

# Concentrations and Trends of Nutrients, Major Ions, Trace Metals and Organic Contaminants in the St. Clair River

1987-1999

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CONCENTRATIONS AND TRENDS OF NUTRIENTS, MAJOR IONS, TRACE  
METALS AND ORGANIC CONTAMINANTS IN THE ST. CLAIR RIVER

1987-1999

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## **1.0 Introduction**

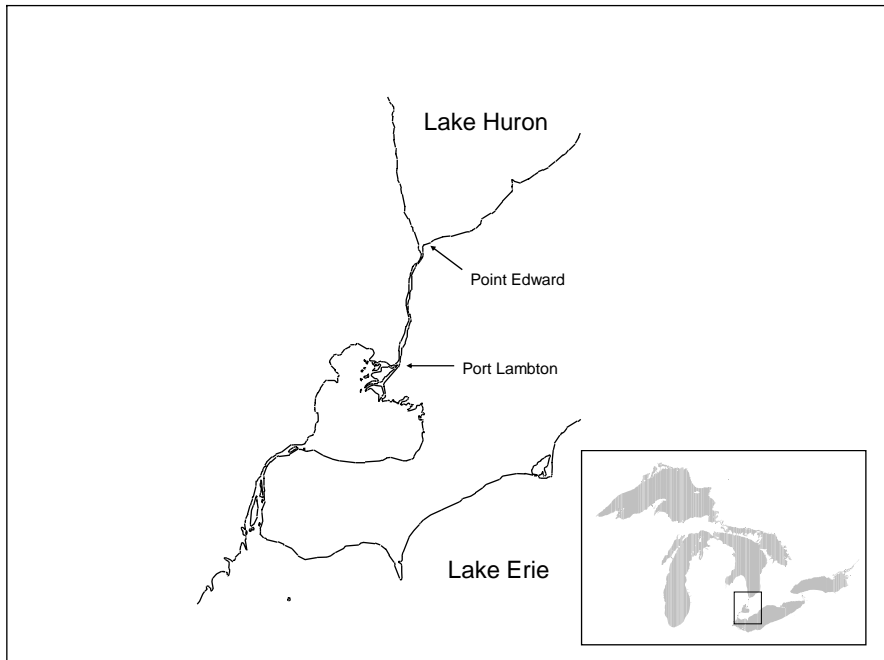
The St. Clair River along with the downstream Lake St. Clair and Detroit River, link the Upper and Lower Great Lakes (i.e., Lakes Superior, Michigan and Huron to Lakes Erie and Ontario). It has one of the heaviest concentrations of chemical industries in Ontario. Petroleum refineries, chemical manufacturers, paper companies, salt producers and thermal electric generating facilities line the Canadian shore of the river from the City of Sarnia to Corunna downstream. The area has been aptly nicknamed “Chemical Valley”. Discharges from these industrial and municipal complexes have resulted in the degradation of river water and sediment quality and aquatic habitat (IJC 1982; IJC 1983; UGLCCS 1988). This state of environmental degradation has resulted in the St. Clair River being designated an “Area of Concern” by the International Joint Commission (IJC 1984). An Area of Concern is an area where “beneficial uses” as identified in Annex 2 to the 1987 Canada/U.S. Great Lakes Water Quality Agreement (Canada 1987) are impaired.

Between 1983 and 1985, Canada and the U.S. conducted a major study to determine the existing environmental conditions and the sources and environmental impact of pollutants in the three Upper Connecting Channels, including the St. Clair River. Appropriate control programs and surveillance activities were recommended (UGLCCS 1988). The major findings for the St. Clair River were that discharges to the Canadian side of the river were the sources of sodium, chloride, metals and organic contaminants to the river. Furthermore, chemicals from these discharges tended to remain close to the shoreline with little cross-river mixing. The long-term monitoring strategy recommended, as a minimum, that monitoring sites be established at the head and mouth of the river.

In 1985, Environment Canada undertook a survey of the St. Clair River to characterize the spatial distribution of persistent organic contaminants with the purpose of identifying strategic sites for monitoring river water quality (Environment Canada 1987). Two permanent monitoring stations were subsequently established in 1987---one at Point Edward and one at Port Lambton, the head and mouth of the river, respectively. Point Edward is located north of Sarnia, on the Lake Huron shore. Port Lambton is located 38 km downstream---just 2 km upstream of Walpole Island where the river branches into several channels and discharges into Lake St. Clair (Figure 1). Biweekly water and suspended sediment samples have been collected at these two sites since April 1987 and analyzed for a variety of chemical parameters including nutrients, major ions, trace metals and organic contaminants. The purpose of this “Upstream/Downstream” monitoring program is to assess the differences in water

quality between the head and mouth of the river and relate these to chemical inputs from the above facilities. The effectiveness of source remediation activities can, thus, be inferred from the trends in water quality at these two stations.

Figure 1. Sampling locations



This monitoring program has been included as an integral component of the St. Clair River Remedial Action Plan (RAP) (OMOEE and MDNR 1995). The program has provided a reliable, long-term database for assessing the changing conditions and trends in river water quality.

This report summarizes the concentrations of nutrients, major ions, trace metals and organic contaminants in centrifuged water and/or suspended sediment for samples collected over the 13-year period 1987/88 to 1999/2000.<sup>1</sup> Changes/trends in these are related to the effectiveness of remedial actions at St. Clair River sources and/or to changes in Lake Huron.

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<sup>1</sup> Samples at each station are collected on a fiscal year basis from April 1 to March 31 each year.



## **2.0 Methodology**

The Point Edward station is located in the Lambton Water Treatment Plant. Three water intake pipes extend out 50 m into the head of the river almost at its confluence with Lake Huron. Water samples are pumped through a 12 mm polyethylene tube attached to the inner wall of one of these pipes and extended far enough into the intake to ensure that the sampled water is not affected by chlorination at the plant. In 1993, a dedicated permanent stainless steel pipe was installed by the Lambton Water Treatment to collect the samples.

The Port Lambton station is located in an abandoned water pumping station. The configuration of the sampling equipment is similar to that at Point Edward, with water being pumped through a 19 mm polyethylene tube from a depth of 7 m about 100 m off shore. The setup at both stations facilitates year-round sampling, even during winter ice-covered periods.


Samples collected at Point Edward essentially represent Lake Huron water. Chemical concentrations at this site establish the baseline water quality conditions for the river. Samples from Port Lambton are indicative of Canadian municipal and industrial inputs to the river. River flow is laterally stratified (Derecki 1985) resulting in contaminants discharged to the river by the chemical industry in Sarnia remaining confined to within 300 m of the Canadian shore, even as far as Port Lambton downstream (Chan et al 1986).

Water was collected at both locations over a 24-hour period using a submersible pump located inside the building and passed through a Westfalia centrifuge at a flow rate of about 6 L/min to separate the suspended sediment and dissolved phases. This resulted in a sample size of about 8600 litres. The centrifuge is about 90-95% efficient in recovering suspended sediments finer than 0.1 $\mu$  (Allan 1986). The suspended sediment was collected from the steel bowls inside the centrifuge and placed in an amber glass jar. The water exiting from the centrifuge (i.e., dissolved phase) was sub-sampled over the 24-hr period to provide a sample size of about 40 litres which was collected into two 20-litre pre-cleaned stainless steel containers. Both sets of samples were sent by courier to the National Laboratory for Environmental Testing (NLET) in Burlington and refrigerated until analysis. Time between collection and analysis generally did not exceed two months.

Dissolved phase samples (centrifuged water) were analyzed for nutrients (phosphorus and nitrogen), major ions, trace metals and persistent organic contaminants. Suspended sediments were analysed only for organic contaminants. Cations (sodium, potassium, magnesium and calcium) were analysed by atomic adsorption from 1987 to 1992. In March 1993, cations and trace metals were analyzed together in acidified samples by ICP-OES (Inductively-Coupled Plasma-Optical Emission Spectrometer). Subsequent

analysis of the data showed that the ICP-OES method generally yields lower cations data in acidified samples, particularly for sodium. Cations data (sodium, potassium, magnesium and calcium) from 1993 to 1997 were thus flagged as suspect and not reported here. In 1998, cations analyses were done separately from metal analyses in un-acidified samples. Nitrate concentrations were determined by ion chromatography until 1993, and then switched to colorimetric methods using a Technicon auto-analyzer. Chloride, sulphate and reactive silicate were analyzed by ion chromatography.

Organic contaminant samples were extracted in the Goulden Large Sample Extractor (GLSE; Goulden and Anthony 1985) with dichloromethane, and the extracts analysed by gas chromatography/mass spectrometry (GC/MSD) and gas chromatography/electron capture detection (GC/ECD) after fractionation and cleanup. Extracts from 1987-1995 were analysed according to methods documented in Detailed Analytical Methods (Environment Canada 1997). From 1996 on, the extracts were analysed according to the Niagara River Protocol (Environment Canada 1997). PCBs are reported here for only the suspended sediment samples.



### 3.0 Data and Statistical Analysis

Table 1 shows the number of water and suspended sediment samples collected at Point Edward and Port Lambton over the period April 1987 to March 2000. Annual statistics are computed from April to March. The number of samples at each station varied due to several factors including changes in plant operation, maintenance, equipment malfunction, and logistics. In 1989, sampling at Point Edward was interrupted to retro-fit the chlorinating unit to combat zebra mussels (*Dreissena polymorpha*). Due to the maintenance shutdown only three samples were taken at Point Edward in 1989-1990, these three samples were taken in April and May. The mean values for this sampling year would therefore show a bias for analytes that show any seasonal trends. The limited number of samples for this station/year results in a mean value of lower confidence than the rest of the data set.

Table 1. Number of samples collected at the St. Clair River

YEAR	WATER		SUSPENDED SEDIMENT	
	Point Edward	Port Lambton	Point Edward	Port Lambton
1987-1988	12	18	9	14
1988-1989	21	25	21	25
1989-1990	3	24	3	24
1990-1991	14	16	15	20
1991-1992	21	23	21	23
1992-1993	15	26	14	24
1993-1994	8	22	7	21
1994-1995	11	16	11	16
1995-1996	10	19	11	16
1996-1997	24	24	24	24
1997-1998	21	22	22	22
1998-1999	23	22	21	20
1999-2000	20	20	20	20

Annual arithmetic means and standard deviations were calculated for the inorganic water quality parameters (i.e., pH, conductance, major ions, nutrients and metals). With the exception of a few metals, these parameters generally were present at concentrations well above their respective analytical detection limits. Means were plotted and regression curves determined for trend analysis. All summarized data is presented in the appendices.

The paired student T test using a 95% confidence level was used to determine any differences between the data sets from the two sites. All "non detects" were replaced with the detection limit for statistical calculations. Changes and rates of

change in concentrations were determined by fitting linear regression lines to the annual mean data.

The maximum likelihood estimate method (MLE; El-Shaarawi 1989) was used to calculate annual means and their 95% confidence intervals for organic contaminants. Many organic contaminants were reported as “less than detection” or at “trace” concentrations. The MLE provides the best way to handle “censored” data (i.e., less than detection). Estimate values are reported in place of annual means for all years where at least three values above detection (including trace) are reported. Where these requirements are not met “ND” is replaces the annual estimate. For some years the absence of collected samples (eg. not enough sediment in centrifuge bowls) may also influence the number of samples above detection. Trends were determined by method of Least Squares. All data have been stored on the Environment Canada ENVIRODAT database.

## 4.0 Results and Discussion

Upstream/downstream differences as well as the changes/trends at each station are both important when attempting to determine the impact of sources and source remediation on chemical concentrations in the river. These are discussed below for conventional chemical parameters, metals and organic contaminants.

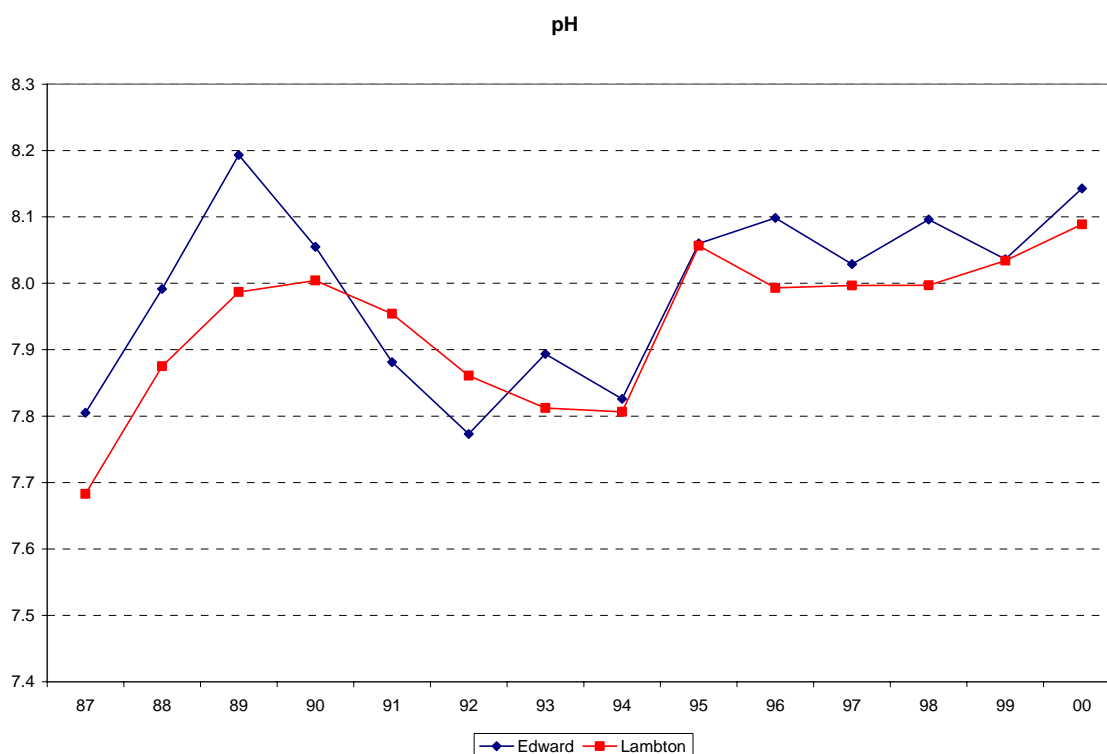
### 4.1 Conventional Chemical Parameters

Annual means and standard deviations for pH, conductance, major ions and nutrients over the thirteen-year period 1987 to 1999 are summarized for both Point Edward and Port Lambton in appendix 2. Figures 2-9 show the annual means.

