of the duplicates but not the other, with the measured concentration being very close to the detection limit. For both of these cases the application of the 50% RPD rule alone might incorrectly suggest a data quality problem. Therefore the criteria used to review RPDs was modified to include two additional screening factors:

1. For detected values five times greater than their sample specific detection limits: Pair values should have RPDs < 50%.

2. For detected values < five times greater than their sample specific detection limit: At least one of the pair values should fall within the range defined by the other sample's concentration plus or minus its sample specific detection limit.

3. For pair values less than five times greater than detection limit with one of the pairs having a "non-detect", the previous rule applies with the exception that the detection limit for the "non-detect" sample is considered to be its sample concentration for the purposes of checking duplicate results.

The solids phase sample results showed forty duplicate criteria exceedences (3% of samples) compared to twelve in the dissolved phase column results (<1% of samples)(Table 6). Dissolved phase duplicate criteria exceedences were limited to 8 PCB and 3 PBDE congeners and Total TCDF. None of the RPDs for analytes detected on both pairs exceeded 100%. Duplicate results for most of the PBDE congeners could not be evaluated because high levels of PBDE lab contamination impacted one of the pair.

The higher frequency of QA criteria exceedences in the solid phase samples is not a major concern because solid phase contaminants in general make up a small (<10%) of total Lake Ontario surface water contaminant concentrations. Of the eight dissolved phase PCB congeners that failed QA criteria, only the coeluting congener pair PCB-153 +168 was found to make up more than 1% of total PCBs (~1.5%) measured in Lake Ontario surface water. This PCB-153+168 duplicate pair only slightly exceeded the QA criteria (54% RPD).

	Dissolved Phase (XAD Resin Column)		Solids Phase (Glass Fiber Cartridge)	
	Detected in both samples	**Detected in only one sample**	**Detected in both samples**	**Detected in only one sample**
Pesticides			BHC alpha (62%) Chlordane (alpha) (51%) Endrin aldehyde (58%) Endrin Ketone (65%) Mirex (76%) trans nonachlor (76%)	4,4'-DDE 4,4"-DDT
PCBs	PCB-153 (54%) PCB-180 (55%) PCB-206 (94%)	PCB-72 PCB-156 PCB-164 PCB-167 PCB-201	PCB-25 (63%), PCB-26 (92%), PCB-31 (59%), PCB-40 (66%), PCB-42 (93%), PCB-44 (59%) PCB-49 (60%), PCB-52 (74%) PCB-56 (66%), PCB-59 (92%) PCB-60 (78%), PCB-61 (71%) PCB-64 (58%), PCB-66 (73%) PCB-77 (76%), PCB-83 (63%) PCB-86 (63%), PCB-88 (52%) PCB-90 (59%), PCB-92 (68%) PCB-93 (57%), PCB-105 (51%) PCB-118 (68%), PCB-128 (77%) PCB-129 (68%), PCB-132 (53%) PCB-141 (70%), PCB-146 (62%) PCB-147 (54%), PCB-153 (61%) PCB-156 (59%), PCB-158 (76%) PCB-164 (60%), PCB-170 (66%) PCB-170 (66%), PCB-172 (65%) PCB-179 (56%), PCB-180 (51%) PCB-183 (61%), PCB-194 (68%) PCB-195 (93%), PCB-203 (57%) PCB-209 (65%)	PCB-1 PCB-109
Dioxins Furans		Total TCDF	OCDD (60%) OCDF (64%) Total HpCDD (57%) 1,2,3,4,6,7,8 HpCDF (63%)	Total TCDD
PBDE	PBDE-15 (78%)	PBDE-37 PBDE-190		PBDE-17 PBDE-190

Table 6. Summary of analytes that did not pass duplicate relative percent difference (RPD) screening criteria. In order to conserve space only the first congener is listed for coeluting groups.

Data Validation

Field sample analyte results less than three times any analyte concentrations detected in associated lab or field blank samples were rejected and not used in any way. Rejected values are provided in the raw data summary only to assist in the planning of future monitoring QA/QC plans and should not be used for modeling or for comparison to water quality criteria.

Field sample analyte results greater than three times but less than five times any analyte concentrations detected in related lab or field blank samples are flagged "B" on the data summaries to indicate that there may be some level of uncertainty associated with these values due the presence of some low levels of field or lab contamination.

Field sample analytes, for which a peak was identified, but the ion ratios were not within the expected range, were flagged by the laboratory as "NDR" (not detected within range). The reported NDR values are maximum possible concentrations and are used in this report in the same way as unflagged data.

Non-detected values were considered to be zero when calculating individual and total contaminant concentrations.

Sampling Results

PCBs

Surface water total PCB concentrations averaged 38 pg/L with more than 90% in the dissolved phase (Fig.7). The types of PCB congeners and their relative proportions to each other were similar across the three basins in the dissolved and suspended solid phases. Trichlorobiphenyls and tetrachlorobiphenyls were the dominant PCB homolog groups (Fig. 8). The dominant PCB homologs in the dissolved phase were trichlorobiphenyls (~30%) followed by tetrachlorobiphenyls (~25%). The relative abundance of PCB homologs found in the dissolved phase is essentially the same as the total PCB (Fig. 8) given the relatively minor percentage of PCBs contributed by the suspended solids phase.

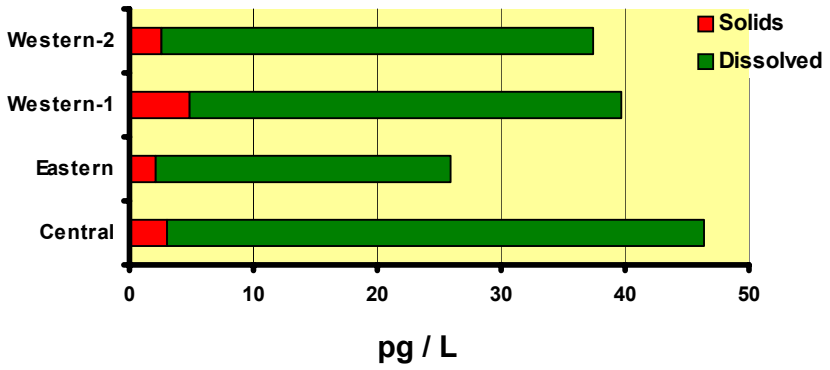

Figure 7. Comparison of Lake Ontario dissolved and solid phase PCB surface water concentrations, eastern, central and western basins.

