CONCENTRATIONS AND TRENDS OF TRACE METALS AND ORGANIC CONTAMINANTS IN THE ST. CLAIR RIVER: 1987 - 2017

Debbie Burniston and Brad Hill Water Quality Monitoring and Surveillance Science and Technology Branch Environment and Climate Change Canada

July, 2020

BACKGROUND

The St. Clair River flows 63 km in a southerly direction from Lake Huron to Lake St. Clair and is a straight channel over much of its length. The flow of the river is controlled by the difference in water level between Lake Huron and Lake St. Clair and by the conveyance of the river. It has a mean discharge of 5150 m3/s and a water retention period of approximately 21 hours. (IJC, 2009; UGLCC, 1988).

The Canadian shoreline is heavily industrialized which has resulted in the St. Clair River being designated as an Area of Concern (AOC) within the Great Lakes. The Canada-United States Great Lakes Water Quality Agreement (GLWQA) designates beneficial use impairments (BUIs) within AOCs which must be restored to levels found elsewhere within the Great Lakes. The St. Clair River has 14 BUI designations for which the five chemicals, octachlorostyrene (OCS), hexachlorobutadiene (HCBD), hexachlorobenzene (HCB), polychlorinated biphenyls (PCBs) and mercury (Hg) are drivers. For example, these chemicals have historically been responsible for the fish and wildlife consumption and degradation of benthos BUIs. These contaminants, referred to as chemicals of mutual concern in the St. Clair River, are part of a larger suite of analytes monitored by Environment and Climate Change Canada (ECCC). Ongoing monitoring of water quality in the Huron-Erie Corridor is needed by Great Lakes managers to assess current status and trends, and to assess the need for, and ultimately the efficacy of, remedial actions.

As part of its Freshwater Quality Monitoring and Surveillance Program, ECCC's St. Clair River Upstream/Downstream (U/D) monitoring measures the concentrations of chemicals in both whole water and suspended sediment at the head (Pt. Edward) and mouth (Port Lambton) of the St. Clair River (Figure 1). The intent of the monitoring is to track organic pollutants in the industrialized Canadian region near Sarnia, Ontario. Results for OCS, HCBD, HCB, PCBs, Hg and polycyclic aromatic hydrocarbons (PAHs) in suspended solids along with Hg in whole water will be reported here.

METHODS

ECCC's St. Clair River U/D monitoring was first established in 1987 using methods based on the well documented U/D monitoring in the Niagara River (NRAP 1992; NRSP 1995; Data Interpretation Group 1997; Data Interpretation Group 1999, NRAP 2000, NRSP 2003). Over the years, these methods have undergone some modifications to meet ongoing operational and management needs; however, the current methods (Harrison et al., 2010) have been in place since 2000 with any changes documented and reported below. Historical data (1987-1999) from the study are available (Chan, 1993; Chan et al, 2007).

Site Locations

Point Edward (PE) is situated on the Lake Huron shore at its outlet, north of Sarnia (Figure 1). Monitoring equipment is housed at the sampling site in the Lambton Area Water Supply Service (LAWSS) Water Treatment Plant which draws Lake Huron water through an intake pipe extending 100 m into Lake Huron immediately upstream of the head of the St. Clair River and 15 m below the water surface. The site therefore can be used to monitor loads exiting Lake Huron and concentrations can be compared with those downstream in the river.

The Port Lambton (PL) site is located 38 km downstream of PE and 2 km upstream of the delta area at the mouth of the St. Clair River (Figure 1). Monitoring equipment is housed in an abandoned water pumping station along the Canadian shore and is similarly configured to the PE station with water being pumped through a 19 mm polyethylene tube from a depth of 7 m about 100 m offshore. The setup at both stations facilitates year-round sampling, even during winter ice-covered periods. Samples from PL are indicative of water quality in the Canadian portion of the river. Flow is laterally stratified (Derecki, 1985), resulting in contaminants discharged to the river by the chemical industry in Sarnia remaining confined within 300 m of the Canadian shore, even as far downstream as PL (Chan et al, 1986). The nearest sources of waste discharges are from the Lambton generating station and a CIL fertilizer plant in Courtright, 18 km upstream.



Figure 1. Locations of St. Clair River stations, Point Edward and Port Lambton

St. Clair River U/D Field Methods

From 1987 to 2012, large-volume, 24-hour time-integrated dissolved and particulate phase samples for trace metals and organic contaminants were collected using a submersible pump, intake line, and Westfalia centrifuge assembly (Anthony, 1994; Kuntz, 1994). After 2012, dissolved phase organic samples were no longer collected; however, particulate sampling continues to the present using the same methods.

Over time, ECCC has changed the sampling frequency for monitoring organics and trace metals on the St. Clair River. Sediment samples were collected approximately every two weeks from 1987 to 2010 for organic contaminants and 2005 to 2012 for trace metals (1992-2012 for Hg) after which sampling was reduced to a monthly frequency that continues to the present day. For dissolved phase organics, bi-weekly samples were collected from 1987 to 2008 when collection switched to monthly until it was discontinued in 2012. Trace metals were collected in whole water on a bi-weekly basis from 2000 to 2012 at which time sampling was reduced to the same monthly frequency used today. Whole water Hg samples have been collected on a monthly basis since being implemented in 2010.

Grab samples of whole water for trace metals analyses are collected directly from the intake line using pre-labelled and pre-cleaned or single use bottles that have been approved by the laboratory. Bottles are rinsed twice with sample water, filled to the maximum level, re-capped and the outside of the bottle rinsed with raw water. Samples are then kept on ice during transportation back to the laboratory.

Whole water Hg grab samples are collected using the "clean hands/dirty hands" method (EPA, 1996) in pre-cleaned Teflon bottles filled with a preservative mixture of water, bromine chloride (BrCl), and hydrochloric acid (HCl) provided by ECCC's Quebec Laboratory for Environmental Testing (QLET). In this case, the preservative is emptied immediately before sampling; the bottles are then rinsed 3 times, filled to the maximum level, capped tightly, stored in two polyethylene bags, and couriered overnight to the laboratory. Note that sampling for mercury in whole water was discontinued periodically prior to August 2010 because the analytical method was not sufficiently sensitive and due to evidence of contamination; however, reliable whole water mercury results have been collected from this date to the present.

St. Clair River U/D Analytical Methods

The analyses of all whole water Hg samples are performed by ECCC's Quebec Laboratory for Analytical Testing (QLET) in Montreal, Quebec using methods accredited by the Canadian Association of Environmental Analytical Laboratories (Table 1).

Analyte	Laboratory Method	Analytical Range	Method Description	Instrument	Detector		
Mercury (Hg)	Q0130E3	0.03 - 10 ng/L	Br-Cl digestion/reduction with SnCl ₂ /gold trap	Analytik Jena	Atomic fluorescence (CV-AFS)		

Table 1: Analytical method information for individual compounds in water

The analyses of all suspended sediment trace metal samples (including Hg) and organic analysis prior to April, 2007 were performed by ECCC's National Laboratory for Analytical Testing (NLET) in Burlington, Ontario using methods accredited by the Canadian Association of Environmental Analytical Laboratories (Table 2). Since April of 2007, organic suspended sediment analysis have been performed by QLET while the analysis of trace metals and Hg in sediments have continued to be provided by NLET.