#### 4.1.1 pH and Conductance

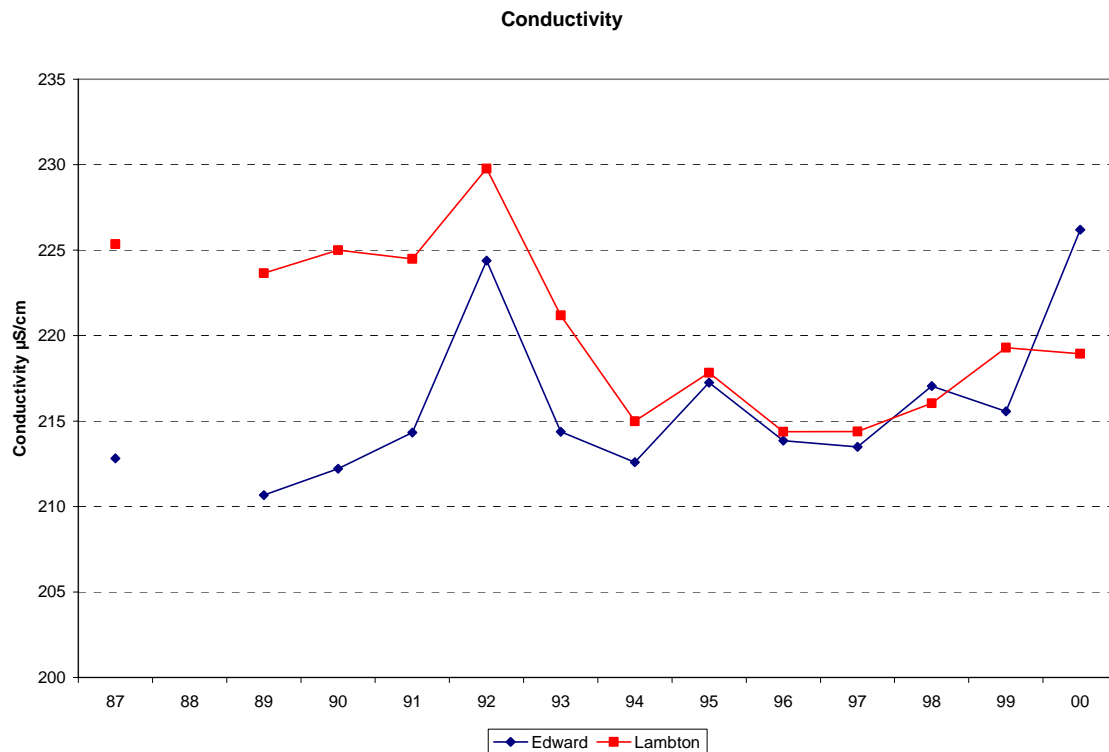
While the pH values at Point Edward and Port Lambton were significantly different ( $p < 0.05$ ) no trend was evident at either station. Values remained within a range of 7.7 to 8.2 pH units (Figure 2).

Figure 2. pH at the St. Clair River 1987-1999



In contrast, conductivity values at Port Lambton were significantly higher than at Point Edward up to 1994 ( $p < 0.05$ ). The mean difference ranged between 10-15 uSie. From 1992, the differences narrowed, and by 1994, there was no longer any significant difference in concentrations between the two stations (Figure 3). The decreases in conductivity at Port Lambton suggest a decrease in major ions inputs along the river. However, it is noteworthy that conductivity at Point Edward showed a gradual increase over the same time period.

Figure 3. Conductivity (uSie) in the St. Clair River 1987-1999.



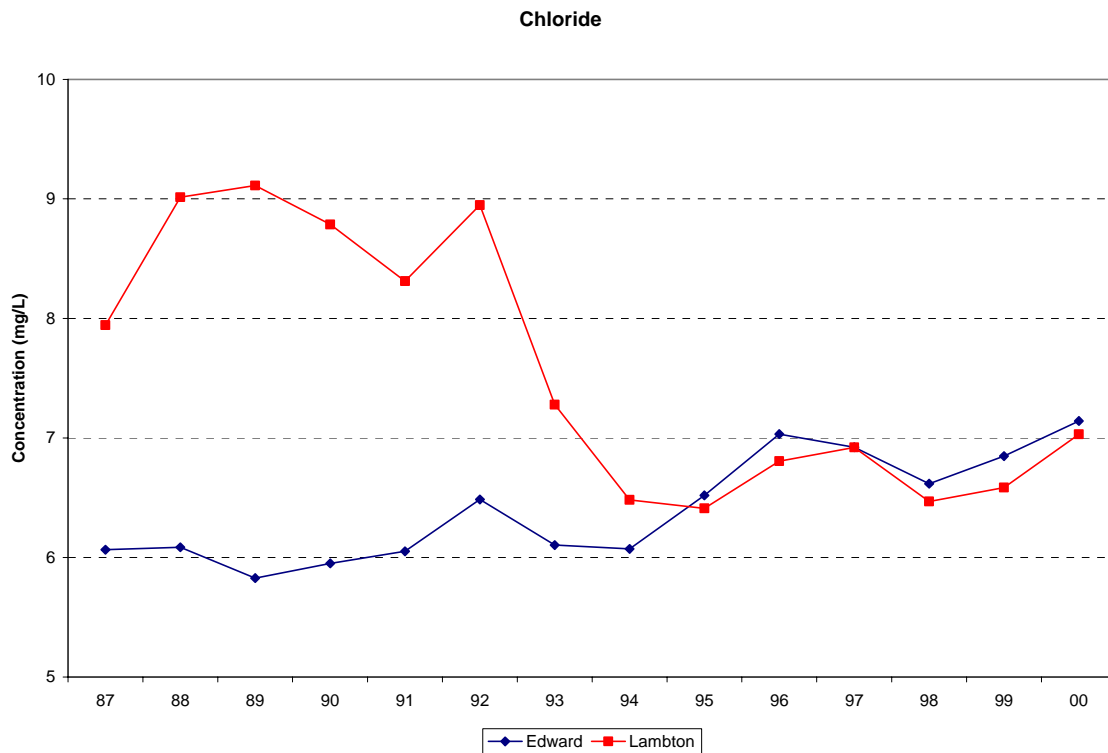
#### 4.1.2 Major Ions

Prior to 1994, mean annual chloride concentrations at Port Lambton were significantly higher than at Point Edward by about 40-50% ( $p < 0.05$ ) (Figure 4). In 1993, the mean concentrations of chloride at Port Lambton showed a 50 % decrease, almost to the same concentration as the upstream station. This decrease in chloride concentration coincides with the corresponding drop in conductivity in Port Lambton. The long term time trend of chloride at Point Edward is on a gradual rise.

Similarly, the mean concentrations of sodium in the late 1980s and early 1990s were significantly higher by about 34% at Port Lambton than at Point Edward

( $p < 0.05$ ). Concentration differences between the two stations for both ions varied between 2 and 3 mg/L. 1998-1999 sodium data using ICP method showed concentrations at Port Lambton and Point Edward were no longer significantly different ( $p > 0.05$ ; Figure 5). The reductions in both sodium and chloride concentrations at Port Lambton suggest better control of the sources of these two chemicals to the river.

Figure 4. Chloride Concentration (mg/L) in the St. Clair River 1987-1999



The concurrent decreases in conductivity and chloride concentration at Port Lambton confirmed the significant decline in chloride concentration in 1993 (Figure 6).

While the changes in sodium and chloride concentrations at Port Lambton are clearly attributable to the effectiveness St. Clair source remediation in reducing their loads to the river, the changes in the concentrations of the other major ions, at both Point Edward and Port Lambton, are probably more related to the changes in the ionic composition of Lake Huron water.

Figure 5. Sodium Concentration (mg/L) in the St. Clair River 1987-1999

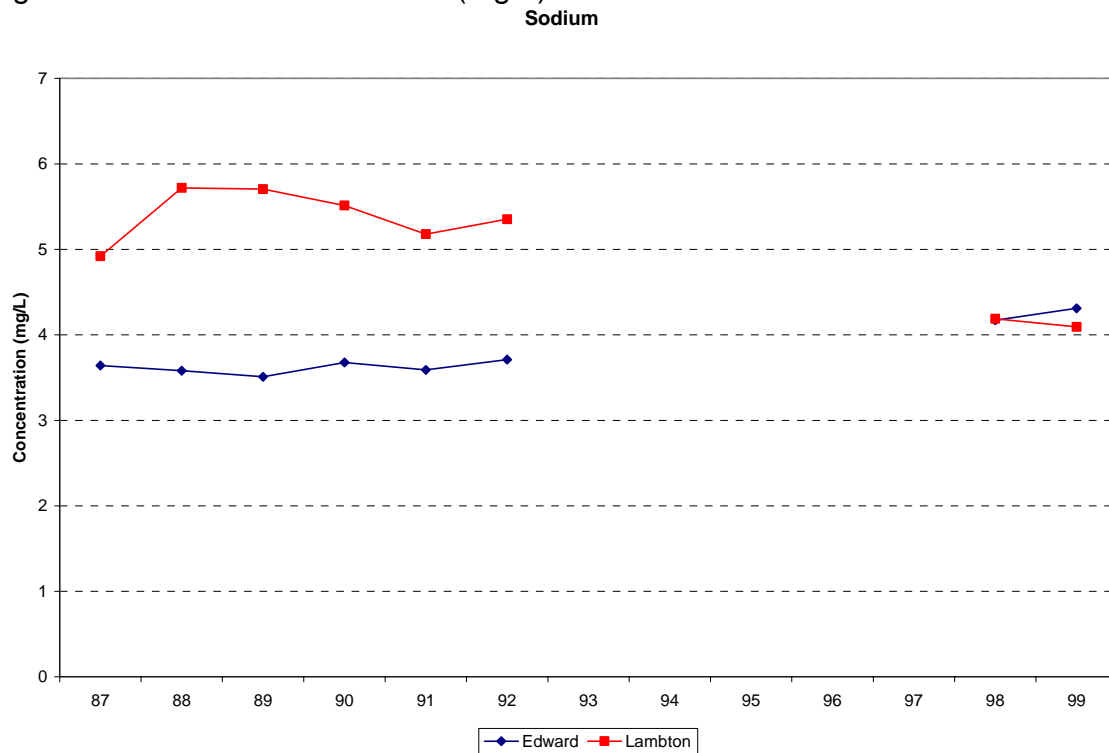


Figure 6. Chloride Concentration and Conductivity at Port Lambton 1987-1999

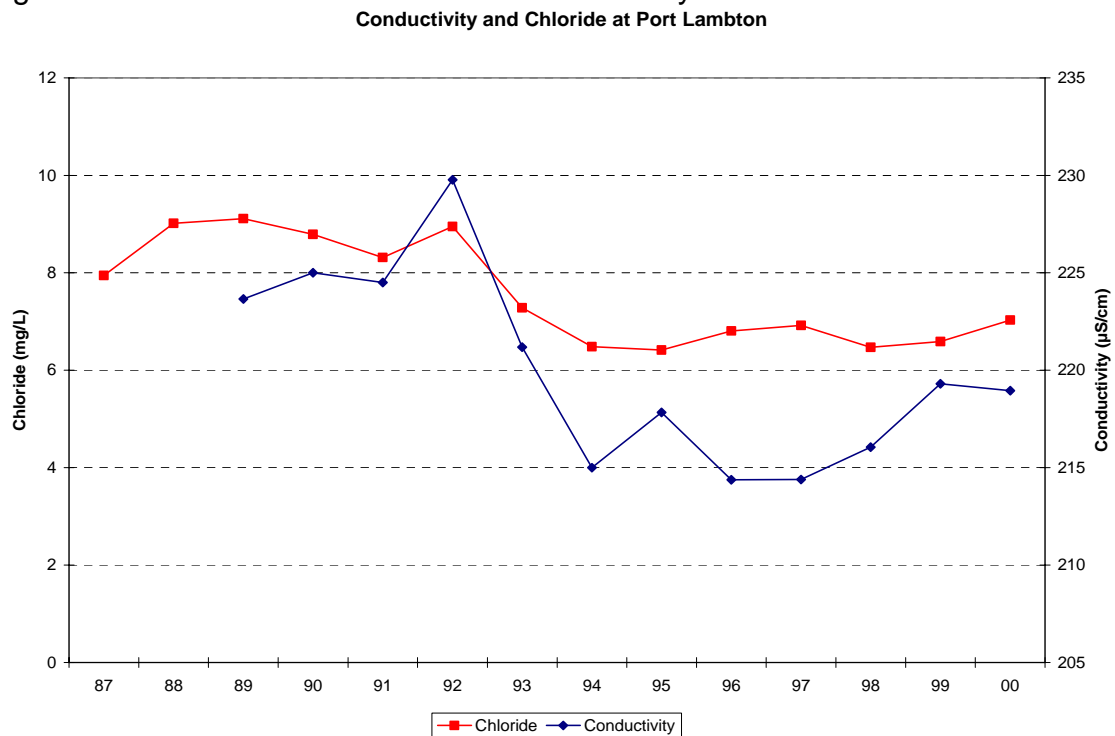
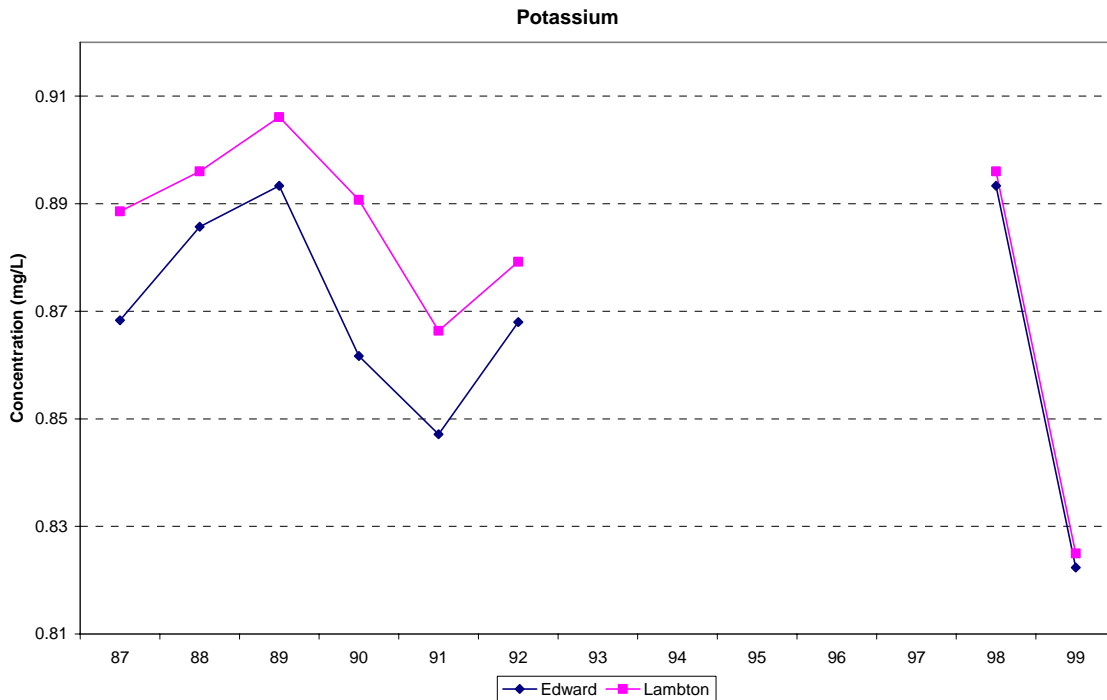




Figure 7. Potassium Concentration in the St. Clair River 1987-1999



Of the rest of the major ions; calcium, potassium, and sulphate, Figure 7, 8, 9 had slightly higher values ( $P < 0.05$ ) downstream at Port Lambton while magnesium, figure 10, had no significant differences between stations ( $p > 0.05$ ). Even though the long term time trend interpretation of cations was compromised by a five year data gap both magnesium and potassium concentrations in 1998 and 1999 were slightly higher then the late eighties whereas calcium showed no clear trend. The gradual increase in cations concentration in Point Edward (Lake Huron) is probably a valid conclusion and it is supported by the increases in conductivity at Point Edward.