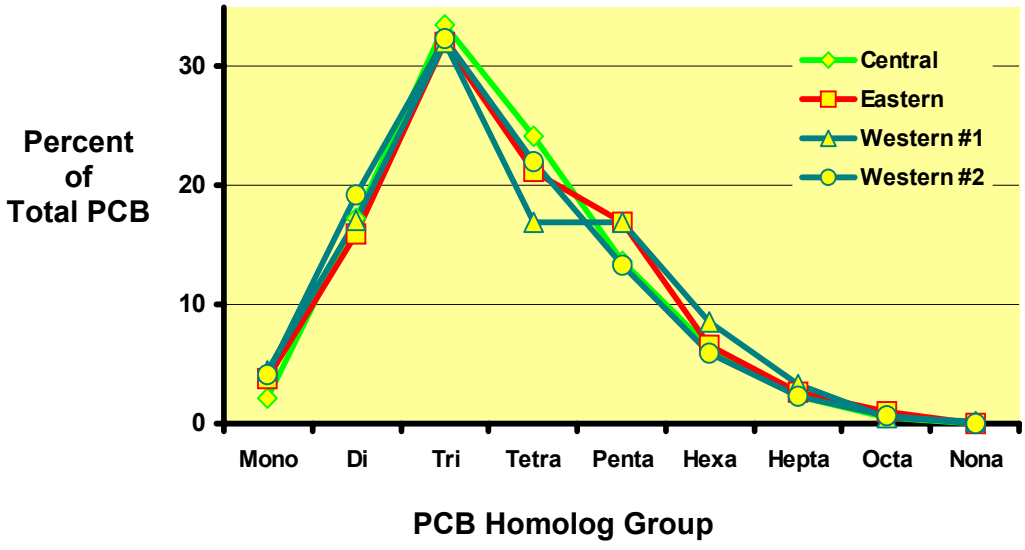

Figure 8. Relative percent abundance of total PCB homologs in Lake Ontario surface water, eastern, central and western basins.

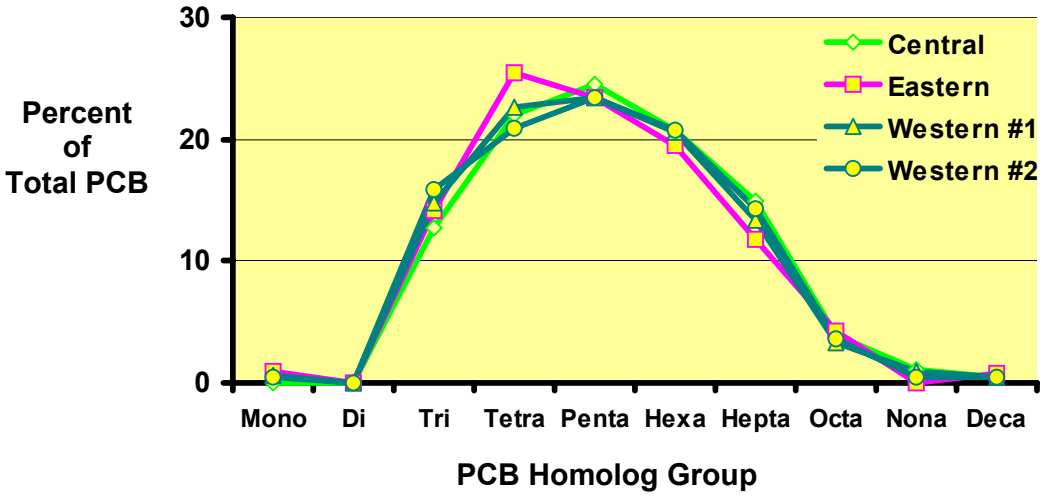

Figure 9. Relative percent abundance of PCB homolog groups measured on Lake Ontario surface water suspended solids, eastern, western and central basins.

The dominant PCB homologs in the solids phase were pentachlorobiphenyls (~23%) followed by roughly equal percentages of tetra- and hexachlorobiphenyls (~20% each) (Fig. 9). The patterns of relative homolog abundance seen in total PCBs and solid phase PCBs were remarkably similar from basin to basin.

The relative abundance of dominant PCB congeners was also very similar from basin to basin. Figure 10 compares the relative abundance of those congeners which, based on a lakewide average, contribute >3% of the total PCB. The relative abundance of these congeners compares well across the three basins suggesting that Lake Ontario surface water PCBs are fairly homogenous, at least in terms of dominant congeners across the three basins.

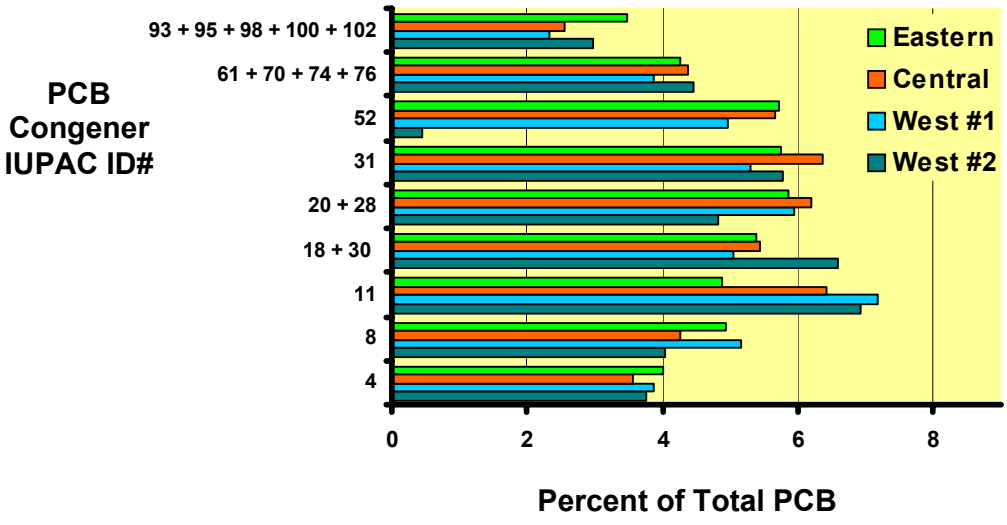

Figure 10. Relative abundance of dominant PCB congeners in Lake Ontario surface water, eastern, central and western basins.

Figure 11 shows PCB congeners that have a relative abundance >1% of total PCBs based on their average concentrations for the three basins. Figure 12 shows the same information broken out to show dissolved and solids phase PCB congener relative abundances. As indicated by the homolog plots, heavier molecular weight PCB congeners dominate the solid phase whereas lighter weight congeners dominate the dissolved phase.

These plots are an attempt to summarize a complex data set. There is fair amount of variability in the relative percent abundance of congeners from basin to basin for those that make up <3% of total PCBs. For such low concentrations it is often difficult to determine if basin-to-basin differences reflect real differences or if they simply reflect normal analytical variability. The raw data would need to be carefully studied before drawing any conclusions on the relative significance of congeners that make up <3% of total PCBs.