Analyte	Laboratory Method	Analytical Range	Method Description	Instrument	Detector
Mercury (Hg)	B0406S	0.001 - 5 mg/kg when 0.1 g of dry weight is taken for analysis	Mercury is analyzed by weighing 0.1 gram of homogenized, freeze dried solid into a non- amalgamating, thermally stable nickel boat. The sample boat is placed on a sample introduction device which rotates and automatically introduces the boat into a quartz decomposition tube. Here the sample is dried at 120°C and then thermally and chemically decomposed at 750°C in an oxygen rich environment. The decomposition products (which includes mercury vapour), are then carried through the catalytic section of the furnace (where oxidation is completed and halogens and nitrogen/sulfer oxides are trapped) to an amalgamator where gold particles selectively trap mercury vapour. After the oxygen has flushed out any remaining decomposition products, the trapped mercury is desorbed rapidly by heating the amalgamator with the mercury release furnace. The oxygen carries the mercury vapour, Hgo, through two absorbance cells, set in series, and positioned in the light path of a single wavelength flameless atomic absorption spectrometer. A mercury lamp is used as the light source and absorbance is measured at 253.7 nm. Quantification is achieved by calibration with known solutions of Hg standards spread across the analytical range. The two cells are of different path lengths, which allows for a low level and a high level calibration line. Reference method: EPA method 7473.	DMA-80	UV with 253.7 nm filter
Polychlorinated biphenyls (PCBS)	Q0506D2	1-50 pg/g	Dry samples are spiked with 13C12-PCB surrogates and then extracted using Soxhlet extraction with toluene. Extracts are cleaned up using copper, then passed on a multilayer column and finally on an alumina column. Samples are evaporated to a small volume and 13C12- PCB congeners are added as internal standard. Samples are then analyzed in a High Resolution Gas Chromatography system couplet to a High Resolution Mass Spectrometer. Final results are corrected for surrogate recoveries.	HRGC-HRMS	HRMS
Hexachlorobenzene, Octachlorostyrene, Hexachlorobutadiene	Q514S0	1-100 pg/g	Dry samples are spiked with 13C-surrogates and then extracted using Soxhlet extraction with toluene. Extracts are cleaned up using copper, then passed on a silica column. Samples are evaporated to a small volume and 13C-compounds are added as internal standard. Samples are then analyzed in a High Resolution Gas Chromatography system couplet to a High Resolution Mass Spectrometer. Final results are corrected for surrogate recoveries.	HRGC-HRMS	HRMS

Table 2:	Analytical	method i	information	for individual	compounds in	sediment

St. Clair River U/D Quality Control

As part of ECCC's quality assurance procedures, replicate samples are collected twice yearly (September and March) at each station by sequential sampling for each container type. Field blanks are processed four times each year by prefilling sampling bottles with ultra-trace clean (MilliQ) water in the Burlington laboratory and subjecting them to field handling, travel, and laboratory processes.

To provide a more meaningful assessment of the results generated from U/D monitoring, ECCC has also developed a flagging procedure which qualifies the data. Table 3 lists the qualifying (Q) flags, with accompanying rationales, which are applied to the data as appropriate.

Q flag	Rationale
Q01	Value qualified since concentration is greatly above the expected range – improbable.
Q02	Value qualified since concentration is greatly below the expected range – improbable.
Q03	Value qualified since surrogate recoveries are high and value above expected range.
Q04	Value qualified since surrogate recoveries are low and value below expected range.
Q05	Value qualified since sample contaminated; interference precludes quantitative assessment.
Q06	Value qualified since blank typically constitutes <a>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>
Q07	Value qualified since indistinguishable from blank population. (Value <uclc)< td=""></uclc)<>
Q08	Value considered biased low since method recovery of analyte is unacceptably low.
Q09	Value considered biased high since method recovery of analyte is unacceptably high.
Q10	Value qualified since inappropriate sampling and/or analytical methods used to generate result.
Q11	Value qualified since noisy baseline precludes quantitative assessment.
Q12	Value qualified as a result of sample loss.
Q13	Value qualified as a result of laboratory contamination issue.
Q14	Value qualified as a result of field contamination issue.
Q15	Value of surrogate is higher than the expected range.
Q16	Value of surrogate is lower than the expected range.
Q17	Value of surrogate is Non-Detect (ND) because the surrogate was not added.
Q18	Value qualified because filtered fraction is greater than unfiltered fraction.
Q19	Value qualified because bottom disturbance suspected during sampling.
Q20	Value qualified as a result of an unidentified event.
Q99	Value qualified for miscellaneous reason.

Table 3. Q Flags and Their Rationales for the St. Clair River Database

Data labeled with a Q01, Q02, Q06, or Q07 flag are done so based on a statistical assessment of the data. Q06 or Q07 flags highlight a problem specifically due to a persistent lab background contamination and are replaced with less than detection limit (<DL) values prior to any statistical analysis. Data qualified by any Q flags other than Q06 and Q07 are not included in any statistical analysis for this report.

St. Clair River U/D Statistical Methods

Long-term monotonic trends for concentrations and loadings were assessed at PE and PL using a Seasonal Kendall test (Kendall, 1938, 1975; Hirsch, et al., 1982; Meals et al., 2011) within the Time Trends software package (Jowett, 2019) to remove any patterns in water quality explained by seasonal variation. The null hypothesis (H_0 = no change in concentration over time) was rejected when p<0.05. Results of the Seasonal Kendall tests, including estimates slopes are compiled in Table 4 and the Appendix. Graphical representations of these trends, generated from the median values and slopes of the Seasonal Kendall test, are plotted for several of the analytes in Figures 2 through 10. Slopes of the trend are estimated within Time Trends using the Sen's Slope (Sen, 1968).

To determine the statistical significance of the upstream (PE) and downstream (PL) concentration differences, a 2-sided Student T-Test (Snedecor and Cochran, 1989) of paired samples was used. The null hypothesis (H_0 = no difference between stations) was rejected when p<0.05. The results of the Student T-Test would also apply to a comparison of loadings between the two stations as the discharge at both is assumed to be the same.

RESULTS

Statistics

A comprehensive table of statistical results including an expanded list of analytes can be found in Appendix A. Presented here are the per cent annual change and the significance of the change as calculated using the Seasonal Kendall test (Tables 4 and 5).

Trend Analysis

Industrial By-products

Octachlorostyrene (OCS) and hexachlorobutadiene (HCBD) are two chemicals that have been identified to have historic active discharges along the St. Clair River. OCS is a compound with no known uses which is produced as a by-product in the manufacture of other chlorinated compounds. Kaminsky and Hites (1984) have suggested that OCS (as well as other chlorinated styrenes and polycyclic aromatic hydrocarbons) originates primarily as a waste product of electrolytic chlorine production. The waste, called "taffy", results from the chlorination of the tar or pitch used to bind graphite electrodes; its improper disposal leads to the introduction of chlorinated aromatic compounds into the environment.