Figure 8. Calcium Concentration in the St. Clair River 1987-1999

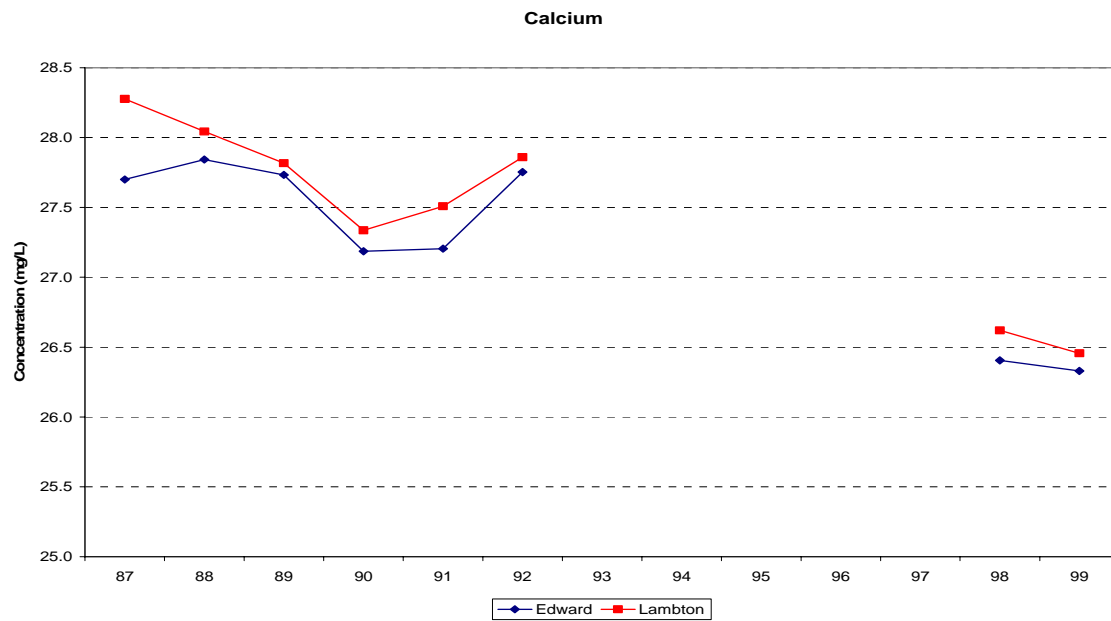


Figure 9. Sulphate Concentration in the St. Clair River 1987-1999

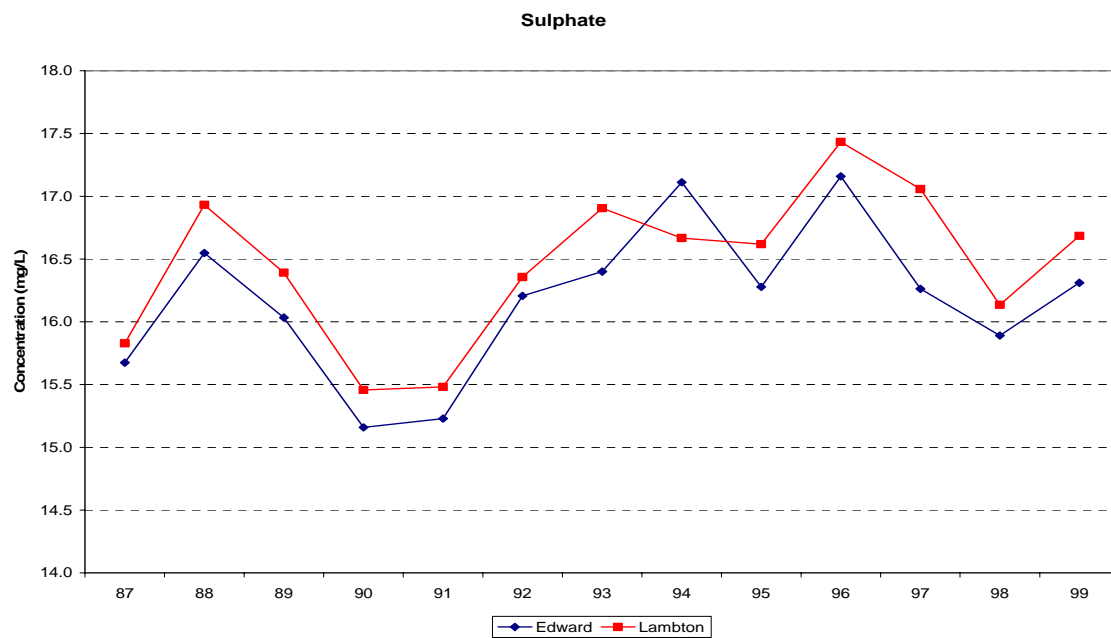
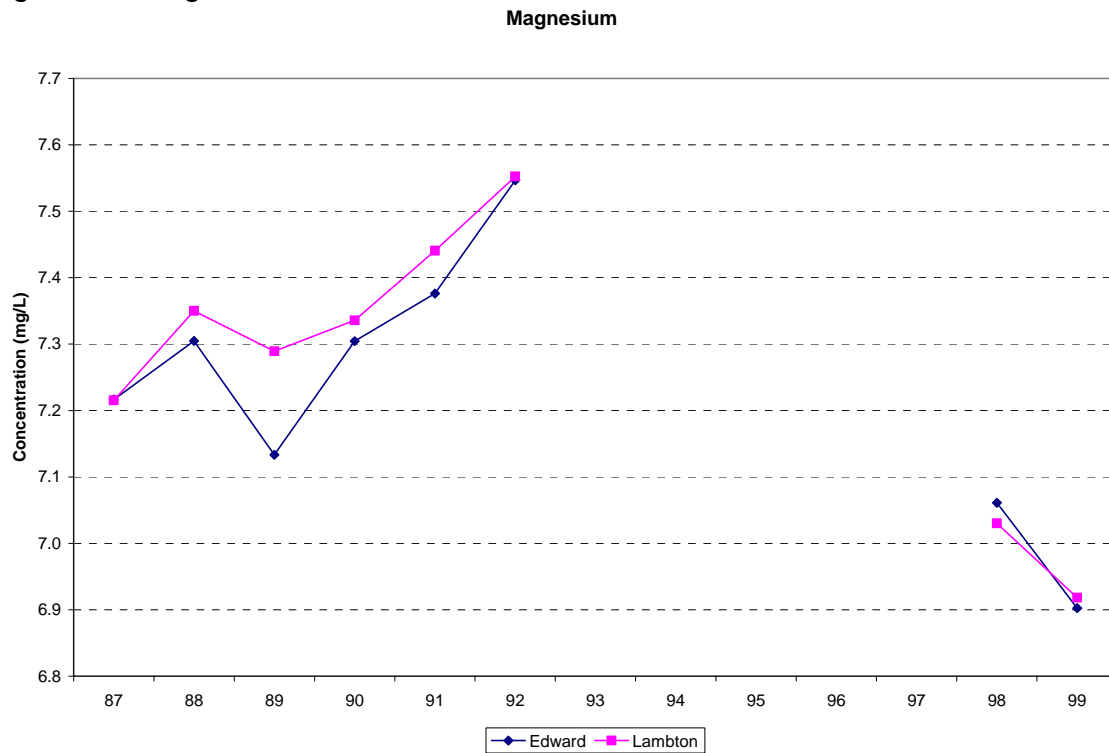


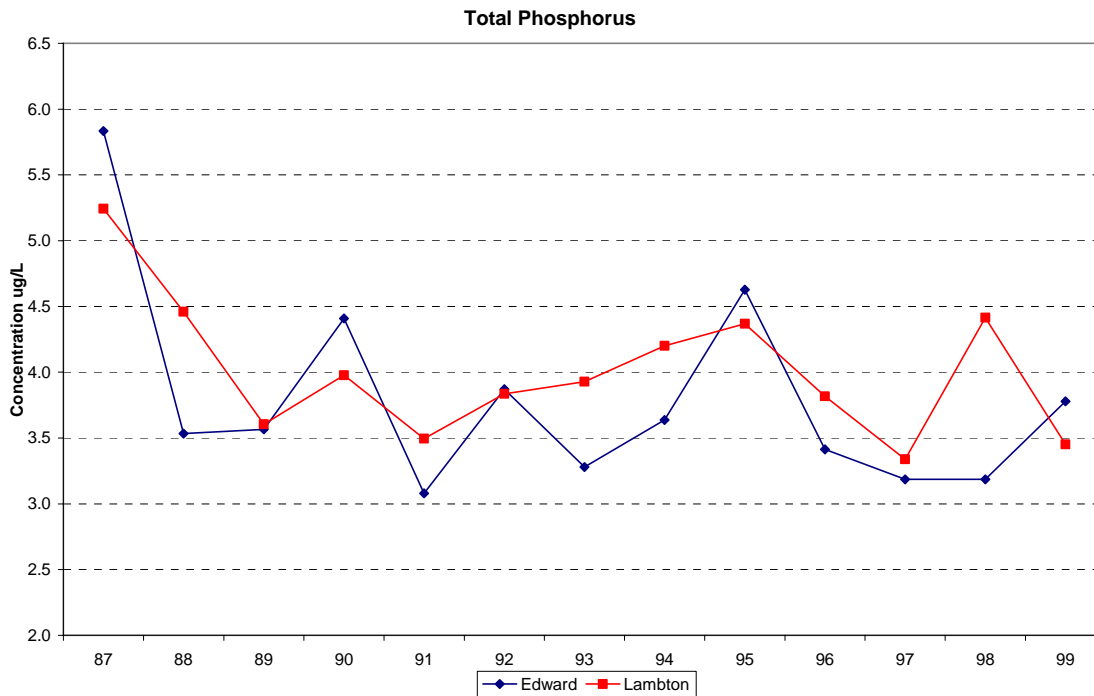
Figure 10. Magnesium Concentration in the St. Clair River 1987-1999



#### 4.1.3 Nutrients (Phosphorus, Nitrogen, Reactive Silicate)

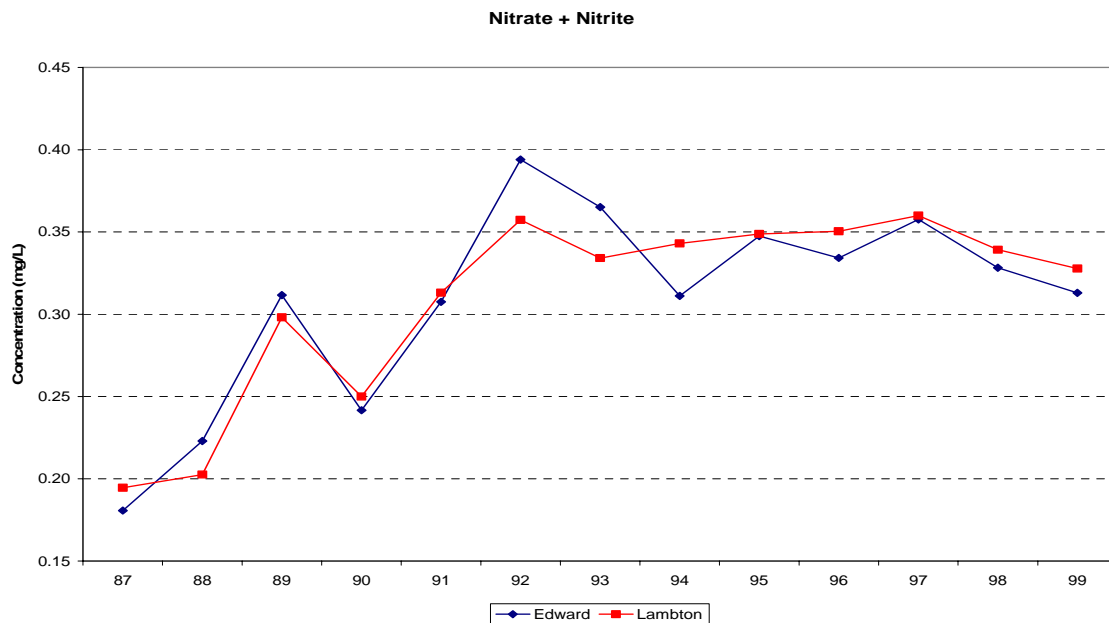
The annual mean phosphorus concentrations exhibited no significant difference between Point Edward and Port Lambton ( $p>0.05$ ). Concentrations at both stations fluctuated between 3 and 7 ug/L. There was no seasonal pattern or significant trend over the 1987 to 1999 period (Figure 11).

Figure 11. Total phosphorus concentration (ug/L) in the St. Clair River 1987-1999.



In contrast, nitrate + nitrite nitrogen concentrations exhibited an increasing trend at Point Edward and Port Lambton (Figure 12).

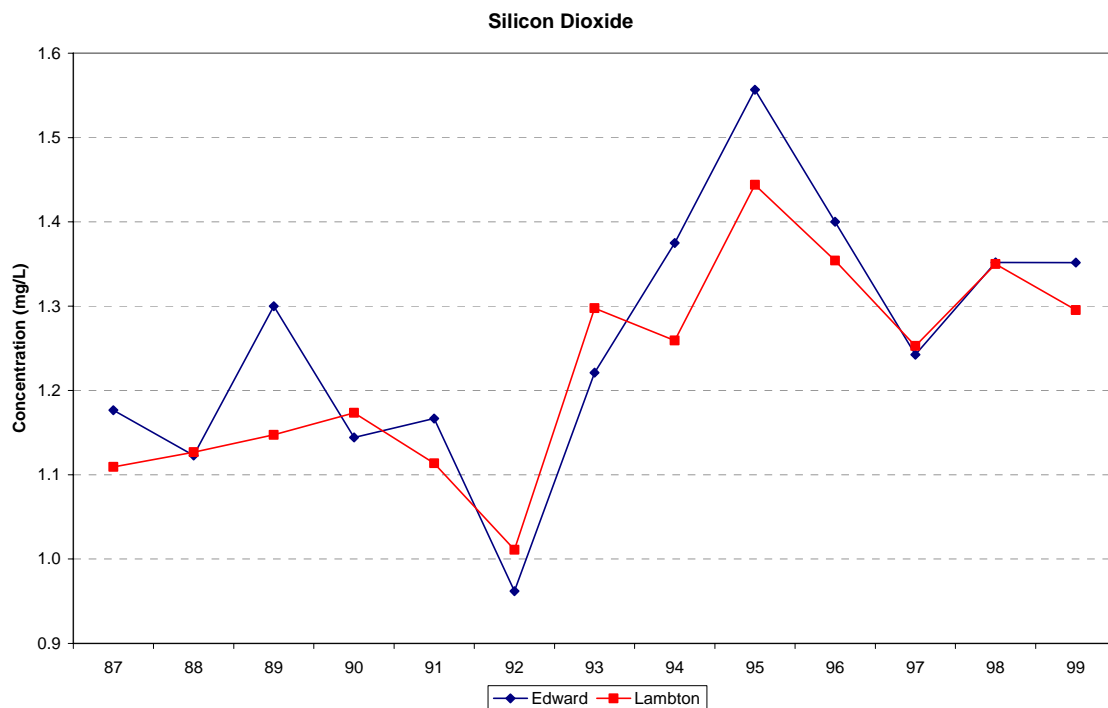
Figure 12. Nitrate + Nitrite concentration (mg/L) in the St. Clair River 1987-1999



Both these results are consistent with those for the open waters of Lake Huron (depth >50m); no significant trend for total phosphorus was noted over the period 1970-2000, while nitrate + nitrite nitrogen increased at a rate of 3.9  $\mu\text{g/L/yr}$  ( $r^2=0.84$ ). The increasing nitrate + nitrite nitrogen trends are also consistent with observations made elsewhere in the Great Lakes (Williams 1992; Neilson et al 1995). Major sources of nitrogen to the Great Lakes include agricultural runoff, municipal sewage treatment plants and atmospheric deposition. For Lake Huron, the atmosphere and tributaries are the major sources of nitrogen contributing 37% and 35% of the total load, respectively (ULR 1977).