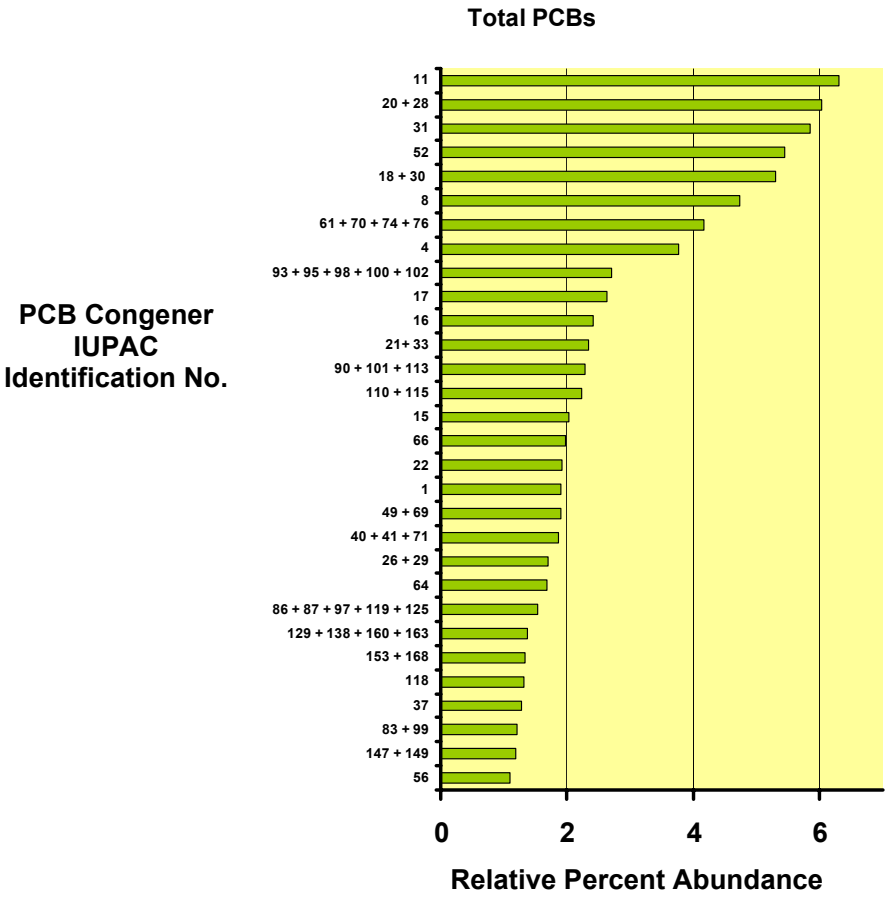

Figure 11. Relative percent abundance of PCB congeners in Lake Ontario surface water based on lakewide average total PCBs (eastern, western and central basins).

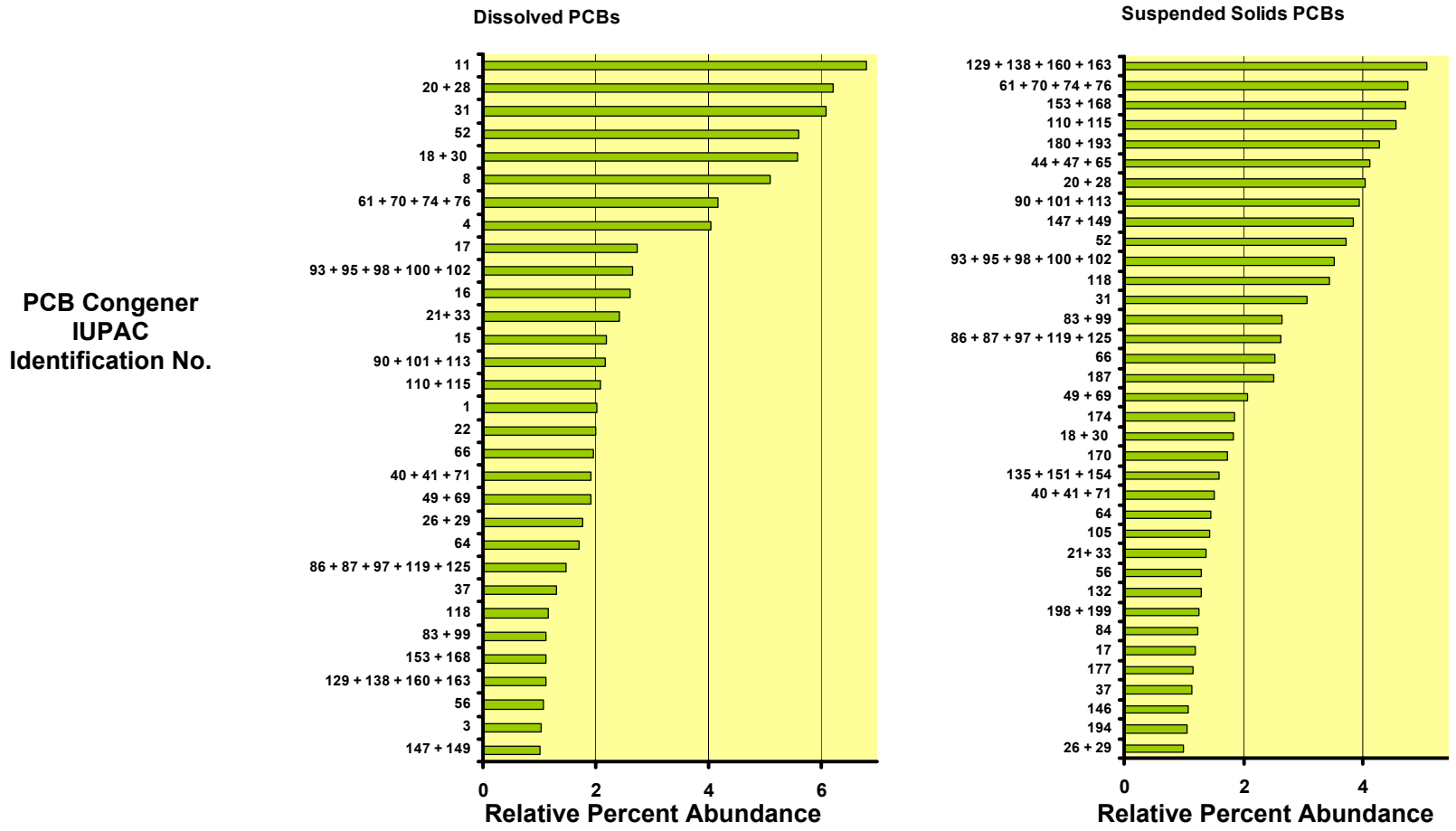

Figure 12. Relative percent abundance of PCB congeners in Lake Ontario surface water dissolved and solids phase. The figure includes those congeners that make up >1% of the total PCBs in the dissolved or solids phase based on the lakewide average concentration.

Pesticides

Most of the pesticides were present almost entirely in the dissolved phase (~90 to 100% of total mass). The one notable exception was mirex of which less than 20% was found in the dissolved phase. Dieldrin, heptachlor epoxide, endosulfan sulfate and HCHs were present in the highest concentrations in the range of 10 to 100 pg/L. Concentrations of other pesticides were ~1 pg/L or less.