Contaminant	Site	Sampling period	% Annual Change	Significance
Octachlorostyrene				
	Point Edward	16/6/87-30/3/17	-1.1	p = 0.817
	Port Lambton	16/6/87-30/3/17	-6.7	p < 0.001
Hexachlorobutadiene				
	Point Edward	16/6/87-30/3/17	-2.6	p = 0.522
	Port Lambton	16/6/87-30/3/17	-24.1	p < 0.001
Hexachlorobenzene				
	Point Edward	16/6/87-30/3/17	-5.3	p < 0.001
	Port Lambton	16/6/87-30/3/17	-8.5	p < 0.001
PCB total				
	Point Edward	16/6/87-30/3/17	-8.6	p < 0.001
	Port Lambton	16/6/87-30/3/17	-5.9	p < 0.001
Mercury total				
	Point Edward	18/4/92-10/10/19	-2.2	p < 0.001
	Port Lambton	18/4/92-10/10/19	-2.4	p < 0.001

 Table 4: Annual change results in Suspended Sediment at Point Edward and Port Lambton (bold results indicate that the trend is significant)

Table 5: Annual change results in dissolved phase water samples at Point Edward and Port Lambton.Mercury total results are for whole water samples (bold results indicate that the trend is
significant)

Contaminant	Site	Sampling period	% Annual Change	Significance
Octachlorostyrene				
	Point Edward	8/4/87-22/3/12	-2.5	p = 0.604
	Port Lambton	24/4/87-22/3/12	-1.7	p = 0.344
Hexachlorobutadiene				
	Point Edward	8/4/87-22/3/12	-2.3	p < 0.001
	Port Lambton	24/4/87-22/3/12	-11.0	p < 0.001
Hexachlorobenzene				
	Point Edward	8/4/87-22/3/12	-1.3	p < 0.001
	Port Lambton	24/4/87-22/3/12	-4.2	p < 0.001
Mercury total				
	Point Edward	9/8/10-5/12/19	-4.8	p = 0.012
	Port Lambton	9/8/10-5/12/19	-8.1	p = 0.003

OCS is mainly found in the non-dissolved (suspended sediment) fraction of the water and the number of samples measured above the detection limit in the dissolved phase are limited at PE. At PL, measurable dissolved values are scattered across the timeline (Figure 2B). In the particulate phase, OCS has no significant trend at PE with most concentrations measured at or below the detection limit while concentrations at PL have a significant decline of 6.71% annually (Figure 2A). HCBD is another compound with limited or no industrial or commercial usage. The major source is as a by-product of the production of perchloroethylene, trichlorethylene and carbon tetrachloride (Mumma and Lawless 1975). Temporal trends are shown graphically in figures 3A and 3B.





Figure 2: Temporal trend of OCS in A) particulate and B) dissolved phase samples at Point Edward and Port Lambton





Figure 3: Temporal trend of HCBD in A) particulate and B) dissolved phase samples at Point Edward and Port Lambton

A)

Concentration trends for HCBD from upstream sources as measured at PE were only statistically significant in the dissolved phase with a 2.3% decline annually (Figure 3B). Significant trends measured at PL in the particulate and dissolve phase represent annual declines of 24% and 11 % respectively (figures 3B and 3A); however, it is important to note that the linear monotonic Seasonal Kendall trend may not be the best fit for the HCBD data sets which appear to follow more of a logarithmic decline.

Given that HCBD concentrations were always low at PE, declining trends measured at PL can be attributed the remedial actions in the St. Clair River. Figure 4 shows the difference in U/D concentrations ([PL]-[PE]) which are an indication of St. Clair River sources and the exceptionally low values observed since the late 1990s suggest that management actions in reducing the in-river sources have been successful.



Figure 4. Inputs of HCBD from St. Clair River sources

Hexachlorobenzene

Hexachlorobenzene (HCB) is ubiquitous within the Great Lakes basin. It is persistent, bioaccumulative, and has been banned globally under the Stockholm Convention on Persistent Organic Pollutants. Past usages were as a fungicide, but it is also produced as a by-product from the manufacture and use of chlorinated solvents and pesticides. HCB is a chemical of mutual concern in the St. Clair River and historically has had considerable sources along the Canadian shoreline.

Figure 5 shows temporal trends for HCB in A) particulate and B) dissolved phases of the water samples. Significant declines in the dissolved and particulate phases at both PE and PL have been measured since 1987. Upstream sources as measured at PE have declined by 5.3% and 1.3% per year in suspended sediment and dissolved concentrations respectively, which is a result of the global banning and international efforts to reduce environmental exposure globally. Concentration declines have been greater from St. Clair River sources as measured at PL with declines of 4.2 and 8.5% per year in the dissolved and particulate phases, respectively.



Figure 5: Temporal trend of HCB in A) Particulate and B) dissolved phase samples at Point Edward and Port Lambton

The temporal trend in U/D differences in St. Clair River HCB is shown in figure 6. While there have been consistent sources within the river, levels have been relatively low since 2000. Spikes in concentrations are evident during periods of remediation while lower overall levels illustrate the effectiveness of these management actions.



Figure 6. HCB inputs from St. Clair River sources

Polychlorinated Biphenyls (PCBs)

PCBs were commonly used in electrical equipment such as transformers and capacitors due to their chemical stability. The manufacture of PCBs was halted in 1977 in the United States and the Great Lakes Water Quality Agreement calls for the virtual elimination of all discharges. PCBs were not produced in Canada but approximately 40,000 tons were imported and used commercially prior the 1980s. Like many other organochlorine compounds, PCB are persistent, bioaccumulative, and toxic and they are considered a priority pollutant by many authorities. PCBs are the cause of most of the fish consumption advisories in each of the Great Lakes (including the St. Clair River) and, along with mercury, they are the driver for the fish and wildlife consumption BUI.

Concentrations of PCBs were only measured in the suspended sediments phase of the water samples in the St. Clair River. Given that these compounds are generally hydrophobic in nature, the trends measured would be highly indicative of the overall trends for PCBs in whole water samples.

In the late 1980s, concentrations of PCBs were higher at PE indicating that the major source of contamination was from upstream sources and that the St. Clair river sources were less contaminated with PCBs. The concentration of St. Clair River PCBs shows declines that are statistically significant at both PE and PL (Figure 7).



Figure 7: Temporal trend of PCBs in suspended particulate samples at Point Edward and Port Lambton

At PE the concentration of PCBs decreased 8.6% per year while at PL the decline was only 5.9%. Although the trend analysis for PCBs may be confounded by the location of PE which may not collect sediment enriched plumes during meteorological events, Student T-Tests show there has been no significant difference in U/D concentrations of PCBs (Table 6) indicating there is little to no input of PCBs from the sources within the river.