Summer concentrations of reactive silica were significantly lower than winter concentrations ( $p<0.05$ ). This is a familiar seasonal pattern in lakes related to the growth cycle of diatoms. Over the 1987-1999 periods, reactive silica exhibited an increasing trend since 1992 (Figure 13).

Figure 13. Reactive Silicate (silicon dioxide) concentration (mg/L) in the St. Clair River 1987-1999



## 4.2 Metals

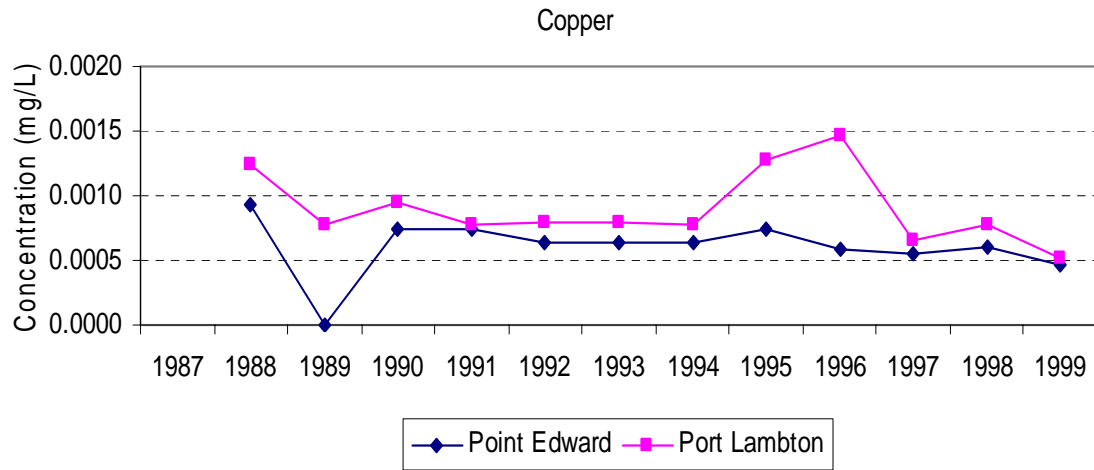
The annual mean concentrations and standard deviations of the sixteen metals measured in the St. Clair River Upstream/Downstream Program are included in the appendices. The concentrations of the alkali earth metals (eg., barium, lithium, strontium) were among the highest, while the concentrations of cadmium, cobalt, lead and vanadium were at or below their detection limits. The concentrations of the industrial metals, aluminium, copper, iron, manganese, nickel and zinc were generally higher at Port Lambton.

While the UGLCCS (1988) did not mention metals as a specific concern in the water it did state that loadings of metals to the St. Clair River continued to compromise local environmental quality. The study also identified point sources which contribute loadings of mercury, lead, chromium, copper and/or nickel to the river. Total loadings to the river would include both dissolved and non dissolved fractions of water, only the dissolved portion is discussed here. While mercury was not measured in the time period of this report the dissolved fractions for lead, chromium, copper and nickel were all measured and interpreted. For chromium, copper and nickel there were significant differences ( $p < 0.05$ ) between the two stations with the Port Lambton generally being slightly higher in concentration. There were no differences found for lead. The temporal trends for copper concentrations (Figure 14) show greater variability at Point Edward than at Port Lambton with concentrations at Port Lambton occasionally exceeding the 5 ug/L criteria. There were no temporal trends in the data for any of these metals suggesting that there have been few changes in the loadings of these metals in the dissolved phase to the river.

For the other metals measured during this time period there were differences in the data sets ( $p < 0.05$ ) between the two stations for barium, and manganese. While Port Lambton is generally higher in concentration than Port Edward, suggesting inputs along the river, differences are often less than the standard deviation for the yearly means. There are no meaningful trends for inputs of these metals. For all of the other metals measured, there were no significant differences between data sets. The overall trends for the metal data are the same as the trends seen for Lake Huron water.

These measurements are comparable to results obtained by Rossmann (1988) and L'Italien (2002) for Lake Huron.

Figure 14. Dissolved Copper concentration (mg/L) in the St. Clair River 1987-1999



### 4.3 Organic Contaminants

Among the 38 organic contaminants (9 chlorobenzenes, 17 organochlorine pesticides, 10 PAHs and 2 industrial by-products), only seventeen were measured in significant concentrations and frequency (> 50 %). Their concentrations and confidence intervals are listed in Table 4a-4c and Table 5a-5c. The detection limits are shown in bracket.

#### 4.3.1 Chlorobenzenes (CBs)

The lower chlorinated CBs are used mainly as solvents; intermediates for dyes, herbicides and insecticides; dye carriers; mothballs; room deodorants and urinal deodorant cake (Kirk Othmer 1979). The more highly chlorinated CBs (tetra, penta and hexa) have very limited industrial or commercial applications. They are mainly produced as unwanted by-products in the manufacture of the lower chlorinated isomers. Also, hexachlorobenzene (HCB) is produced in significant quantities in the production of chlorinated solvents such as perchlorethylene, trichlorethylene, carbon tetrachloride, and in the production of chlorine (Mumma and Lawless 1975).

The CBs most frequently detected in the water (dissolved and/or suspended sediment) in the St. Clair River included 1,4-dichlorobenzene (1,4-DCB), 1,2,4- and 1,3,5- trichlorobenzene (124 and 135TCB) and pentachlorobenzene hexachlorobenzene (HCB). With the exception of 1,4-DCB, their concentrations downstream at Port Lambton were higher than at Point Edward indicating inputs along the river.

1,4-DCB had the highest frequency of detection. Concentrations at Port Lambton showed ambient levels to be less than 4 ng/L (Fig. 15). 1,3,5-trichlorobenzene was rarely detected (4%) in the water at the upstream station but was found in over 79% of the samples at concentrations just slightly above the detection limit of 0.03 ng/L. In suspended sediments, 1,3,5 -trichlorobenzene was occasionally detected at the upstream station, but found to be present in 72 % of the samples at the downstream station. A time plot of 1,3,5-trichlorobenzene in suspended sediments at the downstream station showed a gradual decline in concentration ( Fig. 16) from >9 ng/g to < 4 ng/g.



Figure 15. Concentration of 1,4-dichlorobenzene (ng/L) in the St. Clair River 1987-1999

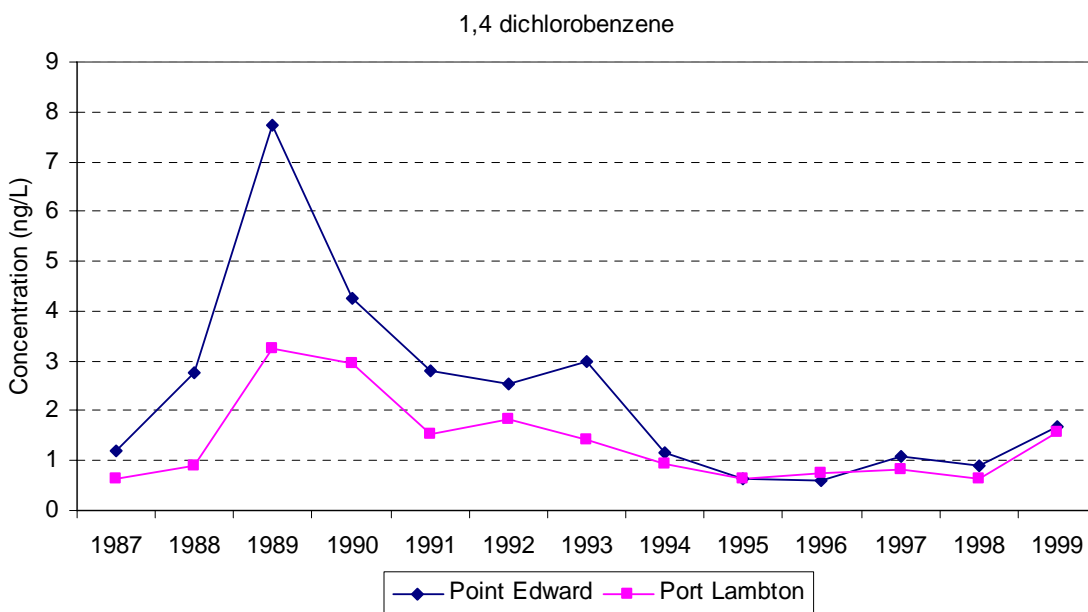
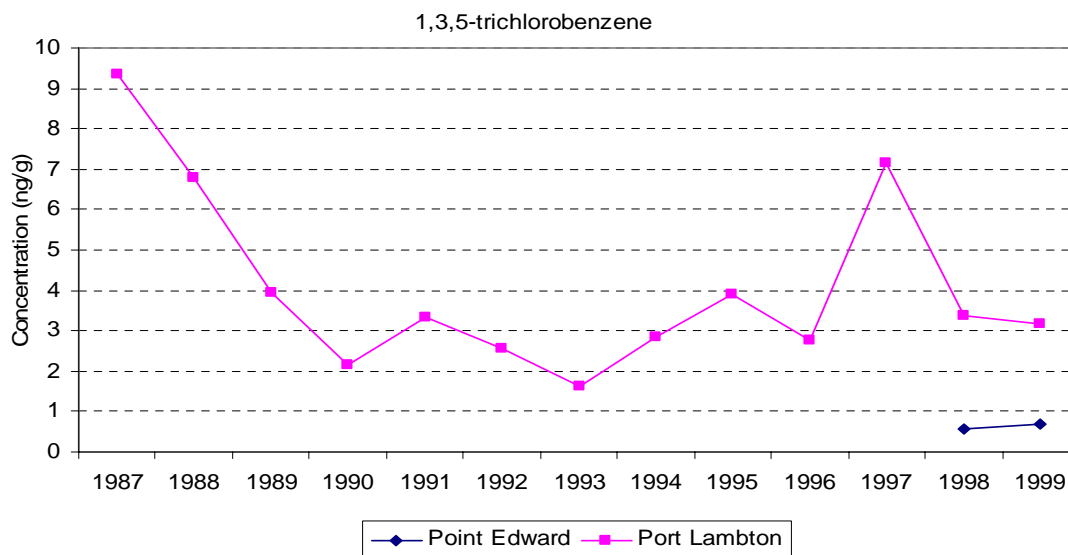


Figure 16. Concentration of 1,3,5-trichlorobenzene in suspended sediments (ng/g) in the St. Clair River 1987-1999



Pentachlorobenzene was found in trace amounts in the water phase at both locations, but in suspended sediments, pentachlorobenzene was found predominantly at the downstream station (>80 %). A plot of pentachlorobenzene (Fig. 17) in suspended sediments at the downstream location showed a decline, similar to the 1,3,5 tri-chlorobenzene, from >10 ng/g to < 2 ng/g.

Figure 17. Concentration of Pentachlorobenzene in suspended sediments (ng/g) in the St. Clair River 1987-1999

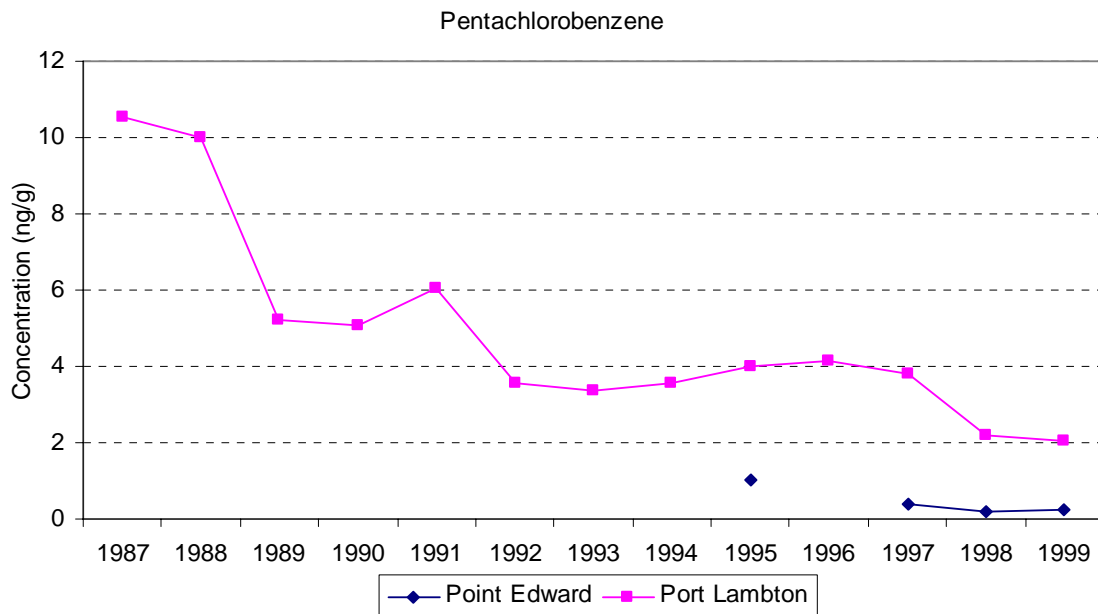
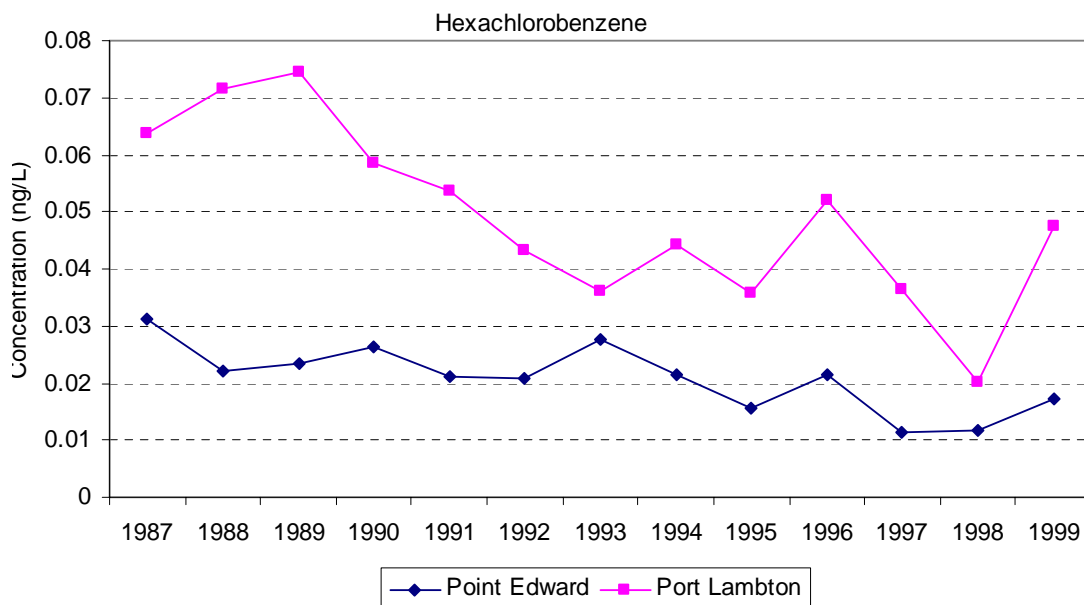