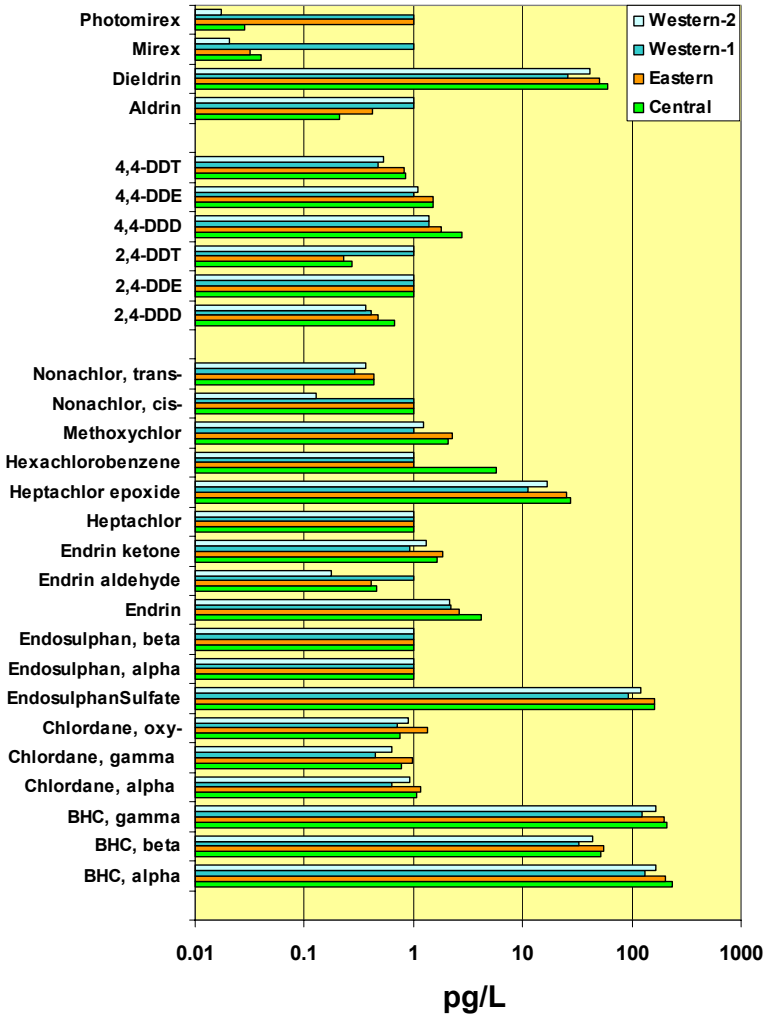

Figure 13. Lake Ontario surface water pesticide concentrations (dissolved + suspended solids) (pg/L), eastern, western and central basins. Note that concentrations are plotted on a logarithmic scale.

Dioxins & Furans

Specific dioxin and furan congeners were selected for analysis based on their relevance to 2,3,7,8-TCDD dioxin-like toxicity. Totals for dioxin and furan homolog groups were also reported by the laboratory. NYSDEC's most stringent ambient water quality standard for dioxins and furans is defined in terms of total 2,3,7,8-TCDD toxicity equivalents (TEQs). 2,3,7,8-TCDD toxicity equivalents for individual dioxin and furan congener are calculated by multiplying their measured concentrations by their respective Toxicity Equivalency Factors (TEFs) and Bioaccumulation Equivalency Factors (BEFs) (Table 7). TEQs for individual congeners and furans are then summed and compared to the NYSDEC ambient water quality value (0.0006 pg/L 2,3,7,8-TCDD TEQs).

Two dioxin congeners were detected on suspended solids. Octochlorodibenzodioxin (OCDD) was the dominant dioxin congener (0.034 to 0.064 pg/L) followed by 1,2,3,4,6,7,8 heptachlorinated dibenzodioxin (1,2,3,4,6,7,8-HpDD) (0.003 to 0.006 pg/L). On a TEQ basis OCDD and 1,2,3,4,6,7,8-HpDD contribute approximately the same to 2,3,7,8-TCDD-like toxicity (~0.000006 pg/L).

Three furan congeners were detected on suspended solids. Octochlorodibenzofuran (OCDF) and 1,2,3,4,6,7,8 heptachlorinated dibenzofuran (1,2,3,4,6,7,8-HpDF) were detected at approximately the same concentrations as the dominant suspended solid dioxin congeners (0.001 to 0.004 pg/L). 2,3,7,8-Tetradibenzofuran was detected at lower concentrations (0.0007 to 0.001 pg/L) but given its higher TEQ factor (0.1 vs. 0.01 & 0.001) contributes the most of the furan contribution to dioxin-like TEQs.

		TEF	BEF
Dioxins	**2,3,7,8-TCDD**	1	1
	1,2,3,7,8-PeCDD	0.5	0.9
	1,2,3,4,7,8-HxCDD	0.1	0.3
	1,2,3,6,7,8-HxCDD	0.1	0.1
	1,2,3,7,8,9-HxCDD	0.1	0.1
	1,2,3,4,6,7,8-HpCDD	0.01	0.05
	OCDD	0.001	0.01
Furans	**2,3,7,8-TCDF**	0.1	0.8
	1,2,3,7,8-PeCDF	0.05	0.2
	2,3,4,7,8-PeCDF	0.5	1.6
	1,2,3,6,7,8-HxCDF	0.1	0.08
	1,2,3,4,7,8-HxCDF	0.1	0.2
	1,2,3,7,8,9-HxCDF	0.1	0.7
	2,3,4,6,7,8-HxCDF	0.1	0.6
	1,2,3,4,6,7,8-HpCDF	0.01	0.01
	1,2,3,4,7,8,9-HpCDF	0.01	0.4
	OCDF	0.001	0.02

Table 7. TEFs & BEFs used in calculating 2,3,7,8-TCDD TEQs of dioxin & furan congeners.