Mercury

Mercury (Hg) is a nonessential trace element that is toxic, persistent and bioaccumulative. Fish consumption advisories are in effect for mercury in much of the Great Lakes ecosystem including the St. Clair River and, along with PCBs, Hg is the cause of the fish and wildlife consumption BUI. Current uses of mercury include some batteries, switches and cathode tubes while other sources of mercury to the environment include mining and smelting, wastewater, fossil fuel combustion and waste incineration.

Compound	Obs. Pairs	Df	Difference In Means	P (T<=t) two-tail
•			(PL-PE)	
BaP (dissolved)	11	10	-0.0022	0.40200
BaP (sediment)	235	234	19.5089	<0.00001
Fluoranthene (dissolved)	221	220	-0.0700	0.05244
Fluoranthene (sediment)	378	377	31.1460	0.00006
HCB (dissolved)	303	302	0.0258	<0.00001
HCB (sediment)	241	240	16.82576767	<0.00001
HCBD (dissolved)	190	189	0.1008	<0.00001
HCBD (sediment)	140	139	11.82984716	0.06036
Hg (dissolved)	98	97	6.0273	<0.00001
Hg (sediment)	263	262	0.108224335	<0.00001
OCS (dissolved)	13	12	0.0032	0.02152
OCS (sediment)	90	89	3.364888889	<0.00001
PCBs (dissolved)	85	84	0.0651	0.47869
PCBs (sediment)	261	260	-7.9420138	0.20311

 Table 6: Upstream/Downstream Differences Based On Student T-Test of Paired Samples

 (bold results indicate that the difference between sites is statistically significant)

Mercury in whole water at both PE and PL are well below the 26 ng/L concentration guidelines for the protection of aquatic life (CCME, 2020). While the Seasonal Kendall test indicate there are significant declines at both stations, the temporal trend is not readily apparent in visual form (Figure 8B). Regardless of these discrepancies, the upstream sources (as measured at PE) are consistently low, ranging from 0.06 to 8 ng/L with a mean value of 0.44 ng/L. At PL, the concentrations range from 0.16 to 103 ng/L with a mean value of 6.2 ng/L and 5 samples that exceed the guideline. It is hypothesised that these guideline exceedances likely occurred during metrological events which can re-suspend contaminated bottom sediment still found in the river.

Concentrations of mercury in suspended sediments (Figure 8A) are low and show a decline of 2.2% per year from upstream sources as measured at PE. Sources upstream of PL have been declining at a rate of 2.3 % annually indicating that sources within the river have also been declining. Current concentrations in suspended sediment are well below the 0.486 ng/g CCME sediment quality guidelines (CCME, 2020) which is indicative of future sediment health at downstream depositional areas.





Figure 8: Temporal trends of Mercury Concentrations in A) particulate and B) whole water at Point Edward and Port Lambton

A)

Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs refer to a group of chemicals whose origins in the environment are from the incomplete combustion of fossil fuels, refuse in municipal incinerators, forest fires and various combustion processes. The chemistry of PAHs is such that they are more readily adsorbed onto particulate matter and are therefore found primarily in suspended sediment.

In the case of fluoranthene at PE, Seasonal Kendall analysis indicates that there is no statistically significant trend at the upstream location (Figure 9). The relatively flat slope of the PE trend line, combined with the lack of statistical significance, indicates that upstream sources have been relatively consistent since the late 1980s.



Figure 9: Temporal trends of fluoranthene concentrations in suspended sediment at Point Edward and Port Lambton

At PL, the Seasonal Kendall test shows a statistically significant increase in concentrations (0.51% per year). The plot of PL concentrations also shows that there appears to be a decrease in variability over time and, while Student T-Tests confirm that there is no statistically significant difference between the upstream and downstream concentrations in the dissolved phase (Table 6), they do show a statistically significant difference between PE and PL sediment concentrations.

Based on Seasonal Kendall analysis, Benzo(a)pyrene (BaP) sediment concentrations shows statistically significant trends at PE and PL (-2% and +1% per year, respectively) between 1987 and 2017 (Figure 10A); however, there are a number of non-detects (194

at PE and 234 at PL) which may be confounding the Kendall results. Using samples collected from 2000 -2017, there are only 27 non-detects at PE and 7 non-detects at PL. The Seasonal Kendall analysis over the more recent period (Figure 10B) shows a similar statistically significant decrease of 1.93% per year at PE and a statistically significant increase of 2.77% per year at PL.







Figure 10: Temporal trends of benzo(a)pyrene concentrations in suspended sediment at Point Edward and Port Lambton over the periods 1987-2017 (A) and 2000-2017 (B)

CONCLUSIONS

Since the designation of the St. Clair River as an area of concern and the inception ECCCs upstream/downstream monitoring program in the St. Clair River in the late 1980s there has been great progress in reducing harmful contaminants to the river and restoring the river to conditions similar to those found elsewhere in the Great Lakes. Results of the thirty years of monitoring indicate that:

- Based on Student T-Tests of paired samples, there are no statistically significant differences in particulate HCBD and PCB concentration between PE and PL, indicating that there is no ongoing source of these contaminants within the river.
- The concentration of mercury in whole water at Port Lambton is below the Canadian
 water quality guidelines for the protection of aquatic life with only a few exceedances
 during meteorological events. The concentration of mercury on particulates has
 decreased significantly from sources upstream of the St. Clair river by 2.2% annually and
 downstream at Port Lambton by 2.4% annually. Hg concentrations on particulates are
 currently below the CCME sediment quality guidelines for the protection of aquatic life
 which may indicate that depositional areas downstream of the St. Clair will not
 endanger aquatic life.
- HCB is ubiquitous in waterways throughout the world which confounds efforts to reduce concentrations in local areas. Notwithstanding, concentrations of HCB on particulate and in dissolved water samples have declined significantly from upstream sources (5.3% and 1.3% per year, respectively). Port Lambton has had greater declines in these matrices of 8.5 and 4.2% annually. While sources in the river are still evident, continued monitoring should confirm continued declines.
- There are virtually no upstream sources of OCS to the St. Clair River. Sources in the river have been steadily declining at a rate of 6.7% annually. Current concentrations are low.
- Interpretation of PAH trends may be confounded by non-detect samples; however, fluoranthene and BaP concentrations appear to be increasing at PL while showing signs of decreasing or remaining relatively constant at PE.
- The upstream/downstream program has been imperative in demonstrating the efficacy of government remedial and management actions.

- Future remediation of mercury-contaminated sediment is being considered and therefore continued monitoring is recommended so that the success of these actions can be verified.
- Continued monitoring is also recommended as this AOC moves into delisting as part of the long term monitoring strategy required by the Great Lakes Water Quality Agreement.