Figure 18. Concentration of Hexachlorobenzene (ng/L) in the St. Clair River 1987-1999

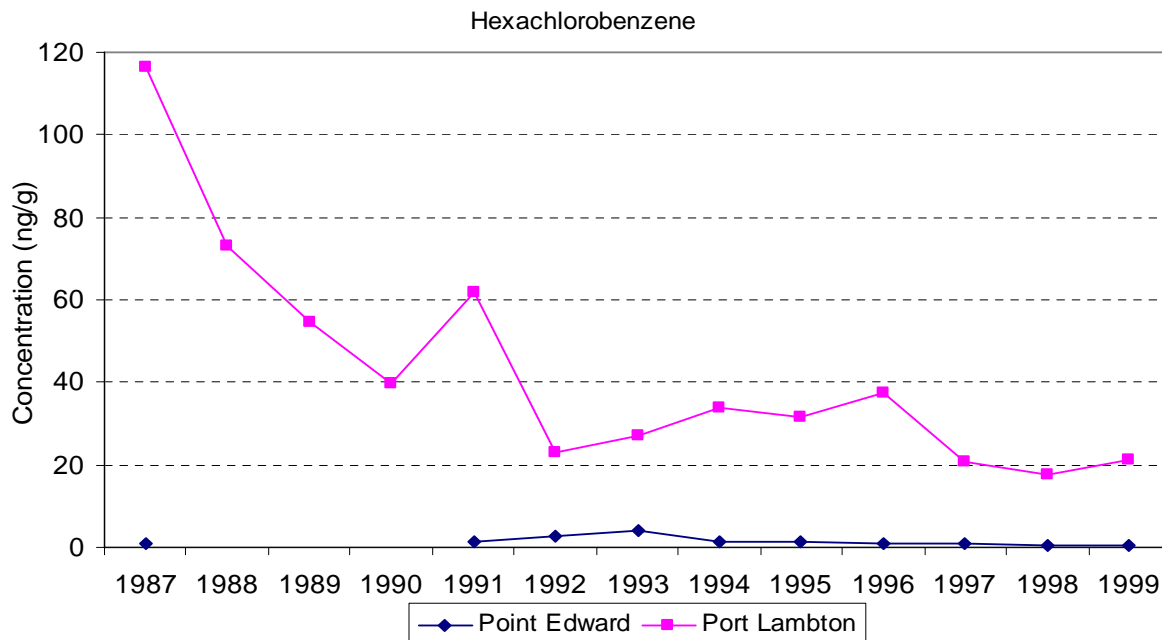


Hexachlorobenzene is readily found in Great Lakes waters (Oliver and Nicol, 1982). Background concentrations of hexachlorobenzene at Point Edward (Lake Huron) remained stable at trace amounts generally around 0.02 ng/L (Fig. 18). Concentrations of hexachlorobenzene downstream were much higher than the

background concentrations upstream and there was a gradual decline over the years from >0.06 ng/L to <0.05 ng/L.

In suspended sediments, trace amounts of hexachlorobenzene were found in the upstream station but the downstream station had concentrations of 20-40 ng/g of hexachlorobenzene. A time plot of hexachlorobenzene in the suspended sediments at the downstream station also showed a substantial (80%) decline from earlier concentrations (Fig. 19) from >110 ng/g to <30 ng/g.

Figure 19. Concentration of Hexachlorobenzene in suspended sediments (ng/g) in the St. Clair River 1987-1999



#### 4.3.2 Organochlorine Pesticides (OCs)

Unlike chlorobenzenes, organochlorine pesticides were found mostly to be present in the water phase and less associated with suspended sediments (Table 4a, 4b). HCHs, dieldrin and heptachlor epoxide were the most frequently found pesticides in the St. Clair River. There were no changes in organochlorine pesticides concentrations in the River.

HCHs are the most widely globally used pesticides. a-HCH and g-HCH were found in most media in the Great Lakes. They were found more readily in the water than in suspended sediments. Both HCHs showed significant decline in the St. Clair River ( Fig 20, 21) a-HCH concentration decreased from 2- 4 ng/L in the late eighties to less than 1 ng/L in the mid nineties. The decline of HCH could be

attributed to the decline in global usage of HCH (Li, 1999). Similarly, g-HCH concentration declined from 0.40 ng/L to 0.25 ng/L in the same period. Time plots of both HCHs showed definite seasonal pattern with higher concentrations towards summer and lower in winter. A plot of a-HCH/g-HCH ratio (Fig. 22) showed a declining ratio over the years. The ratio in the winter months was consistently higher than the summer. If this seasonal change is related to changing inputs, this would imply a very fast response in the Lake which is highly improbable in large bodies of water like the Great Lakes. A more likely explanation for this seasonal behaviour is related to air exchanges between lake water and the atmosphere. Ridel (1996) made simultaneous air and water measurements of HCH in Lake Ontario, and he estimated that the semi-annual (May-October) deposition of g-HCH of 178 kg/6 months, but volatilisation of 90 kg/6 months of a-HCH. The deposition of g-HCH in the summer months coupled with the loss of a-HCH through volatilization would give a lower ratio in the summer months and a higher ratio in the winter months. The declining ratio also suggests that use of lindane, the commercial name for g-HCH, is on the rise.

Figure 20. Concentration of a-HCH (ng/L) in the St. Clair River 1987-1999

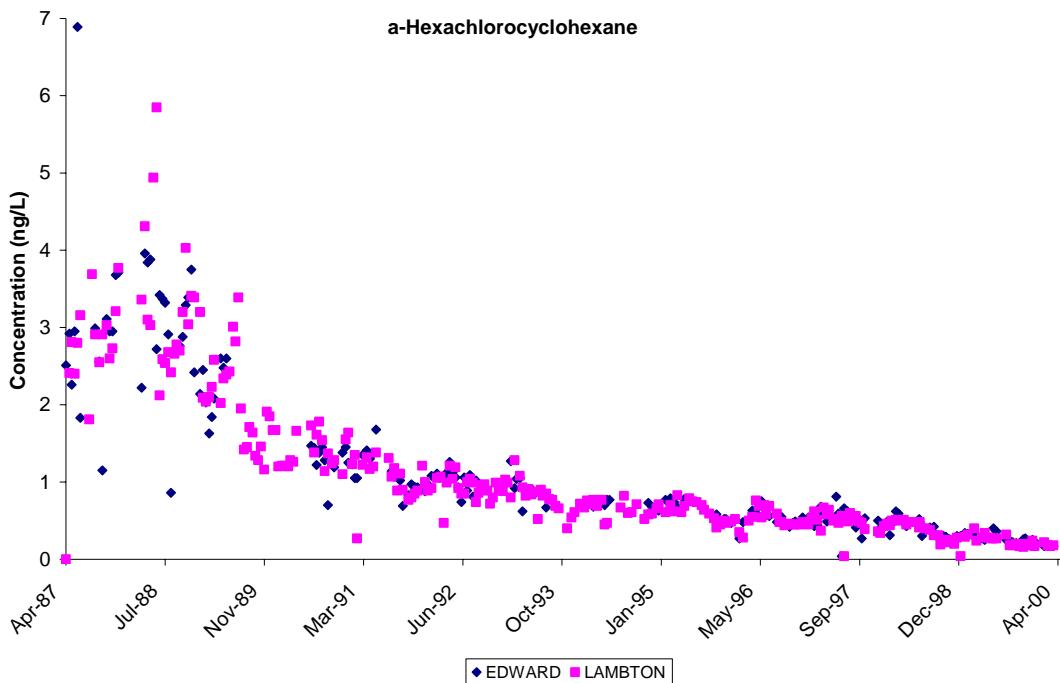


Figure 21. Concentration of g-HCH (ng/L) in the St. Clair River 1987-1999

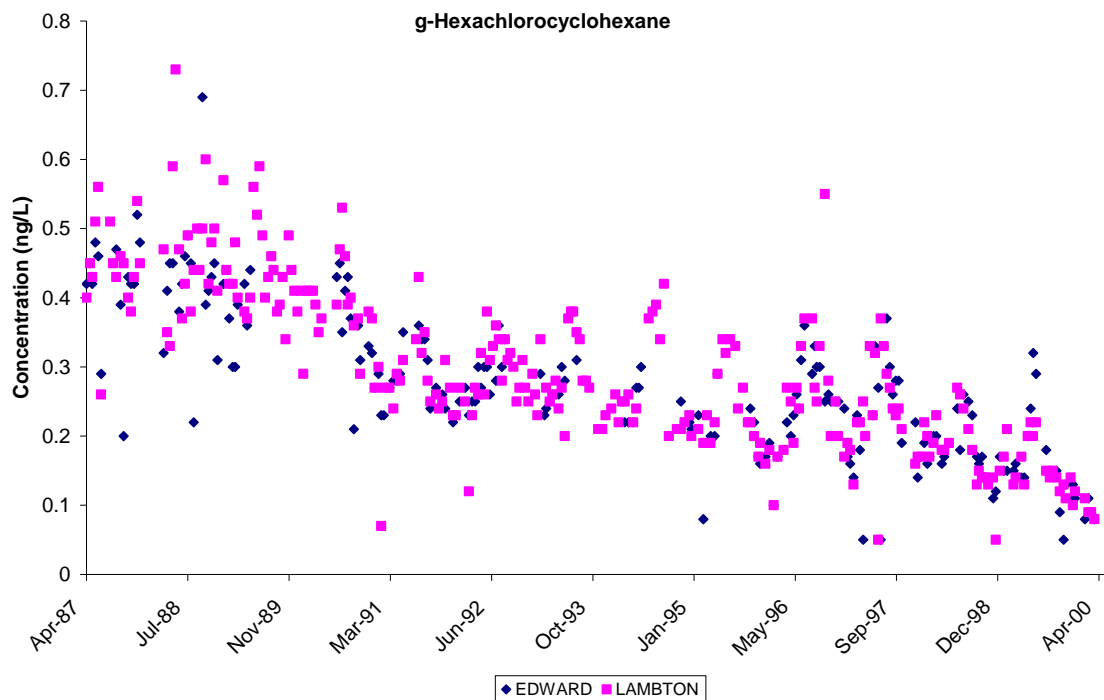


Figure 22. Ratio of a-HCH/g-HCH in the St. Clair River 1987-1999

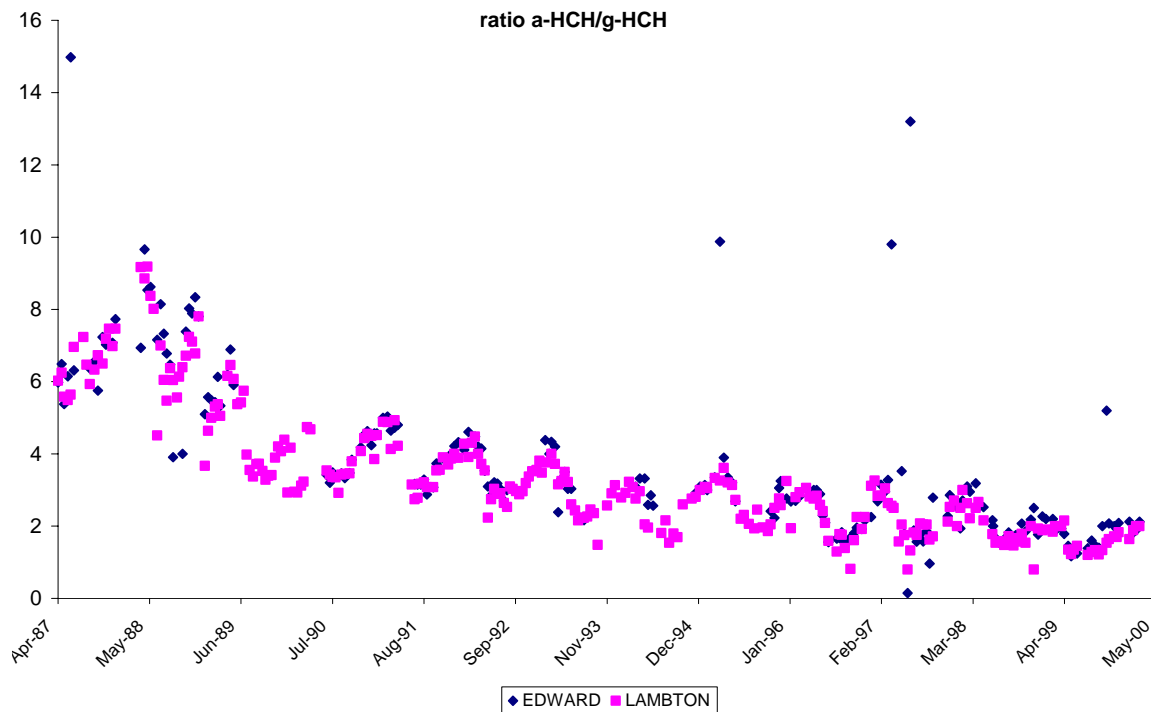
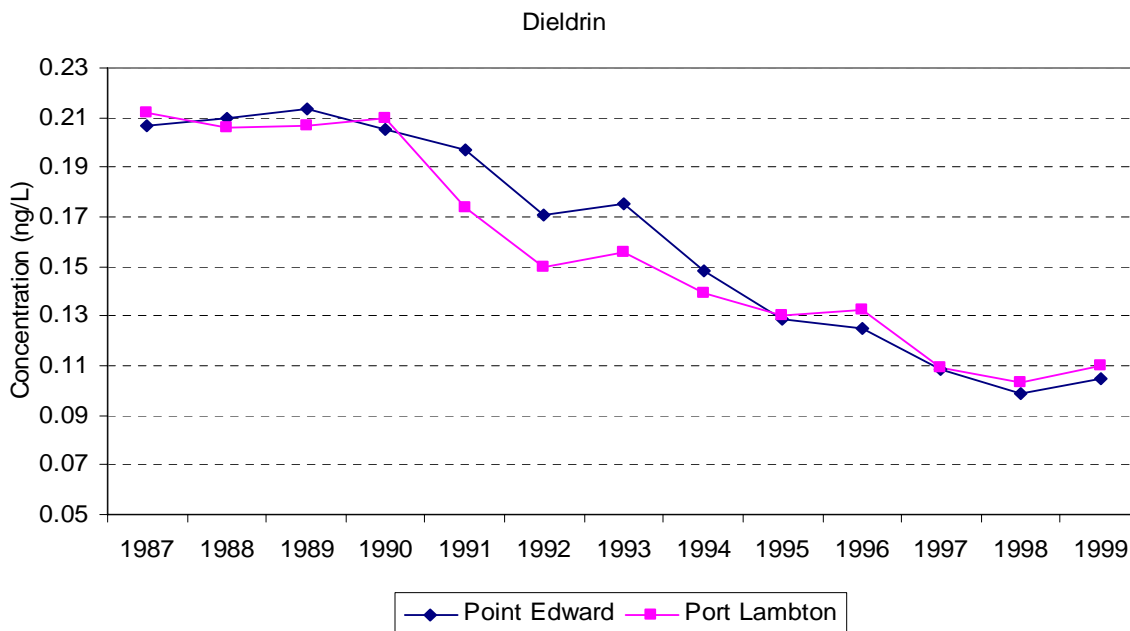