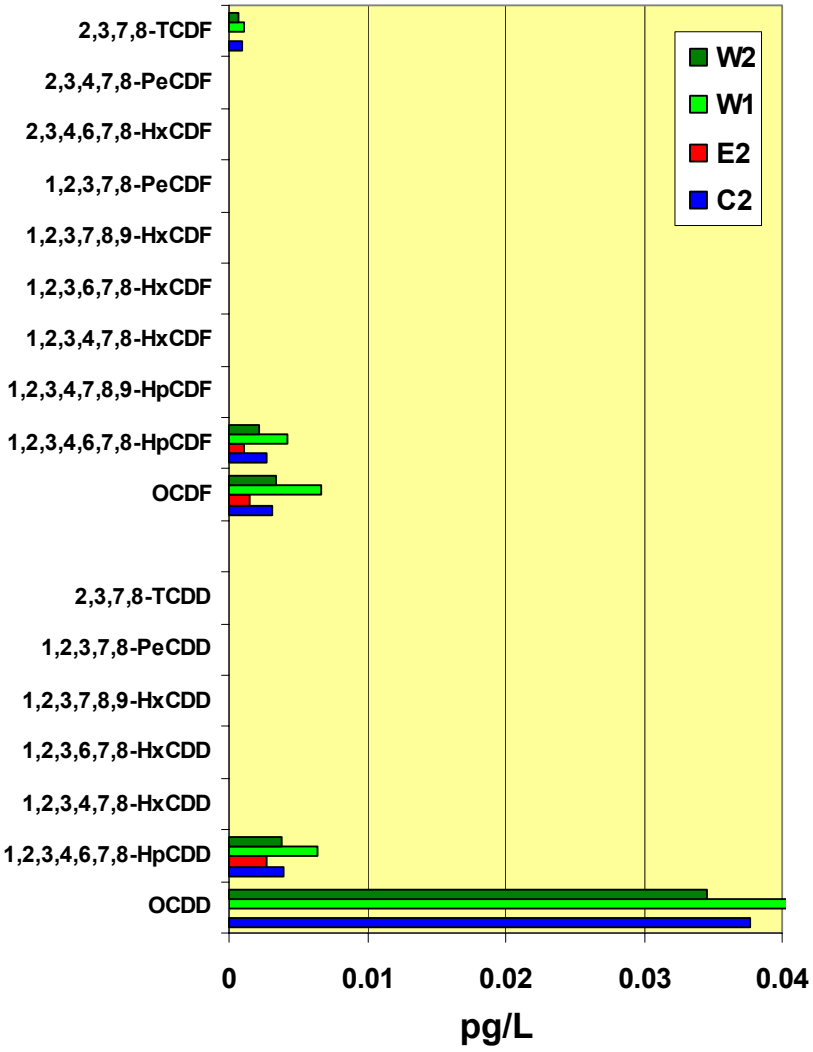

Figure 14. Summary of dioxin & furan congener concentrations detected on Lake Ontario surface water suspended solids, eastern (E2) central (C2) & western (W1 & W2) basins.

When concentrations of non-detected congeners are assumed to be zero, total 2,3,7,8-TCDD toxicity of all suspended solid phase dioxin and furans is approximately one order of magnitude less than NYSDEC's ambient water quality value (0.0006 pg/L TEFs)(Figure 15). TEQs were also calculated using the detection limit as the concentration for congeners not detected to help estimate the potential contribution of undetected congeners to the total TEQ. This showed that a potential "worst case" upper limit of suspended solids 2,3,7,8-TCDD TEQs was approximately three orders of magnitude greater than New York State's ambient water quality value.

2,3,7,8-tetradibenzo-p-dioxin (2,3,7,8-TCDD) was detected in the central basin and 2,3,7,8-TCDF was detected in the central and eastern basins. These were the only congeners detected in the dissolved phase. These detections are suspect because: 1) 2,3,7,8-TCDD was not detected on the suspended solids with much lower detections limits than those achieved for the dissolved phase; 2) 2,3,7,8-TCDD was not detected in the western basin where known historical sources of 2,3,7,8-TCDD are located and; 3) they were only detected in one sample. Based on NYSDEC's experience using XAD resin to measure dioxin in surface waters in the years since 1999, a number of additional QA measures would need to be taken in order to develop more reliable dissolved phase results.

Despite the extremely low detection limits achieved by the TOPS large volume sampling method, these detection limits were insufficient to determine if Lake Ontario water meets NYSDEC's ambient water quality value for 2,3,7,8-TCDD-like toxicity.

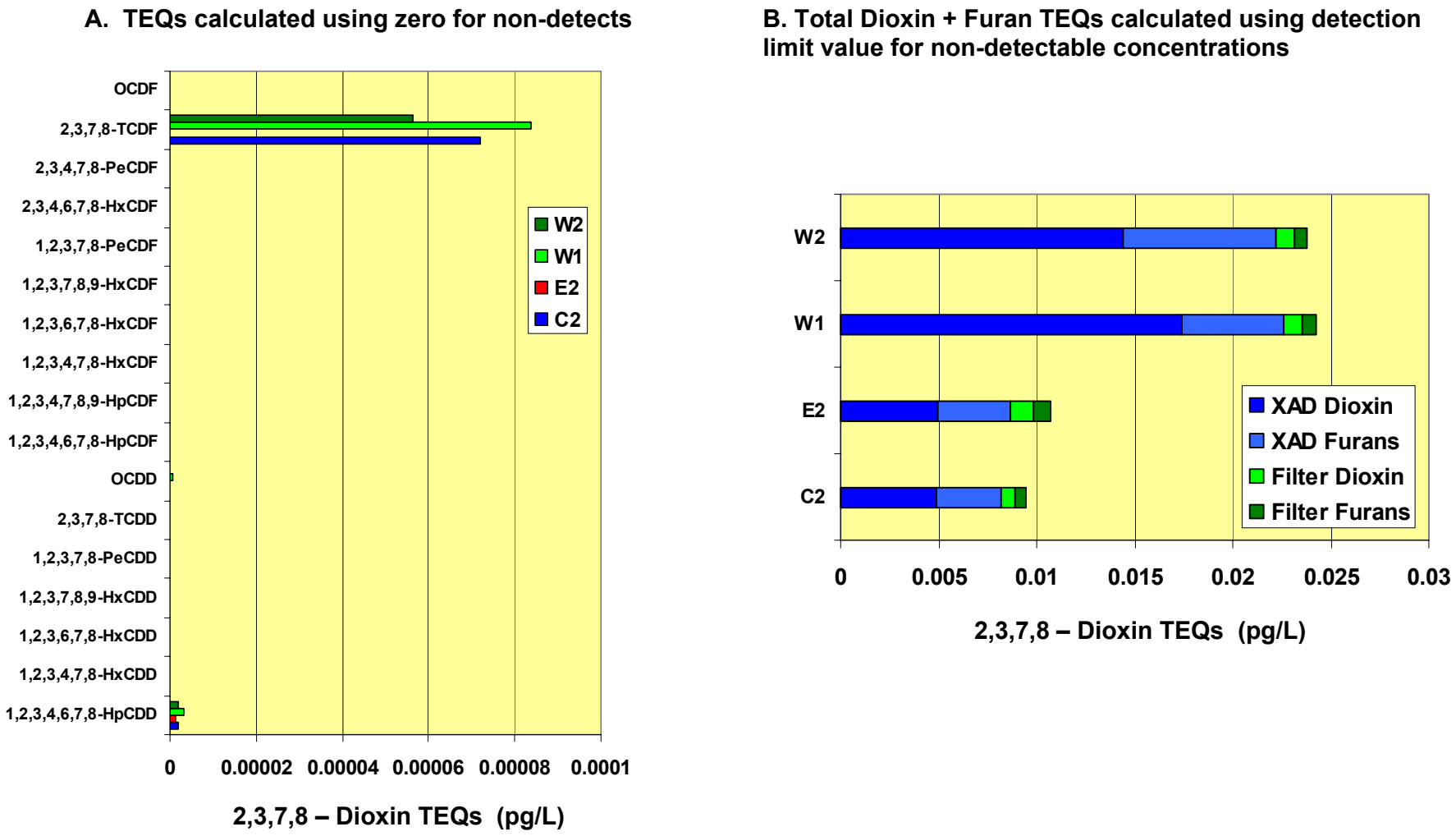

Figure 15. Lake Ontario surface water suspended solid dioxins and furans 2,3,7,8-TCDD toxicity equivalents (pg/L), eastern (E2), central (C2) and western (W1 & W2) basins. TEQs were calculated using zero for non-detections (A) and using the detection limit value for non-detects (B). The graph on the left only shows congeners that were detected in at least one sample.