ACKNOWLEDGEMENTS

The authors gratefully recognize Bob McCrae, John Fisher, C.H. Chan, Bruce Harrison, Mary Lou Archer, Jeff Hanna, Tina Hooey, Jesse Baillargeon, John Kraft, Andrew Mummery, Tina Mamone, Leah Peacock, Jasmine Waltho, and Allison Puhl for their invaluable contributions to ECCC's monitoring operations on the St. Clair River. We also acknowledge the technical expertise of staff at ECCC's National Laboratory for Environmental Testing, Quebec Laboratory for Environmental Testing; and Technical Operations. Water quality monitoring in the St. Clair Niagara River is supported by Freshwater Water Quality Monitoring and the Great Lakes Action Plan at ECCC.

REFERENCES

Anthony, D.J. 1994. Large sample extraction systems with analytical solvent recovery for low flow applications. NWRI Contribution No. 94-69. Environment Canada, Burlington.

International Joint Commission (IJC), 2009. International upper Great Lakes study: Impacts on upper Great Lakes water levels: St. Clair River Final report. http://www.iugls.org/St. Clair River Results. (Retrieved April 25, 2017).

CCME. 2020. *Canadian Environmental Quality Guidelines*. Retrieved from <u>http://ceqg-rcqe.ccme.ca/en/index.html#void</u>. July 8, 2020.

Chan, C.H., Y.L. Lau, B.G Oliver, 1986. Measured and modelled chlorinated contaminant distribution in St. Clair River water. *Water Pollution Research Journal of Canada*. 21, 332–343.

Chan, C.H. 1993 St. Clair River head and mouth water quality monitoring, 1987-89. *Water Pollution Research Journal of Canada*. 28(2):451-471.

Chan, C.H. D.J. Williams, M. Neilson, J. Waltho, S.M. Backus and D.Burniston. 2007. Concentrations And Trends Of Nutrients, Major Ions, Trace Metals And Organic Contaminants In The St. Clair River: 1987-1999. Environment Canada. Environmental Conservation Branch/Ontario Region/Ecosystem Health Division. Report No.: EHD/ECB-OR/05-01/I

Data Interpretation Group. 1997. Joint Evaluation of Upstream/Downstream Niagara River Data 1995-96. A joint publication of New York State Department of Environmental Conservation, Environment Canada, U.S. Environmental Protection Agency, and Ontario Ministry of the Environment.

Data Interpretation Group. 1999. Joint Evaluation of Upstream/Downstream Niagara River Data 1996-97. A joint publication of New York State Department of Environmental Conservation, Environment Canada, U.S. Environmental Protection Agency, and Ontario Ministry of the Environment.

Data Interpretation Group. 2002. Upstream/Downstream Niagara River Monitoring Program Final Report - 1997-98 and 1998-99. A joint publication of New York State Department of Environmental Conservation, Environment Canada, U.S. Environmental Protection Agency, and Ontario Ministry of the Environment. Derecki, J.A., 1985. Effect of channel changes in the St. Clair River during the present century. *Journal of Great Lakes Research*. 11, 201–207.

EPA. 1996. *Method 1669: Sampling Ambient Water For Trace Metals At EPA Water Quality Criteria Levels* [PDF File]. Retrieved from https://www.epa.gov/sites/production/files/2015-10/documents/method_1669_1996.pdf

Harrison, B., C. Lochner, M.L Archer, B. Hill and P. Klawunn. 2010. SOP WQMS11 - 001. Standard Operating Procedure For The Collection Of Water And Suspended Sediment Samples At The St. Clair River Monitoring Stations (Point Edwards And Port Lambton). Environment Canada. Water Quality Monitoring and Surveillance. Burlington, Ontario.

Hirsch, R.M., Slack, J.R., Smith, R.A., 1982. Techniques of trend analysis for monthly waterquality data. *Water Resources Research*. 18 (1), 107–121.

Jowett, Ian. 2019. TimeTrends: Trend Analysis and Equivalence testing for environmental data. Version 6.30. Updated 9 September 2019

Kaminsky, R. and R A Hites. 1984. Octachlorostyrene in Lake Ontario: Sources and Fates. *Environ Science and Technology*. April 1984. 18(4):275-9. doi: 10.1021/es00122a013.

Kendall, M.G., 1938. A new measure of rank correlation. Biometrika 30 (1/2), 81–93.

Kendall, M.G., 1975. Rank Correlation Methods. 4th edition. Charles Griffin, London.

Kuntz, K.W. 1994. A Comparison of Extraction Efficiencies of Organic Contaminants in the Niagara River between the Goulden Large Sample Extractor (GLSE) and the New (GLSE/SR) with Solvent Recovery. Environment Canada, Burlington, (Draft Report).

Meals, D.W., Spooner, J., Dressing, S.A., Harcum, J.B., 2011. Statistical Analysis for Monotonic Trends, Tech Notes 6, November 2011. Developed for U.S. Environmental Protection Agency by Tetra Tech, Inc., Fairfax, VA (23 pp.).

Mumma, C.E., and E.W. Lawless. 1975. Survey of industrial processing data. Task 1 -Hexachlorobenzene and hexochlorobutadiene. EPA 560/3-75-003, National Technical Information Service NRAP. 2000. Method Guide for the Analysis of Chlorobenzenes, Organochlorine Pesticides, Total Polychlorinated Biphenyls and Polynuclear Aromatic Hydrocarbons in Niagara River Samples. Prepared by M. E. Comba, P.J. Klawunn and E. Sverko, National Laboratory for Environmental Testing (NLET), Environment Canada, October 2000.

NRAP. 1992. Analytical Protocol for Monitoring Ambient Water Quality at the Niagara-on-the-Lake and Fort Erie Stations. Analytical Protocol Group. A joint report by Environment Canada, U.S. Environmental Protection Agency, New York State Department of Environmental Conservation, and the Ontario Ministry of the Environment.

NRSP. 1995. Upstream/Downstream Sampling Protocol. Joint report of Environment Canada, United States Environmental Protection Agency, New York State Department of Environmental Conservation, and Ontario Ministry of Environment.

NRSP. 2003. Upstream/Downstream Sampling Protocol. Joint report of Environment Canada, United States Environmental Protection Agency, New York State Department of Environmental Conservation, and Ontario Ministry of Environment, Report No. EHD/ECB-OR/03-05/I. Environment Canada, Burlington.

Sen, P.K. (1968), Estimates of the regression coefficient based on Kendall's tau, *Journal of the American Statistical Association* 63, 1379--1389.

Snedecor, G.W., Cochran, W.G., 1989. Statistical Methods. Iowa State University Press, Eighth edition.

Upper Great Lakes Connecting Channels Study (UGLCCS), 1988. Upper Great Lakes Connecting Channel Study Final Report V.II. pp. 25–27.