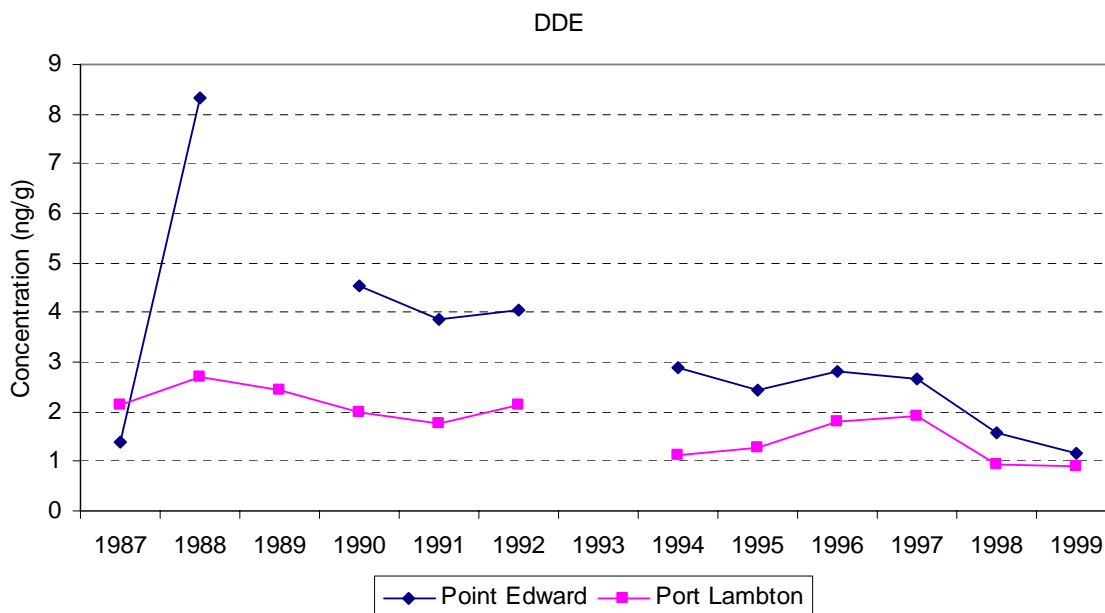
Figure 23. Concentration of dieldrin (ng/L) in the St. Clair River 1987-1999



Dieldrin is another organochlorine pesticide which is widely distributed in the Great Lakes. They were frequently found both in water and suspended sediments. Time plot of dieldrin in water showed that there were little or no upstream/downstream differences and that like HCHs, their concentrations on the decline from 0.20 ng/L to 0.12 ng/L (Fig. 23).

At both sites, DDE concentrations in water were less than the detection limits, but it was one of the pesticides most frequently detected in suspended sediments. Earlier data showed that DDE concentrations in suspended sediments were about 6 ng/g, 2 ng/g higher than the downstream station. However, by the late nineties, DDE concentrations at both stations were lowered to less than 2 ng/g (Fig 24). The lowering of DDE concentration at the downstream could be a result of increase sediment in the river causing a dilution.

Figure 24. Concentration of DDE in suspended sediments (ng/g) in the St. Clair River 1987-1999



#### 4.3.3 Industrial By-product Chemicals

Hexachlorobutadiene (HCBd) and octachlorostyrene (OCS) are two chemicals which have been identified to have active discharges along the St. Clair River (King 1986).

Hexachlorobutadiene is another compound with limited or no industrial or commercial usage. Its major source is as a by-product of the production of perchlorethylene, trichlorethylene and carbon tetrachloride, with lesser amounts from the manufacture of chlorine (Mumma and Lawless 1975).

Octachlorostyrene is a compound with no known uses which is probably 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", resulted from the chlorination of the tar or pitch used to bind graphite electrodes; its improper disposal led to the introduction of chlorinated aromatic compounds into the environment.

Results showed that these two compounds were found almost exclusively at the downstream station and they were mostly associated with particulate matter. Trace concentration of HCBd (<0.04 ng/L) were found in the dissolved phase at the upstream station, while detectable quantities were measured downstream. Water concentrations at Port Lambton declined from >1 ng/L to 0.1 ng/L over the period of record. Similar declines were seen in the suspended sediment phase (Fig 25).

Figure 25. Concentration of hexachlorobutadiene in suspended sediments (ng/g) and water (dissolved phase) in the St. Clair River 1987-1999

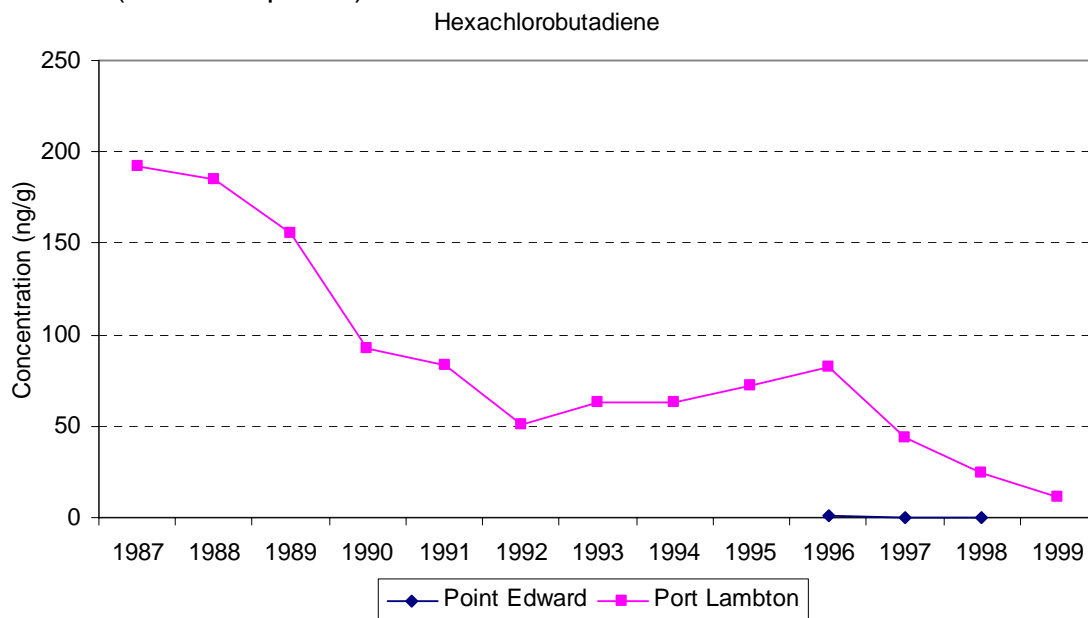
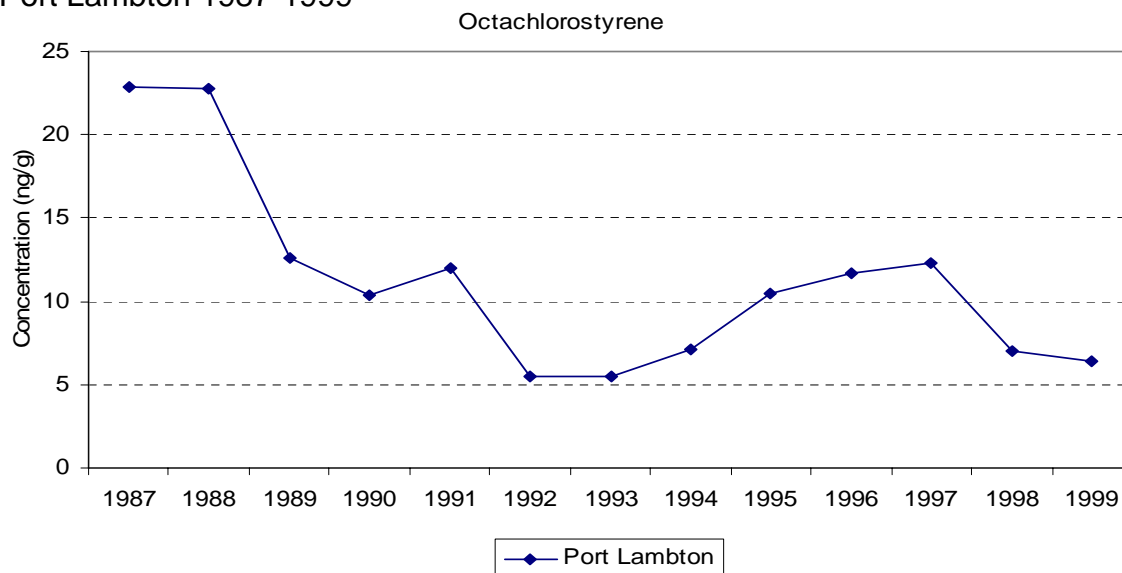


Figure 26. Concentration of octachlorostyrene in suspended sediments (ng/g) at Port Lambton 1987-1999



Octachlorostyrene was undetected at the upstream station in both phases, water and suspended sediment, and at the downstream station, this compound was



found only in suspended sediments. Concentrations of octachlorostyrene in suspended sediment declined from 22 ng/g to 6 ng/g (Fig. 26).

#### 4.3.4 Polyaromatic Hydrocarbons (PAHs)

PAHs refer to a group of chemicals whose origins in the environment are from incomplete burning 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 therefore found in suspended sediments. Ambient levels of PAHs in the dissolved phase are quite low (< 2 ng/L, see Table 4c) and showed no upstream and downstream differences and temporal trends over the study period. Concentrations of PAHs in suspended sediments are much higher (Table 5c). Phenanthrene, fluoranthene and pyrene were the most frequently detected in both the dissolved and suspended sediment phases at both stations. Typical distributions of PAHs in suspended sediments are shown in (Fig 27-29).

Figure 27. Concentration of phenanthrene in suspended sediments (ng/g) 1987-1999

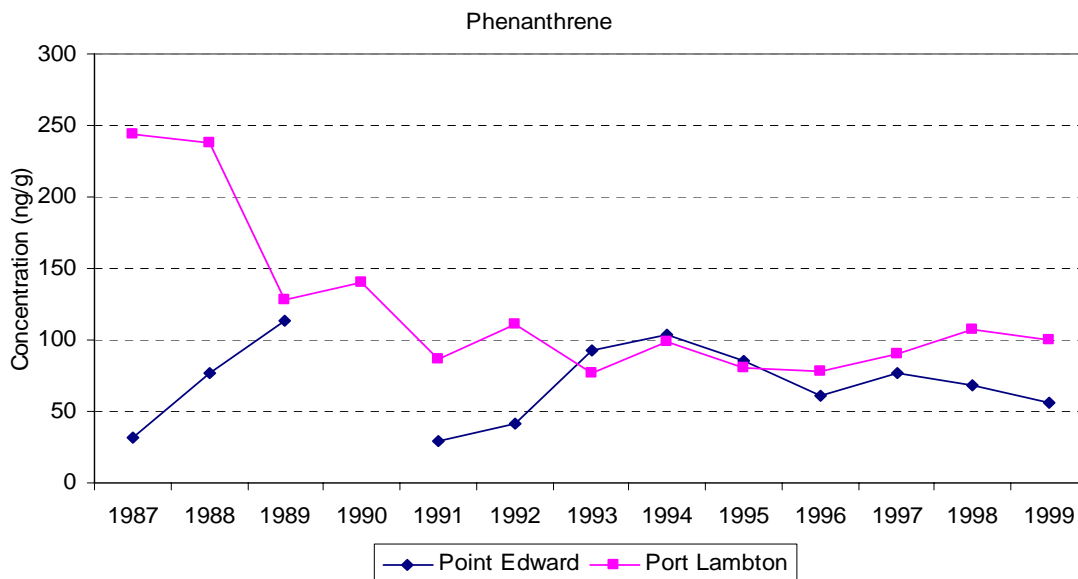


Figure 28. Concentration of fluoranthene in suspended sediments (ng/g) in the St. Clair River 1987-1999