PBDE

PBDEs were added to the analyte list after the samples had been collected in response to reports that polybrominated diphenyl ethers (PBDEs), a widely used bioaccumulative flame retardant, had been detected in Great Lakes fish and herring gull eggs (Luross *et al.* 2000).

Total concentrations of PBDEs in Lake Ontario surface water were ~ 4 pg/L with 80 to 90 percent present in the dissolved phase (Figs. 16 & 17). 2',4,4',5-pentabromodiphenyl ether (BDE-99) was the most abundant congener making up > 50% of the total (Figs.18 & 19). Next in relative abundance were 2,2',4,4',5,5'-hexabromodiphenyl ether (BDE-153) and 2,2',4,4',5,6'-hexabromodiphenyl ether (BDE-154) each contributing ~10% of the total.

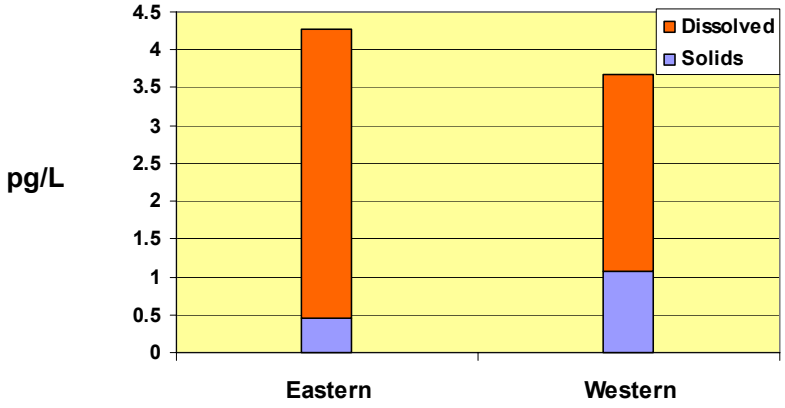

Figure 16. Lake Ontario surface water dissolved and suspended solids PBDE concentrations (pg/L), eastern and western basins.

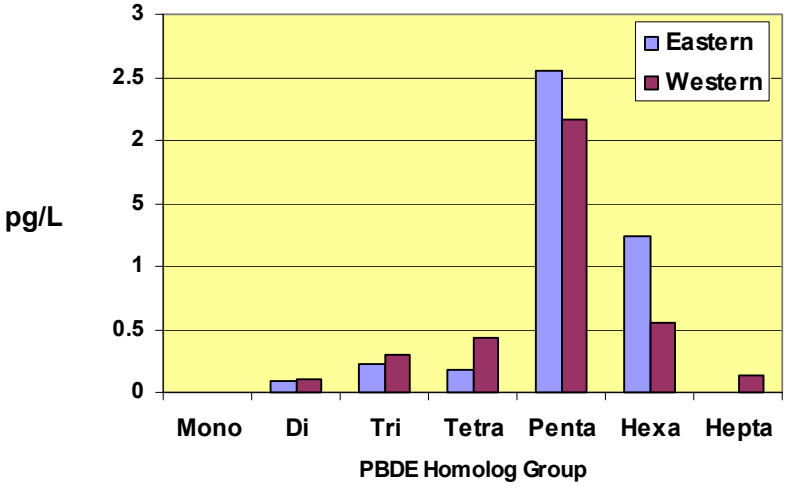

Figure 17. Comparison of Total PBDE homolog concentrations (pg/L) in Lake Ontario surface water, eastern & western basins.

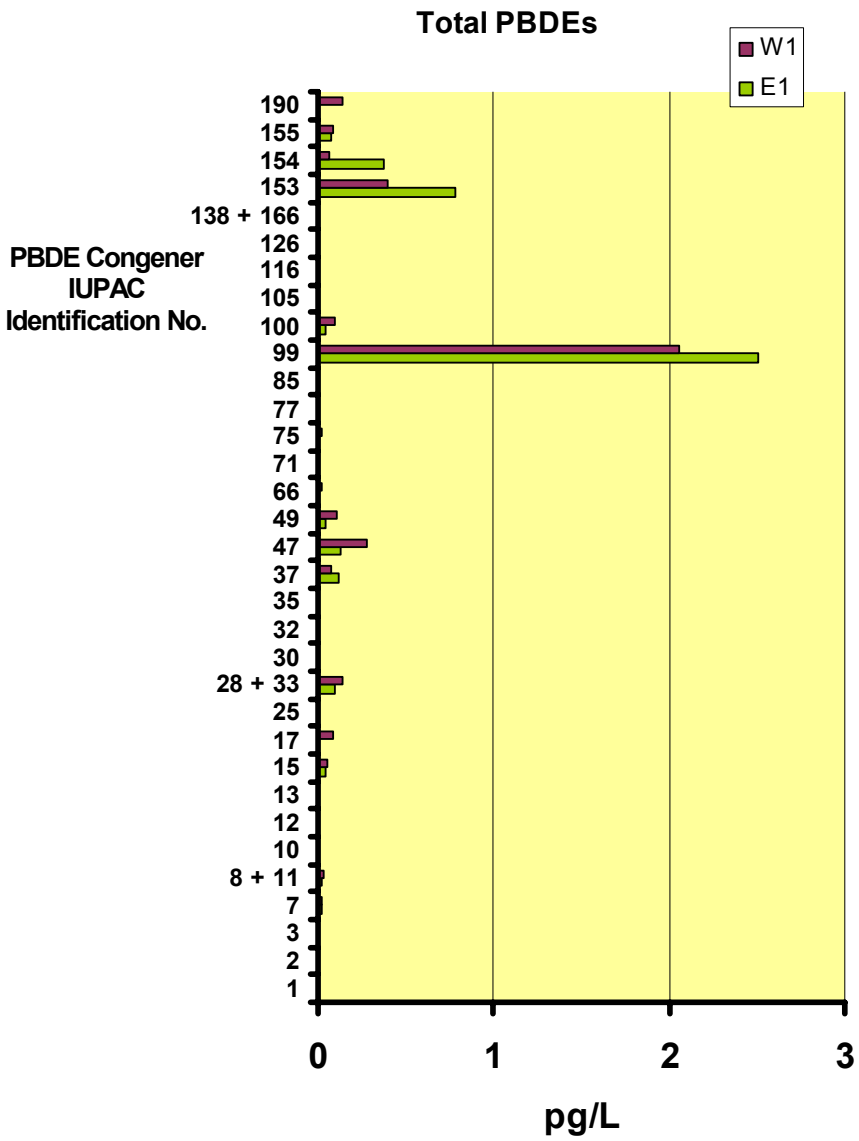

Figure 18. Concentrations of Total PBDE congeners (dissolved + solids) (pg/L) in Lake Ontario surface water, eastern (E1) & western (W1) basins.