APPENDIX

Table A-1 Statistical results for suspended sediment samples. Bold numbers indicate a significant trend (p<0.05)

Site/ Analyte	Non- detects	Sample size (N)	Sample period	Mean	Max	Min	Median	Kendall Stat	Variance	Z	Ρ	Slopes	Median Sen slope (annual)	95 % confidence limits for slope	% annual change
Octachlorosty	rene					1									
Point Edward	356	458	16/6/87- 30/3/17	0.12	4	<0.028	<0.200	-711	9432767	-0.2	0.817	102	-0.001	-0.00410833 to 0.00000001	-1.14
Port Lambton	28	567	16/6/87- 30/3/17	7.14	150	0.1	3.80	-53905	20301551	-12.0	<0.001	539	-0.255	-0.29377370 to -0.21853141	-6.71
Hexachlorobe	nzene														
Point Edward	89	500	16/6/87- 30/3/17	0.77	21	0.1	0.58	-35963	13845278	-9.7	<0.001	411	-0.031	-0.03587662 to -0.02615075	-5.32
Port Lambton	8	563	16/6/87- 30/3/17	24.52	286	0.3	12.00	-64930	19878227	-14.6	<0.001	555	-1.021	-1.16748499 to -0.88103708	-8.51
Hexachlorobu	tadiene								•						
Point Edward	296	464	16/6/87- 30/3/17	0.11	3	0.0	0.10	-2054	10298559	-0.6	0.522	168	-0.003	-0.00388767 to -0.00064728	-2.56
Port Lambton	13	567	16/6/87- 30/3/17	37.00	1400	0.0	7.40	-92809	20304149	-20.6	<0.001	554	-1.780	-1.99817752 to -1.56211775	-24.06
Hexachlorocy	clopentadie	ene					1	1	1	I					1
Point Edward	191	313	2/8/96- 30/3/17	0.68	20	<0.011	<0.410	-8421	3314544	-4.6	<0.001	122	-0.100	-0.13095813 to -0.06961410	-48.59
Port Lambton	241	245	2/8/96- 30/3/17	0.03	2	<0.015	<0.41	-289	1434213	-0.2	0.810	4	-0.054	<-0.63583171 to 8.91349145	-26.29
PCB total															
Point Edward	78	460	16/6/87- 30/3/17	43.87	1460	3.1	32.83	-37219	10793424	-11.3	<0.001	382	-2.809	-3.14674157 to -2.49670617	-8.56
Port Lambton	145	545	16/6/87- 30/3/17	37.04	454	3.4	31.90	-40765	17824367	-9.7	<0.001	400	-1.881	-2.12649167 to -1.65055544	-5.90

alpha- BHC OF	R НСН														
Point Edward	0	409	16/6/87- 30/3/17	-0.32	16	-2.3	-0.20	16073	7331765	5.9	<0.001	409	0.017	0.00000001 to 0.06920821	-8.52
Port Lambton	0	493	16/6/87- 30/3/17	-0.71	6	-2.3	-0.18	23691	12532197	6.7	<0.001	493	0.009	0.00000001 to 0.07380851	-5.04
gamma-BHC C	OR HCH (Lin	idane)													
Point Edward	297	355	16/6/87- 19/8/09	0.27	7	0.0	<3.5	-2110	4244104	-1.0	0.306	58	-0.048	-0.09499218 to -0.01664908	-2.76
Port Lambton	354	431	16/6/87- 9/9/09	0.16	4	0.0	<3.5	-3147	7074442	-1.2	0.237	77	-0.022	-0.03159193 to -0.01528281	-1.24
14-dichlorobe	nzene (par	a)													
Point Edward	125	344	16/6/87- 13/6/07	8.94	36	2.7	7.46	3090	4385885	1.5	0.140	219	-0.021	-0.21595643 to 0.00000001	-0.28
Port Lambton	175	407	16/6/87- 20/3/07	8.64	48	1.9	5.90	-867	6951766	-0.3	0.743	232	0.000	-0.13384182 to 0.00000001	0.00
Pentachlorobe	enzene														
Point Edward	174	433	16/6/87- 30/3/17	0.23	5	0.0	0.27	-10057	8665125	-3.4	0.001	259	-0.007	-0.00917180 to -0.00500171	-2.63
Port Lambton	35	495	16/6/87- 30/3/17	3.13	66	0.1	1.52	-58649	13509504	-16.0	<0.001	460	-0.164	-0.18511375 to -0.14518885	-10.79
o,p'-DDE (2,4'-	-DDE)	•									•				
Point Edward	26	86	26/6/07- 30/3/17	0.05	<0.30	0.0	0.05	51	68978	0.2	0.849	60	0.000	0.00000001 to 0.009166098	0.00
Port Lambton	26	89	4/4/07- 30/3/17	0.07	<0.51	0.0	<0.13	-88	76099	-0.3	0.752	63	0.000	-0.00496320 to 0.00035102	0.00
p,p'-DDE (4,4'	-DDE)														
Point Edward	75	486	16/6/87- 30/3/17	1.70	15	<0.30	1.30	-41572	12734202	-11.6	<0.001	411	-0.088	-0.10151377 to -0.07584463	-6.78
Port Lambton	117	546	16/6/87- 30/3/17	1.11	6	0.2	1.10	-44878	17950766	-10.6	<0.001	429	-0.047	-0.05282801 to -0.04074970	-4.25

Phenanthrene	!														
Point Edward	48	489	16/6/87- 30/3/17	72.96	302	4.2	69.00	27695	13016632	7.7	<0.001	441	0.978	0.57496929 to 1.38705087	1.42
Port Lambton	20	553	16/6/87- 30/3/17	118.89	2026	<10	97.90	27221	18832281	6.3	<0.001	533	1.332	0.85909075 to 1.80509158	1.36
Fluoranthene															
Point Edward	23	493	16/6/87- 30/3/17	78.31	520	6.6	71.00	1237	13348766	0.3	0.735	470	-0.400	-0.85061736 to 0.01772799	-0.56
Port Lambton	17	551	16/6/87- 30/3/17	114.61	1952	<15	83.10	11684	18631850	2.7	0.007	534	0.426	0.00000001 to 0.87052651	0.51
Pyrene				•	•		•								
Point Edward	0	26	30/4/15- 30/3/17	48.31	98	19.0	39.00	8	2014	0.2	0.876	26	1.449	-2.09948673 to 18.88144974	3.72
Port Lambton	0	26	30/4/15- 30/3/17	85.31	290	39.0	70.00	-22	2016	-0.5	0.640	26	-3.727	-0.50028685 to 20.92861000	-5.32
Lead total reco	overable														
Point Edward	0	213	30/3/05- 10/10/19	20.35	44	9.1	19.10	-2602	1080471	-2.5	0.012	213	-0.221	-0.40176349 to -0.05084175	-1.15
Port Lambton	0	219	30/3/05- 10/10/19	19.36	39	8.0	19.10	-2806	1174071	-2.6	0.010	219	-0.224	-0.38034463 to -0.06071670	-1.17
Benzo(a)pyrer	ne														
Point Edward	194	487	16/6/87- 30/3/17	28.58	150	<4.04	25.10	8617	12651070	2.4	0.015	293	-0.499	084386522 to -0.15484089	-1.99
Port Lambton	234	555	16/6/87- 30/3/17	46.98	943	7.1	35.00	37365	18481110	8.7	<0.001	321	0.338	-0.09582291 to 0.78403038	0.97
Point Edward	25	314	3/2/00- 30/3/17	31.36	150	<4.04	26.45	-1146	217727	-2.5	0.014	289	-0.511	-0.86594059 to -0.19902542	-1.93
Port Lambton	7	295	3/2/00- 30/3/17	48.96	420	7.10	41.00	1876	181884	4.4	<0.001	288	1.135	0.63629548 to 1.65436870	2.77