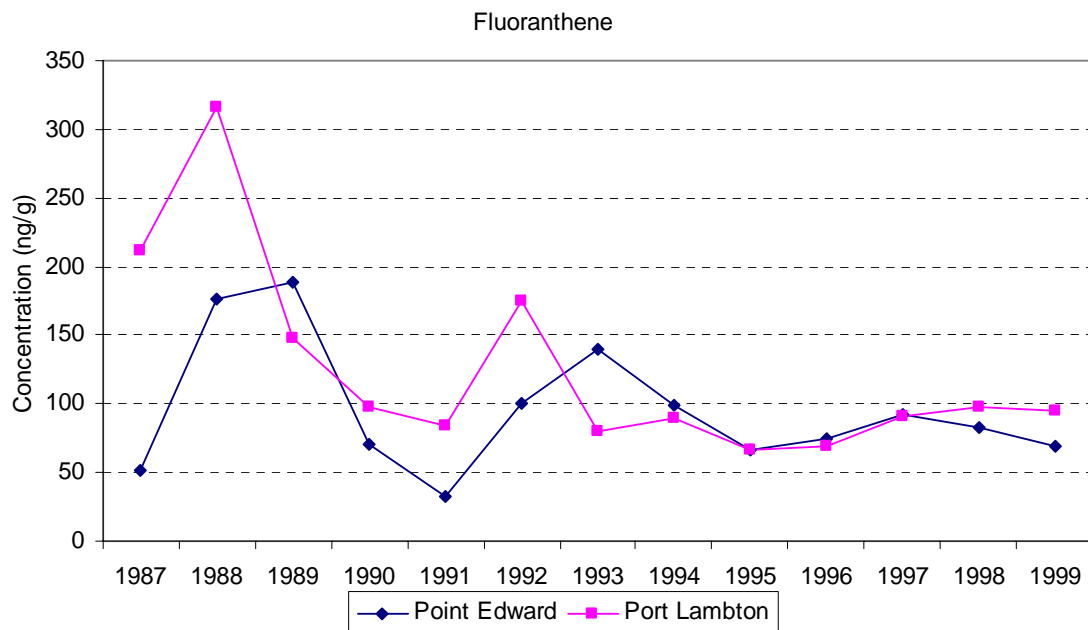
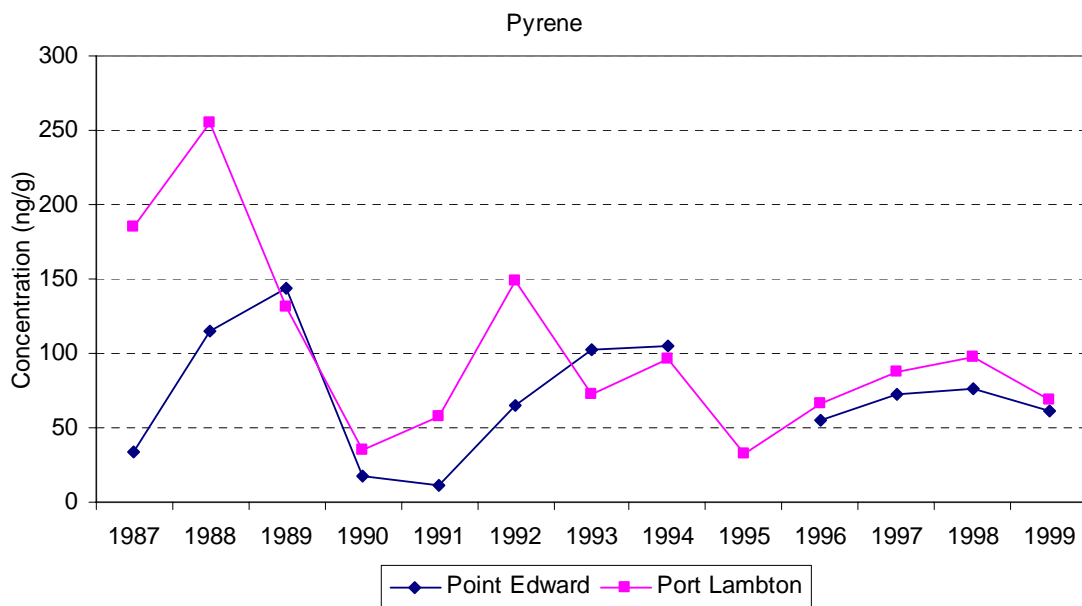


Figure 29. Concentration of pyrene in suspended sediments (ng/g) in the St. Clair River 1987-1999



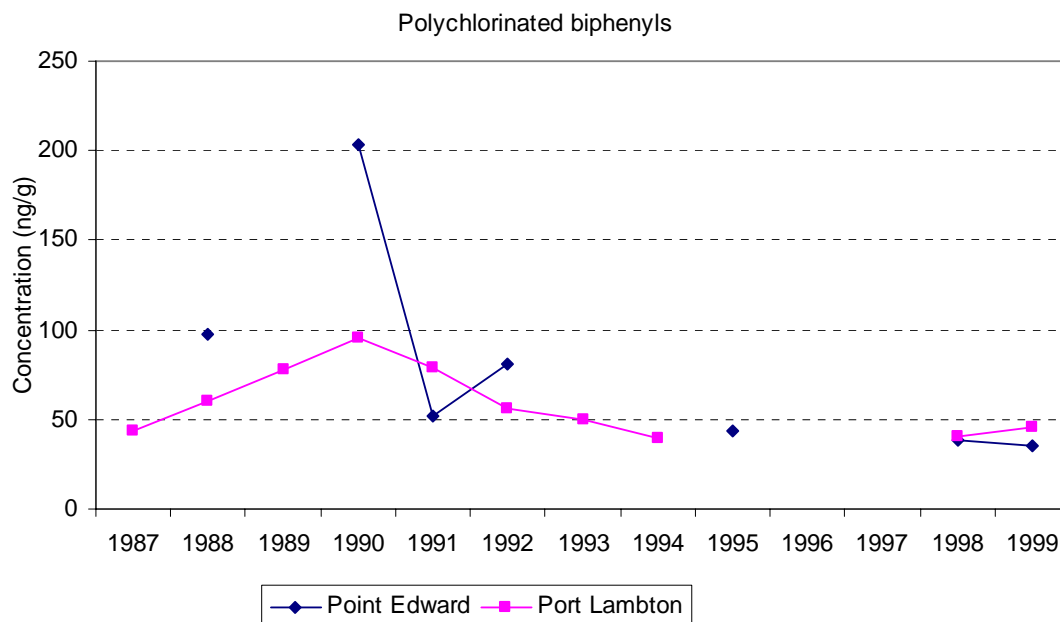
#### 4.3.5 Polychlorinated Biphenyls (PCBs)

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. PCBs were not produced in Canada but approximately 40,000 tons were imported and used commercially prior to the 1980s. Like many other organochlorine compounds, PCBs are persistent, bioaccumulative and toxic. They are the cause of the majority of the fish consumption advisories in each of the Great Lakes and they are considered a priority pollutant by many authorities. The Great Lakes Water Quality Agreement calls for the virtual elimination of discharges of PCBs.

The GLSE methodology (used during this reporting period) for the extraction of PCBs from the water is very susceptible to contamination from the surrounding air due to the large volumes of dichloromethane exposed to the air. Background levels in the dissolved phase were determined to be too high and therefore the data flagged and not reported here.

Annual mean estimates for PCBs can only be determined if three samples for the year are reported as real numbers. (i.e. not reported as a < detection limit). The detection limit for PCB analysis of sediment was 77 ng/g prior to 1998. Estimates, when they could be determined are shown in Figure 30 and are generally below detection limit. Estimates could not be determined at Point Edward for most of the years prior to 1998 and at Port Lambton from 1995-1997. This proves difficult in assessing temporal trends however there are several points which can be made. Twice as many estimates could be determined at Port Lambton than at Point Edward prior to 1995 indicating that samples are more often higher at Port Lambton. Between 1993 and 1999 there were no changes in the estimates when they could be determined suggesting no temporal change over this period and also suggesting minimal change in the concentration of the suspended material as it moved down the river down the river.

Figure 30. Concentration of PCBs in suspended sediments (ng/g) in the St. Clair River 1987-1999



## 5.0 Conclusions

Major ions at the head of the St Clair River (Point Edward) showed gradual increases in concentrations over the thirteen year period. This increase is probably due to the natural aging of Great Lakes water.

Conventional water quality parameters (cations, anions and nutrients) showed no significant changes along the river with the exception of sodium and chloride which were consistently higher at the downstream station at Port Lambton indicating active inputs along the River. However, the data also suggested that salt inputs have been greatly reduced and that the salt concentrations at Port Lambton approached that of the upstream station.

Aluminium, copper, iron, manganese and zinc all showed slightly higher concentrations at the downstream station while concentrations of cadmium, cobalt, chromium, molybdenum, nickel and lead were detected at trace levels and below the detection limits. None of the dissolved metals data showed any visible trend over the years.

Notable chlorobenzenes found in the St. Clair River are 1,3,5 trichlorobenzene, pentachlorobenzene and hexachlorobenzene. These chlorobenzenes were found in higher concentrations in the suspended sediment at the downstream location.

The temporal trends of hexachlorobenzene, hexachlorobutadiene and octachlorostyrene data showed their inputs along the River were on the decline.

Organochlorine pesticides were found mostly to be present in the water phase and less associated with suspended sediments. There was no change in concentrations of organochlorine pesticides from Point Edward to Port Lambton. Several organochlorine pesticides (HCHs, dieldrin and DDE) showed a gradual decline over the thirteen year period.

PCBs on the suspended sediment were more consistently above detection at the Port Lambton site in the earlier years of this reporting period while estimates could not be determined for either site in the mid nineties suggesting a decrease in concentration from the late eighties. Lower detection limits in 1997 and 1998 showed no differences in the concentrations between the sites as well as no difference from the estimates determined in 1994.

## **6.0 Recommendations**

1. Samples should be taken and analysed for metals in whole water. Metals may have very high concentrations on the suspended particulate fraction in the water which may show substantially different trends than the dissolved phase.
2. Samples should be taken and analysed for mercury in whole water. Mercury has been found at elevated levels in the sediment and fish in the St. Clair R. Temporal trend data for this contaminant should be determined.
3. A method with sufficiently low background levels should be used for the analysis of PCBs in water.
4. Results should be compared to available environmental criteria.

## **7.0 Acknowledgements**

Environment Canada wishes to thank the Ontario Clean Water Agency for providing the space and support for sampling at Point Edward and we express our gratitude to Mr. Alex Bej for his dedicated efforts in collecting water and sediment samples over the years.

## 8.0 References

- Allan, R. J. 1986. The Role of particulate matter in the fate of contaminants in aquatic ecosystems. Scientific Series No. 142, Inland Waters Directorate, Ontario Region.
- Chan, C. H., Y. L. Lau, and B. G. Oliver. 1986. Measured and Modelled Chlorinated Contaminant Distribution in St. Clair . River Water. Water Poll. Res. J. Canada, vol 21, No 3, p332.
- Chan, C.H. 1993 St. Clair River head and mouth water quality monitoring, 1987-89. Wat. Poll. Res. J. Canada. 28(2):451-471.
- Derecki, J. A. 1985. Effect of channel changes in the St. Clair River during the present century. Journal of Great Lakes Res., 11:201-207.
- Environment Canada. 1987. Survey of Trace Contaminants in the St. Clair River, 1985. Scientific Series No. 158, Inland Waters Directorate, Ontario Region.
- Environment Canada, 1997. Manual of Analytical Methods. National Laboratory of Environmental Testing.
- Environment Canada, 1997. The Niagara River Protocol. National Laboratory of Environmental Testing.
- El-Shaarawi, A.H. 1989. Inferences about the mean from censored water quality data. Water Resour. Res. 25:685-690, 1989.
- Goulden, P.D., and D. H. J. Anthony. 1985. Design of a large sample extractor for the determination of organics in water. National Water Research Institute, contribution no. 83-121. Unpublished report.
- International Joint Commission, 1982. Report on Great Lakes Water Quality. Great Lakes Water Quality Board, November 1982. Windsor, Ontario.
- International Joint Commission, 1983. Report on Great Lakes Water Quality. Great Lakes Water Quality Board, November 1982. Windsor, Ontario.
- International Joint Commission, 1984. Report on Great Lakes Water Quality. Great Lakes Water Quality Board, November 1982. Windsor, Ontario.
- Kaminsky, R. and R. A. Hites 1984. Octachlorostyrene in Lake Ontario: sources and Fates. Environ. Sci. Technol. 18, 275-263.

King, Lawrence and G. Sherbin (1986). Point Sources of Toxic Organic in the Upper St. Clair River. *Water Poll. Res. J. Canada*, vol 21, 3, p433-445.

Kirk Othmer Encyclopedia of Chemical Technology. 1979. John Wiley and Sons, New York.

L'Italien 2002. Lake Huron and Georgian Bay Surveillance Program, Spatial distribution and temporal trends of selected parameters with emphasis on 1999-2000 results. (in preparation).

Li, Y. F. 1999. Global technical hexachlorocyclohexane usage and its contamination consequences in the environment: from 1948 to 1997. *Sci. Tot. Environ.* 232:121-158.

Mumma, C.E., and E.W. Lawless. Survey of Industrial Processing Data. Task I.: Hexachlorobutadiene and Hexachlorobenzene Pollution from Chlorocarbon Processing. EPA 560/3-75-003.

Neilson, M., S. L'Italien, C. Glumac, D. Williams, and P. Bertram. 1995. Nutrients: Trends and System Response. State of the lakes Ecosystem Conference Background Paper, Environment Canada and the United States Environmental Protection Agency, EPA 905-R-95-015.

Oliver, B. G., Nicol, K.D., 1982. Chlorobenzenes in sediments, water, and selected fish from Lake Superior, Huron, Erie, and Ontario. *Environ. Sci. Technol.* 16, 532-536.

OMOEE and MDNR. 1995. The St. Clair River Area of Concern: Water Use Goals, Remedial Measures and Implementation Strategy. Remedial Action Plan - Stage 2 - Recommended Plan. Ontario Ministry of Environment and Energy and Michigan Department of Natural Resources. March 7, 1995. 121pp.

Ridal J.J., Kerman B.R., and Fox M.E. 1996. Seasonality of air-water fluxes of hexachlorocyclohexanes in Lake Ontario. *Envir. Sci. Technol.* 30:852-858.

Rossmann, R. and Barres, J. 1988. Trace element concentrations in near-surface waters of the Great Lakes and methods of collection, storage, and analysis. *J. Great Lakes Res.* 14(2):188-204.

UGLCCS 1988. Final report of the Upper Great Lakes Connecting Channels Study. Environment Canada, U.S.EPA, Ontario Ministry of Environment and Michigan Department of Natural Resources. 3 Volumes.

Upper Lakes Reference Group 1977. International Joint Commission. The waters of Lake Huron and Lake Superior volume II.

Williams, D.J. 1992. Great Lakes Water Quality: A Case Study. In Dunnette and O'Brien [Eds] The Science of Global change : The Impact of Human Activities on the Environment. American Chemical Society Symposium Series 483, Washington. pp. 207-223.

Williams, D. J. , Merriman, J. and Neilson, M. A. 1998 Surveillance and Monitoring of Lake Ontario and the Niagara and St. Lawrence Rivers. Great Lakes Research Review Vol. 4, 1998 pp 21-34.