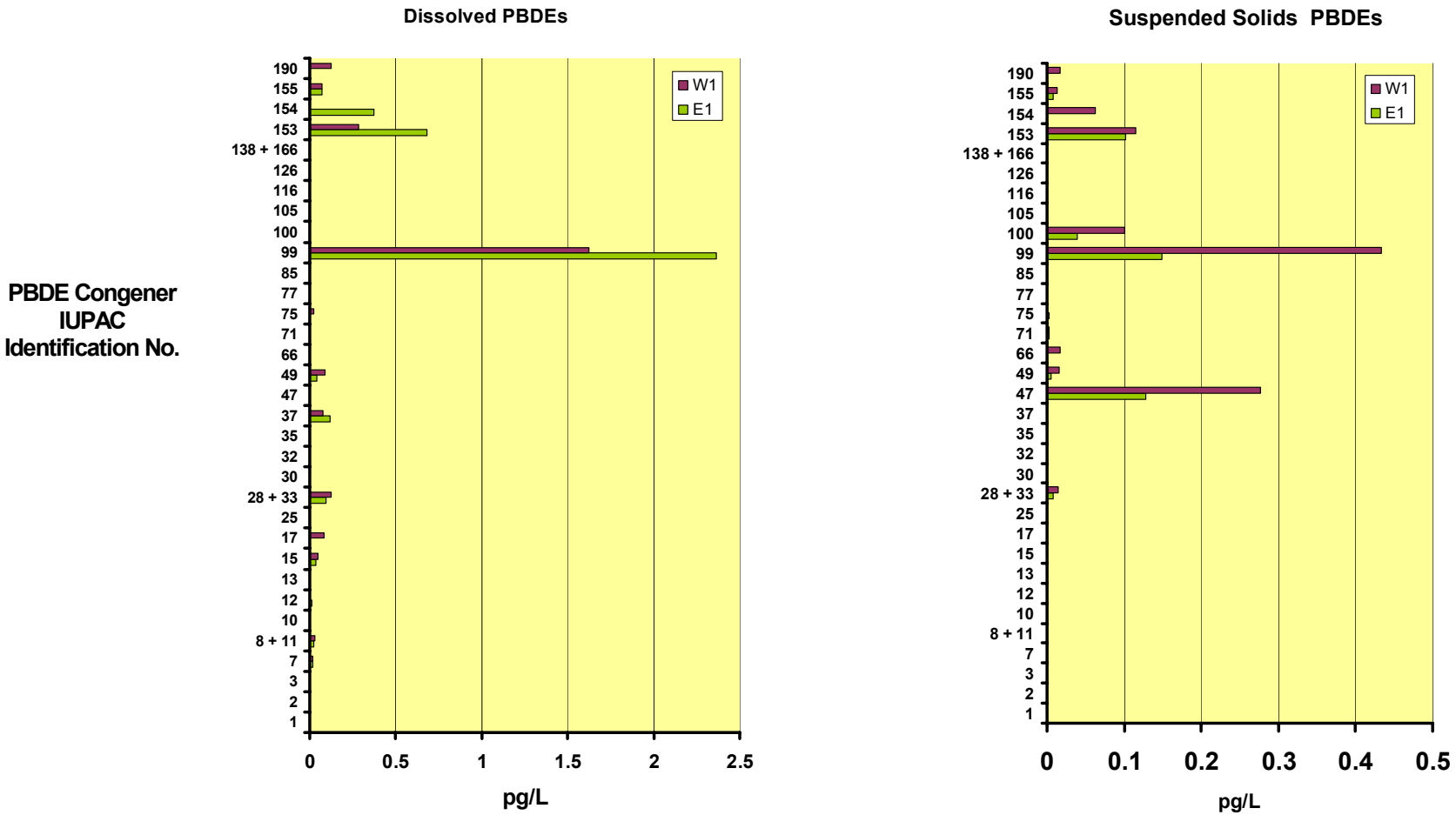

Figure 19. PBDE congener concentrations (pg/L) detected in dissolved and suspended solid phases in Lake Ontario surface water, eastern (E1) and western (W1) basins. Note that the concentration scales are not the same for the dissolved and solid phase results.

Mercury

Methyl mercury was not detected (< 0.018 ng/L) in any field samples or field blanks. Total mercury and total dissolved mercury results were rejected because they were less than three times the field blank levels (~0.75 ng/L) (Table 8).

Field-Filtered Methyl-Mercury - EPA Method 1638 - CVAFS

Location	Conc.	QA Flag	Units	Detection Limit
Western Basin	ND		ng/l	0.018
Central Basin	ND		ng/l	0.018
Eastern Basin	ND		ng/l	0.018
Field Blank	ND		ng/l	0.018

Field-Filtered Total Mercury - EPA Method 1638 - CVAFS

Location	Conc.	QA Flag	Units	Detection Limit
Western Basin	0.43	R	ng/l	0.12
Central Basin	1.04	R	ng/l	0.12
Eastern Basin	0.4	R	ng/l	0.12
Field Blank	0.75		ng/l	0.12

Unfiltered Total Mercury - EPA Method 1638 - CVAFS

Location	Conc.	QA Flag	Units	Detection Limit
Western Basin	1.2	R	ng/l	0.12
Central Basin	0.51	R	ng/l	0.12
Eastern Basin	1.34	R	ng/l	0.12
Field Blank	0.75		ng/l	0.12

Table 8. Mercury sampling results for Lake Ontario surface water (ng/l). Note that filtered and unfiltered "total" mercury results were rejected due to field blank contamination.

Discussion

Exceedences of New York State Ambient Water Quality Values

PCBs and dieldrin exceeded New York State's very stringent, Great Lakes Initiative based ambient water quality values designed to limit bioaccumulation of contaminants in fish in order to protect fish-eating wildlife and reduce human exposures related to fish consumption (Table 9). PCB concentrations ranged from 25 to 46 times above NYSDEC's 1 pg/L ambient water quality value. Dieldrin exceeded NYSDEC's 0.6 pg/L value by up to two orders of magnitude. The majority of the other pesticides were three or more orders of magnitude lower than their respective NYSDEC ambient water quality value.