Arsenic total r	recoverable	2													
								-	•				r	1	
Point	0	213	30/3/05-	9.44	19	4.0	9.00	-3442	1070147	-3.3	0.001	213	-0.142	-0.24838112	-1.58
Edward			10/10/19											to	
														0.0000001	
Port	0	219	30/3/05-	9.46	18	4.0	9.00	-7101	1155802	-6.6	<0.001	219	-0.240	-0.30716899	-2.67
Lambton			10/10/19											to	
														-0.16459076	
Copper total r	ecoverable	2	•	•	•				•	•	•				
Point	0	213	30/3/05-	28.69	61	9.0	27.00	-809	1078337	-0.8	0.437	213	-0.075	-0 33477370	-0.28
Edward	U	215	10/10/19	20.05	01	5.0	27.00	005	10/035/	0.0	0.437	215	0.075	to	0.20
Luwaru			10/10/15											0 11000760	
Dort	0	210	20/2/05	25.05	127	12.1	25.00	6966	1172160	6.2	<0.001	210	1 1 4 0	1 46020255	2.26
Pull	0	219	30/3/05-	55.95	127	12.1	55.00	-0000	11/5100	-0.5	<0.001	219	-1.140	-1.45056555	-5.20
Lampton			10/10/19											0 02222062	
														-0.83233802	
Dieldrin															
Point	130	500	16/6/87-	2.33	41	< 0.14	1.00	-51222	13850364	-13.8	<0.001	370	-0.144	-0.17067194	-14.51
Edward			30/3/17											to	
														-0.12202575	
Port	97	560	16/6/87-	1.11	17	<0.22	0.94	-64705	19451427	-14.7	<0.001	463	-0.057	-0.06376597	-6.11
Lambton	_		30/3/17			-								to	
														-0.05147886	
Mercury total												1		0.002.0000	
wiched y total		r		-				-	•				1		
Point	1	328	18/4/92-	0.05	0	< 0.004	0.04	-9418	3936051	-4.7	<0.001	327	-0.001	-0.00125622	-2.16
Edward			10/10/19											to	
														-0.00053735	
Port	0	366	18/4/92-	0.16	1	0.03	0.15	-13949	5468042	-6.0	<0.001	366	-0.004	-0.00470662	-2.35
Lambton			10/10/19											to	
														-0.00239897	
Mirex			1												
			T									1			
Point	368	380	16/6/87-	0.07	<4.4	<0.021	<4.4	-704	5070306	-0.3	0.755	12	-0.031	-0.10222220	-1.40
Edward			30/3/17											to	
														-0.01333932	
Port	426	433	16/6/87-	0.06	<4.4	<0.024	<4.4	-163	6558403	-0.1	0.950	7	-0.006	<-0.05253295	-0.29
Lambton			30/3/17		1]					to	
	1					1								0.10319176	

Site/ Analyte	Non- detects	Sample size (N)	Sample period	Mean	Max	Min	Median	Kendall Stat	Variance	Z	Ρ	Slopes	Median Sen slope (annual)	95 % confidence limits for slope	% annual change
Hexachlorob	enzene			4			1					1	•	1	
Point Edward	42	433	8/4/87- 22/3/12	0.02	0.27	0.00	0.02	-20623	8685966	-7.0	0.000	391	0.000	-0.00036895 to -0.00008399	-1.33
Port Lambton	26	484	24/4/87- 22/3/12	0.04	0.54	<0.0 05	0.03	-36476	1248072 9	-10.3	0.000	458	-0.001	-0.00148587 to -0.00099847	-4.16
Hexachlorob	utadiene														
Point Edward	180	432	8/4/87- 22/3/12	0.04	1.16	0.00	<0.04	12532	8373968	4.3	0.000	252	0.000	-0.00095936 to 0.00000001	-2.34
Port Lambton	15	485	24/4/87- 22/3/12	0.26	4.68	0.00	0.14	-57529	1270774 5	-16.1	0.000	470	-0.015	-0.01719434 to -0.01357015	-11.03
Hexachlorocy	clopentad	iene											·		
Point Edward	100	148	27/6/96- 22/3/12	0.36	11.3 0	0.00	0.02	-1300	310511	-2.3	0.020	48	-0.002	-0.00421780 to 0.01372141	-8.29
Port Lambton	212	250	6/4/96- 22/3/12	0.00	0.04	0.00	<0.04	-453	1058800	-0.4	0.660	38	-0.001	-0.00093120 to -0.00036174	-2.55
Octachlorost	yrene														
Point Edward	412	433	8/4/87- 22/3/12	0.00	<0.0 7	0.00	<0.07	-1254	5836147	-0.5	0.604	21	-0.001	-0.00119981 to -0.00059164	-2.52
Port Lambton	352	486	24/4/87- 22/3/12	0.01	0.12	0.00	<0.07	-2706	8181358	-0.9	0.344	134	-0.001	-0.00079207 to -0.00034789	-1.66
PCB total															
Point Edward	0	124	14/4/95- 5/3/08	0.87	9.18	0.00	0.60	-3478	213736	-7.5	0.000	124	-0.112	-0.14597277 to -0.08496776	-18.89
Port Lambton	0	116	14/4/95- 5/3/08	1.15	11.8 5	0.00	0.76	-3288	175152	-7.9	0.000	116	-0.104	-0.12427352 to -0.08632672	-13.65

Table A-2 Statistical results for dissolved samples. Hg statistics is for whole water. Bold numbers indicate a significant trend (p<0.05)