Mercury, dioxins and furans could not be fully evaluated due to data quality issues. All other contaminants such as DDT, Mirex and hexachlorobenzene were well below all NYSDEC's ambient water quality values. Endosulfan sulfate, alpha HCH and gamma HCH were the only organic contaminants to exceed 100 pg/L although they were approximately one order of magnitude below NYSDEC's ambient water quality values. No NYSDEC ambient water quality values have been developed for PBDE.

Comparison of results with 1997 Lake Ontario TOPS collection effort

TOPS samplers were first used to measure bioaccumulative contaminants in Lake Ontario surface water in September 1997 (Litten & Donlon, 1998). There were some differences in the sampling and analytical approaches used in the 1997 and 1999 surveys that limit the usefulness of a direct comparison of their results. The 1997 survey collected water samples in shallower waters and the water collection method had to be modified due to equipment damage. This 1999 effort utilized a more advanced analytical methods than the 1997 effort. Only one set of the 1997 XAD resin columns and glass fiber filter samples was judged to be relatively free of significant quality assurance issues. A gross comparison of analytes measured in both surveys, and both passed quality control review suggests that these survey results are generally consistent with each other (Table 10).

Dominant PCB congener detected not included in routine monitoring programs

The list of PCB congeners detected using EPA's PCB full-scan congener method (1668A), was compared with congener reporting lists used by the International Atmospheric Deposition Network (IADN) and the Niagara River Upstream/Downstream (US/DS) long term monitoring programs. The purpose of this was to see if the PCB congener reporting lists used by IADN and US/DS include all significant congeners present in Lake Ontario surface water. This comparison showed that these lists capture all of the significant congeners measured as part of this effort with the exception of 3,3'-Dichlorobiphenyl (PCB-11). PCB-11 was the dominant congener detected by accounting for ~6% of the total PCB concentrations. This low-weight PCB congener is probably of little concern from a bioaccumulation point of view. However, as NYSDEC's ambient water quality value is defined in terms of "total" PCB congeners it would be important to include this congener on future congener reporting lists.

	Units =pg/l				NYSDEC Ambient Water Quality	
	Central	East	West-1	West-2	Value & Basis Code	
PCB	46	26	40	37	1	H (FC)
Dioxin + Furan TEQs	?[1]	?[1]	?[1]	?[1]	0.0006	H (FC)
4,4-DDD	3	2	2	1	80	H (FC)
4,4-DDE	2	1	0	1	7	H (FC)
4,4-DDT	0.95	0.81	0.64	0.54	10	H (FC)
Total DDT	6	4	3	3	11	W
HCH, alpha	237	204	133	165	2000	H (FC)
HCH, beta	52	55	32	44	7000	H (FC)
HCH, gamma	210	199	125	167	8000	H (FC)
Total Chlordane	3	4	2	3	20	H (FC)
Aldrin	0.23	0.43	0.03	0.02	1000	H (FC)
Dieldrin	62	53	29	44	0.6	H (FC)
Aldrin + Dieldrin	62	53	29	44	1000	H (FC)
Total Endosulfan	161	162	96	124	9000	A(C)
Endrin	4	3	3	3	2000	H (FC)
Endrin aldehyde	0.55	0.50	0.10	0.23	5,000,000	H (WS)[2]
Endrin ketone	2	2	1	1	5,000,000	H (WS)[2]
Heptachlor	<0.03	<0.06	<0.04	<0.07	200	H (FC)
Heptachlor epoxide	27	25	11	17	300	H (FC)
Hexachlorobenzene	6	4 R	5 R	5 R	30	H (FC)
Methoxychlor	2	2	0	1	30,000	A(C)
Mirex	0.26	0.18	0.30	0.15	1	H(FC)
Photomirex	0.03	<0.03	<0.02	0.02	None	None
PBDE	14.96 R	4	4	19.50 R	None	None
Methyl-mercury	<18	<18	<18	NS	None	None
Total Dissoved Mercury	1040 R	400 R	410 R	NS	700	H (FC)
Total Mercury	510 R	1340 R	1200 R	NS	None	None

Table Notes

[1] - Could not be fully evaluated
[2] - Guidance Value
ND - Not Dectected
R - Rejected (<3X Blank Concentration)
NS - Not sampled

Value Basis Codes:

H (FC) - Human Health Fish Consumption
H (WS) - Source of Drinking Water
A(C) - Aquatic Propoagation
W - Wildlife Protection

Table 9. Concentrations of bioaccumulative contaminants in Lake Ontario surface water, October 1999. This table compares surface water contaminant concentrations with NYSDEC's ambient water quality values for Lake Ontario. All values are NYSDEC standards with the exception of the two guidance values as noted.

	1997 n =1	1999 n = 4
PCB	110	26 - 46
4,4-DDD	16	1. - 3.
4,4-DDE	10	0.5 - 2.0
4,4-DDT	3	0.5 - 1.0
HCH, alpha	440	133 - 236
HCH, beta	59	32 - 55
HCH, gamma	270	125 - 209
Total Chlordane	14	2. - 4.
Endrin	51	29 - 61
Methoxychlor	1	0.1 - 2.0

Table 10. Comparison of 1997 and 1999 TOPS Lake Ontario surface water sampling results (pg/L).

Recommendations

1) Use high resolution PCB analytical methods when possible – Currently the cost of performing high-resolution PCB congener analyses is more than $2000 per sample if the dissolved and suspended solids concentrations are analyzed separately. This is too expensive to be routinely used by many monitoring programs. At least some high resolution PCB congener analyses should be included in a monitoring program to ensure that all environmentally significant congeners are recognized and to check on the accuracy of total PCB values provided by less comprehensive methods.

2) Collect larger dioxin/furan suspended solids sample volumes –Despite the fact that high resolution analytical methods combined with the large volume sampling methods produced parts per quintillion detection limits, these detection limits were still too high to determine if Lake Ontario water meets NYSDEC's ambient water quality value for 2,3,7,8-TCDD TEQs. Dioxin and furan congeners were detected much more reliably on suspended solids than the dissolved phase, often one to two orders of magnitude above the detection limit, although the congener with the highest TEQ (2,3,7,8-TCDD) was not detected. This could be remedied by collecting larger suspended solid sample volumes in the future if it is determined that this information is needed. The measurement of reliable dissolved phase concentrations may not be feasible using XAD resin as pumping larger volumes of water through the XAD resin may introduce greater uncertainty related to poorly understood physical and chemical interactions between the sample water, filter and XAD resin.

3) PBDE Lab Contamination – Given the ubiquitous and largely unregulated use of PBDEs in many types of building materials, furniture and electronics, recent PBDE lab blanks should be carefully reviewed before sending PBDE samples to a lab for extraction. This may help prevent valuable samples from being compromised by gross lab contamination as was the case with some our PBDE samples. The same concern exists for other new, largely unregulated contaminants of concern that may be the focus of future monitoring efforts.

Acknowledgements

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