Mercury total															
Point	0	104	9/8/10-	0.44	8.05	0.06	0.32	-894	126467	-2.5	0.012	104	-0.015	-0.02879322	-4.79
Edward			5/12/19											to	
														-0.00348859	
Port	1	107	9/8/10-	6.06	102	<0.0	1.93	-1090	137842	-2.9	0.003	106	-0.156	-0.28775187	-8.06
Lambton			5/12/19			3								to	
														-0.05581297	
Copper total															
Point	0	377	26/6/00-	0.64	6.67	0.00	0.47	-4585	5972569	-1.9	0.061	377	-0.003	-0.00692669	-0.66
Edward	•	0	30/1/20	0.01	0.07	0.00	0		0072000	1.5	0.001	0//	0.000	to	0.00
2411414			00, 2 20											0.00000001	
Port	0	357	26/6/00-	0.93	9.62	0.00	0.76	5016	5074460	2.2	0.026	357	0.011	0.00023373	1.41
Lambton	-		30/1/20											to	
														0.02490165	
14-dichlorob	enzene (pa	ira)	_ I												
Point	84	338	8/4/87-	1.61	9.67	<0.2	1.00	-6989	4286192	-3.4	0.001	254	-0.018	-0.03763562	-1 82
Edward	04	550	22/3/12	1.01	5.07	7	1.00	0505	4200152	5.4	0.001	234	0.010	to	1.02
Lawara			22) 3/ 12											-0.00194238	
Port	37	485	8/4/87-	1.24	7.02	<0.2	1.00	-10979	1264677	-3.1	0.002	448	-0.006	-0.01623102	-0.63
Lambton	57	100	22/3/12	1.2.1	7.02	7	1.00	10575	8	5.1	0.002	110	0.000	to	0.00
Lumbton			22 0/ 22			-			0					0.00000001	
135-trichloro	benzene (s	sym)	_ I												
Point	311	126	8/1/87-	0.01	0.14	0.00	<0.02	-3367	8115144	-1.2	0.237	115	-0.001	-0.00210210	-1/ 87
Edward	511	420	22/3/12	0.01	0.14	0.00	VU.UZ	3307	0110144	1.2	0.237	115	0.001	to	14.07
Lawara			22/3/12											-0 00096959	
Port	62	487	8/4/87-	0.05	0.19	0.00	0.04	-21987	1281001	-6.1	0.000	425	-0.002	-0.00223060	-4 70
Lambton	02	407	22/3/12	0.05	0.15	0.00	0.04	21507	3	0.1	0.000	723	0.002	to	4.70
Lambton			22 3, 12						5					-0.00151996	
Pentachlorob	enzene			1				1		1		1		0.00101000	
Doint	140	422	0/4/07	0.01	0.09	0.00	0.01	24720	9510225	0 5	0.000	202	0.000	0.00012605	0.27
Foint	140	432	8/4/8/-	0.01	0.08	0.00	0.01	-24729	8519235	-8.5	0.000	292	0.000	-0.00012605	-0.37
Euwaru			22/5/12											0.0000001	
Dort	21	100	24/4/97	0.02	0.26	0.01	0.02	40105	1240060	11.4	0.000	155	0.001	0.00000001	2 71
Lambton	21	400	24/4/07-	0.02	0.30	0.01	0.02	-40195	1240000	-11.4	0.000	455	-0.001	-0.00080380	-5.71
Lambton			22/3/12						1					-0.00060334	
alpha PUC UC	าน			<u> </u>										-0.00000334	
арпа вне не					-	-	-						-		
Point	0	39	8/4/87-	2.85	6.89	0.86	2.88	-113	6683	-1.4	0.171	39	-0.248	-0.73202610	-8.60
Edward			15/5/89											to	
														0.17159495	
Port	0	60	8/4/87-	2.63	5.85	1.16	2.59	-712	24287	-4.6	0.000	60	-0.584	-0.78243000	-22.49
Lambton			23/12/89		1									to	
	1	1	1		1	1				1		1		-0.37693261	1

gamma- BHC OR HCH (Lindane)															
Point Edward	3	434	8/4/87- 22/3/12	0.18	0.69	0.02	0.15	-66364	9106327	-22.0	0.000	431	-0.013	-0.01419237 to -0.01250396	-8.88
Port Lambton	2	486	8/4/87- 22/3/12	0.21	0.73	0.02	0.17	-90270	1278574 8	-25.2	0.000	484	-0.016	-0.01693241 to -0.01518689	-9.45
p,p'-DDE (4,4'-DDE)															
Point Edward	201	431	8/4/87- 22/3/12	0.03	0.13	0.00	<0.08	-6054	8623453	-2.1	0.039	230	-0.001	-0.00188681 to -0.00058946	-3.02
Port Lambton	258	487	8/4/87- 22/3/12	0.03	0.17	0.00	<0.08	-6313	1219827 1	-1.8	0.071	229	-0.001	-0.00177905 to -0.00040928	-2.73
Phenanthren	ie			•	•			•	•			•		•	
Point Edward	47	383	8/4/87- 5/3/08	0.92	16.5	<0.1 2	0.68	-3466	6259240	-1.4	0.166	336	-0.033	-0.04286765 to -0.02339622	-4.91
Port Lambton	85	436	24/4/87- 5/3/08	0.75	25.1	0.05	0.48	-5091	9207371	-1.7	0.093	351	-0.034	-0.04287558 to -0.02464661	-7.08
Fluoranthen	e	•	•	•	•		•	•	•		•	•			•
Point Edward	58	385	8/4/87- 5/3/08	0.57	9.75	0.07	0.36	-15692	6340205	-6.2	0.000	327	-0.034	-0.03959549 to -0.02806036	-9.36
Port Lambton	82	437	8/4/87- 5/3/08	0.56	8.55	0.07	0.34	-8359	9238768	-2.7	0.006	355	-0.024	-0.03075705 to -0.01769339	-7.06
Lead total		•	•	•	•		•	•	•		•	•			•
Point Edward	29	376	26/6/00- 30/1/20	0.22	5.77	<0.0 00	0.05	-3024	5925134	-1.2	0.214	347	-0.004	-0.00536427 to -0.00210352	-7.56
Port Lambton	12	358	26/6/00- 30/1/20	0.41	6.83	<0.0 00	0.22	8255	5117587	3.6	0.000	346	0.004	0.00042929 to 0.00937231	2.02
Arsenic total															
Point Edward	0	312	25/3/03- 30/1/20	0.59	3.09	0.31	0.53	-12082	3377086	-6.6	0.000	312	-0.005	-0.00618644 to -0.00330094	-0.88
Port Lambton	0	294	26/3/03- 30/1/20	0.71	4.32	0.27	0.62	-3764	2834036	-2.2	0.025	294	-0.003	-0.00603221 to 0.00000001	-0.52

Benzo(a)pyrene															
Point	352	385	8/4/87-	0.15	0.29	0.00	<0.17	-128	5440628	-0.1	0.957	33	-0.001	-0.00617474	-1.22
Edward			5/3/08											to	
														0.0000001	
Port	384	438	8/4/87-	0.03	0.38	0.01	<0.17	-41	7958129	0.0	0.989	54	0.000	-0.00302427	0.00
Lambton			5/3/08											to	
														0.0000001	
Dieldrin															
Point	11	434	8/4/87-	0.12	0.30	<0.0	0.10	-51739	9089602	-17.2	0.000	423	-0.006	-0.00629433	-5.80
Edward			22/3/12			12								to	
														-0.00526296	
Port	6	483	8/4/87-	0.13	0.37	0.00	0.12	-70023	1252932	-19.8	0.000	477	-0.006	-0.00656580	-5.13
Lambton			22/3/12						9					to	
														-0.00574033	
Mirex										-		-			-
Point	409	434	8/4/87-	0.00	0.06	0.00	<0.05	-1356	8048207	-0.5	0.633	25	-0.001	-0.00128646	-3.33
Edward			22/3/12											to	
														-0.00063342	
Port	462	488	8/4/87-	0.01	0.07	0.00	<0.05	-1199	1139902	-0.4	0.723	26	-0.001	-0.00143100	-3.76
Lambton			22/3/12						4					to	
		1				1			1		1			-0.00074193	