# **Appendices**

**Appendix 1- Detection Limits**

**Appendix 2- Data**

## **Appendix 1- Detection Limits**

	units	Dissolved	units	Particulate		units	Dissolved	units	Particulate
pH		0.1			<b>OC Pesticides</b>				
Conductivity	USIE/CM	0.1			α-Hexachlorocyclohexane (a-HCH)	ng/L	0.04	ng/g	2.3
<b>Metals</b>					γ-Hexachlorocyclohexane (g-HCH)	ng/L	0.05	ng/g	1.5
Aluminum (Al)	µg/L	0.2			α-chlordane	ng/L	0.09	ng/g	2.3
Barium (Ba)	µg/L	0.2			γ-Chlordane	ng/L	0.07	ng/g	1.5
Cadmium (Cd)	µg/L	0.1			α-Endosulphan	ng/L	0.04	ng/g	1.4
Chromium (Cr)	µg/L	0.2			β-Endosulphan	ng/L	0.10	ng/g	2.9
Cobalt (Co)	µg/L	0.1			Dieldrin	ng/L	0.08	ng/g	3.2
Copper (Cu)	µg/L	0.2			Endrin	ng/L	0.18	ng/g	2.9
Iron (Fe)	µg/L	0.4			Aldrin	ng/L	0.05	ng/g	160
Lithium (Li)	µg/L	0.1			Heptachlor	ng/L	0.03	ng/g	1.4
Manganese (Mn)	µg/L	0.1			Heptachlor Epoxide	ng/L	0.03	ng/g	1.9
Molybdenum (Mo)	µg/L	0.1			p,p'-DDE	ng/L	0.08	ng/g	5.6
Nickel (Ni)	µg/L	0.2			p,p'-DDD	ng/L	0.38	ng/g	6
Lead (Pb)	µg/L	0.2			o,p'-DDT	ng/L	0.15	ng/g	7
Strontium (Sr)	µg/L	0.1			p,p'-DDT	ng/L	0.17	ng/g	7.5
Vanadium (V)	µg/L	0.1			Mirex	ng/L	0.05	ng/g	4.3
Zinc (Zn)	µg/L	0.2			Methoxychlor	ng/L	0.84	ng/g	18
<b>Nutrients</b>					<b>PAHs</b>				
Total Kjeldahl Nitrogen (TKN)	mg/L	0.01			Acenaphthylene	ng/L	0.19	ng/g	10
Total Phosphorus (TP)	mg/L	0.0002			Acenaphthene	ng/L		ng/g	10
<b>Major ions</b>					Fluorene	ng/L	0.55	ng/g	15
Chloride (Cl)	mg/L	0.05			Phenanthrene	ng/L	0.19	ng/g	15
Sulphate (SO <sub>4</sub> )	mg/L	0.01			Fluoranthene	ng/L	0.26	ng/g	15
Sodium (Na)	mg/L	0.03			Pyrene	ng/L	0.30	ng/g	15
Potassium (K)	mg/L	0.02			Benzo(b/k)fluoranthene	ng/L	0.30	ng/g	30
Calcium (Ca)	mg/L	0.05			Benzo(a)pyrene	ng/L	0.17	ng/g	30
Magnesium (Mg)	mg/L	0.01			Indeno(123-cd)pyrene	ng/L	0.83	ng/g	30
Silicate (SiO <sub>2</sub> )	mg/L	0.02			Benzo(ghi)perylene	ng/L	0.54	ng/g	30
Ammonia (NH <sub>3</sub> )	mg/L	0.001			<b>Industrial by-products</b>				
Nitrogen (Nitrate + Nitrite)	mg/L	0.010			Octachlorostyrene (OCS)	ng/L	0.07	ng/g	2.7
<b>Organic Contaminants</b>					Hexachlorobutadiene (HCBd)	ng/L	0.04	ng/g	4.2
<b>Chlorobenzenes</b>									
1,3-Dichlorobenzene	ng/L	0.26	ng/g	11.1					
1,4-Dichlorobenzene	ng/L	0.27	ng/g	11.7					
1,2-Dichlorobenzene	ng/L	0.25	ng/g	14.7					
1,3,5-Trichlorobenzene	ng/L	0.03	ng/g	1.8					
1,2,4-Trichlorobenzene	ng/L	0.03	ng/g	3.6					
1,2,3-Trichlorobenzene	ng/L	0.03	ng/g	1.9					
1,2,3,4-Tetrachlorobenzene	ng/L	0.03	ng/g	2.7					
Pentachlorobenzene	ng/L	0.03	ng/g	3.7					
Hexachlorobenzene (HCB)	ng/L	0.04	ng/g	6.3					

## **Appendix 2- Data**

# **Chemical parameters**

<b>Pt. Edward</b>	<b>pH</b>			<b>Conductivity</b>		
Mean	units	n	S.D.	USIE/CM (n)	n	S.D.
1987	7.8	12	0.3	213	12	5
1988	8.0	20	0.3		0	
1989	8.2	3	0.1	211	3	4
1990	8.1	14	0.2	212	14	6
1991	7.9	21	0.4	214	21	4
1992	7.8	13	0.3	224	13	7
1993	7.9	8	0.1	214	8	6
1994	7.8	5	0.2	213	5	2
1995	8.1	4	0.1	217	4	2
1996	8.1	22	0.1	214	22	4
1997	8.0	18	0.2	214	18	5
1998	8.1	21	0.1	217	21	10
1999	8.0	19	0.2	216	19	3
<b>Port Lambton</b>						
1987	7.7	14	0.3	225	14	11
1988	7.9	25	0.3		0	
1989	8.0	23	0.3	224	23	5
1990	8.0	16	0.2	225	16	9
1991	8.0	23	0.3	225	22	7
1992	7.9	22	0.2	230	22	6
1993	7.8	22	0.2	221	22	6
1994	7.8	3	0.1	215	3	5
1995	8.1	6	0.1	218	6	2
1996	8.0	22	0.2	214	22	5
1997	8.0	18	0.2	214	18	4
1998	8.0	20	0.2	216	20	6
1999	8.0	20	0.2	219	20	19
p (student t)	0.02			0.004		

n            number of samples  
S.D.        Standard Deviation

## Major Ions

Pt. Edward				SO <sub>4</sub>			Na			K		
	mg/L	n	S.D.	mg/L	n	S.D.	mg/L	n	S.D.	mg/L	n	S.D.
Mean												
1987	6.07	12	0.5	15.68	12	0.4	3.64	12	0.37	0.87	12	0.03
1988	6.09	21	0.4	16.55	21	0.5	3.58	21	0.09	0.89	21	0.02
1989	5.83	3	0.3	16.03	3	1.2	3.51	3	0.05	0.89	3	0.04
1990	5.95	12	0.5	15.16	12	0.6	3.68	12	0.22	0.86	12	0.05
1991	6.05	21	0.6	15.23	21	1.1	3.59	21	0.17	0.85	21	0.04
1992	6.49	15	0.3	16.21	15	0.7	3.71	15	0.13	0.87	15	0.03
1993	6.10	8	0.3	16.40	9	0.7	N.A.			N.A.		
1994	6.07	10	0.3	17.11	9	0.7	N.A.			N.A.		
1995	6.52	9	0.7	16.28	9	0.7	N.A.			N.A.		
1996	7.03	24	0.5	17.16	24	1.3	N.A.			N.A.		
1997	6.92	21	0.7	16.26	21	1.7	N.A.			N.A.		
1998	6.62	21	0.6	15.89	21	1.3	4.17	21	0.55	0.89	21	0.11
1999	6.85	19	0.6	16.31	19	4.5	4.31	17	0.31	0.82	17	0.07
<b>Port Lambton</b>												
1987	7.94	14	1.2	15.83	14	0.8	4.92	14	0.68	0.89	14	0.04
1988	9.01	25	0.8	16.93	25	0.6	5.72	25	0.53	0.90	25	0.04
1989	9.11	22	1.2	16.39	24	1.0	5.70	23	0.80	0.91	23	0.03
1990	8.79	14	1.1	15.46	14	1.3	5.51	14	0.67	0.89	14	0.04
1991	8.31	22	1.3	15.48	22	0.9	5.18	22	0.84	0.87	22	0.05
1992	8.95	25	0.9	16.36	25	0.9	5.35	25	0.56	0.88	25	0.04
1993	7.28	21	1.1	16.90	22	0.9	N.A.			N.A.		
1994	6.48	15	0.3	16.67	15	1.0	N.A.			N.A.		
1995	6.41	16	0.3	16.62	16	0.8	N.A.			N.A.		
1996	6.81	24	0.3	17.43	24	1.1	N.A.			N.A.		
1997	6.92	21	0.5	17.06	21	1.7	N.A.			N.A.		
1998	6.47	20	0.6	16.14	20	0.9	4.19	20	0.39	0.90	20	0.08
1999	6.59	18	0.2	16.68	19	0.5	4.09	18	0.13	0.83	18	0.07
Detection Limit	0.05			0.01			0.03			0.02		
p	0.003			0.001			0.003			0.002		

n        number of samples  
S.D.     Standard Deviation

## Major Ions

Pt. Edward	Ca			Mg			SiO <sub>2</sub>			NH <sub>3</sub>			NO <sub>3</sub> +NO <sub>2</sub>		
	mg/L	n	S.D.	mg/L	n	S.D.	mg/L	n	S.D.	mg/L	n	S.D.	mg/L	n	S.D.
Mean															
1987	27.70	12	0.67	7.22	12	0.10	0.15	12	0.15				0.181	11	0.124
1988	27.84	21	0.43	7.30	21	0.20	0.30	21	0.30	0.010	20	0.007	0.223	20	0.085
1989	27.73	3	0.25	7.13	3	0.15	0.50	3	0.50	0.014	3	0.004	0.312	3	0.008
1990	27.19	14	0.72	7.30	14	0.19	0.31	12	0.31	0.009	12	0.004	0.242	12	0.111
1991	27.20	21	0.54	7.38	21	0.18	0.26	21	0.26	0.019	20	0.024	0.308	21	0.037
1992	27.75	15	1.06	7.55	15	0.19	0.38	15	0.38	0.032	15	0.041	0.394	15	0.054
1993	N.A.			N.A.			0.14	8	0.14	0.016	8	0.012	0.365	8	0.050
1994	N.A.			N.A.			0.22	10	0.22	0.023	5	0.024	0.311	10	0.048
1995	N.A.			N.A.			0.17	9	0.17	0.020	15	0.015	0.347	11	0.029
1996	N.A.			N.A.			0.19	24	0.19	0.012	16	0.010	0.334	23	0.059
1997	N.A.			N.A.			0.19	21	0.19	0.012	16	0.008	0.358	21	0.066
1998	26.41	20	0.77	7.06	21	0.29	0.23	21	0.23	0.014	18	0.007	0.328	18	0.055
1999	26.33	17	0.61	6.90	17	0.27	0.25	19	0.25	0.009	15	0.006	0.313	19	0.052
<b>Port Lambton</b>															
1987	28.28	13	2.11	7.22	13	0.10	0.20	13	0.20				0.195	13	0.125
1988	28.04	25	0.56	7.35	26	0.20	0.30	25	0.30	0.015	24	0.008	0.203	25	0.113
1989	27.82	23	0.47	7.29	22	0.12	0.47	22	0.47	0.012	22	0.006	0.298	22	0.149
1990	27.34	14	0.64	7.34	14	0.16	0.32	14	0.32	0.010	12	0.007	0.250	13	0.095
1991	27.51	22	0.47	7.44	22	0.18	0.34	22	0.34	0.017	23	0.010	0.313	23	0.051
1992	27.86	25	1.51	7.55	25	0.30	0.32	25	0.32	0.016	25	0.008	0.357	25	0.049
1993	N.A.			N.A.			0.29	21	0.29	0.018	22	0.011	0.334	22	0.071
1994	N.A.			N.A.			0.34	14	0.34	0.021	15	0.011	0.343	16	0.090
1995	N.A.			N.A.			0.20	16	0.20	0.026	17	0.020	0.349	17	0.028
1996	N.A.			N.A.			0.20	24	0.20	0.018	22	0.008	0.350	23	0.101
1997	N.A.			N.A.			0.20	21	0.20	0.014	21	0.007	0.360	20	0.043
1998	26.62	20	0.93	7.03	20	0.19	0.19	20	0.19	0.016	17	0.007	0.339	17	0.062
1999	26.46	18	0.70	6.92	18	0.26	0.18	19	0.18	0.019	17	0.012	0.328	19	0.057
Detection Limit	0.05			0.01			0.02			0.001			0.010		
p	0.003			0.059			0.163			0.289			0.480		

n  
S.D.

## Nutrients

<b>Pt. Edward</b>	<b>TKN</b>			<b>TP</b>		
Mean	µg/L	n	S.D.	µg/L	n	S.D.
1987	0.137	6	0.029	5.8	9	0.0029
1988	0.138	20	0.040	3.5	18	0.0010
1989	0.140	3	0.071	3.6	3	0.0004
1990	0.141	13	0.029	4.4	11	0.0036
1991	0.125	21	0.041	3.1	19	0.0008
1992	0.140	14	0.036	3.9	14	0.0021
1993	0.136	8	0.024	3.3	5	0.0008
1994	0.150	11	0.031	3.6	11	0.0011
1995	0.167	11	0.036	4.6	11	0.0023
1996	0.142	23	0.031	3.4	23	0.0008
1997	0.141	21	0.018	3.2	21	0.0010
1998	0.145	21	0.032	3.2	21	0.0024
1999	0.149	19	0.031	3.8	19	0.0018
<b>Port Lambton</b>						
1987	0.143	6	0.037	5.2	7	0.002
1988	0.164	24	0.060	4.5	25	0.001
1989	0.124	22	0.026	3.6	20	0.001
1990	0.137	16	0.026	4.0	13	0.001
1991	0.129	22	0.026	3.5	23	0.001
1992	0.126	24	0.044	3.8	22	0.001
1993	0.146	22	0.051	3.9	21	0.002
1994	0.158	16	0.038	4.2	15	0.002
1995	0.182	19	0.070	4.4	17	0.002
1996	0.147	22	0.033	3.8	24	0.001
1997	0.148	21	0.022	3.3	21	0.001
1998	0.140	20	0.020	4.4	20	0.004
1999	0.149	19	0.022	3.5	19	0.001
p value (student t)	0.16			0.10		

n                      number of samples  
S.D.                  Standard Deviation



# Chlorobenzenes

Pt. Edward	1,4-Dichlorobenzene						1,2-Dichlorobenzene						1,3,5-Trichlorobenzene					
	dissolved			particulate			dissolved			particulate			dissolved			particulate		
	ng/L (n)	Lower 90% CI	Upper 90% CI	ng/g (n)	Lower 90% CI	Upper 90% CI	ng/L (n)	Lower 90% CI	Upper 90% CI	ng/g (n)	Lower 90% CI	Upper 90% CI	ng/L (n)	Lower 90% CI	Upper 90% CI	ng/g (n)	Lower 90% CI	Upper 90% CI
Mean																		
1987	1.21	0.535	2.75	ins. data			0.160	0.153	0.167	ins. data			ins. data			ins. data		
1988	2.75	2.04	3.70	ins. data			ins. data			ins. data			ins. data			ins. data		
1989	7.72	6.55	9.09	ins. data			ins. data			ins. data			ins. data			ins. data		
1990	4.24	2.78	6.47	ins. data			0.267	0.211	0.339	ins. data			ins. data			ins. data		
1991	2.80	2.11	3.73	ins. data			0.335	0.311	0.361	ins. data			ins. data			ins. data		
1992	2.54	2.06	3.14	ins. data			0.398	0.290	0.547	ins. data			ins. data			ins. data		
1993	2.98	2.32	3.82	ins. data			0.553	0.291	1.05	ins. data			ins. data			ins. data		
1994	1.15	1.03	1.28	21.4	17.2	26.8	0.130	0.100	0.168	7.10	6.28	8.01	ins. data			ins. data		
1995	0.642	0.415	0.993	13.9	10.9	17.7	0.508	0.184	1.40	ins. data			ins. data			ins. data		
1996	0.599	0.428	0.838	7.77	7.01	8.60	0.395	0.257	0.608	ins. data			ins. data			ins. data		
1997	1.09	0.854	1.40	9.12	7.73	10.8	0.243	0.070	0.844	ins. data			ins. data			ins. data		
1998	0.909	0.636	1.30	5.44	4.84	6.11	0.178	0.086	0.371	1.36	1.07	1.73	ins. data			0.581	0.391	0.863
1999	1.67	1.56	1.79	7.12	5.83	8.69	0.368	0.203	0.666	1.97	1.38	2.80	0.025	0.019	0.033	0.705	0.467	1.07
Port Lambton																		
Mean																		
1987	0.649	0.506	0.833	ins. data			0.180	0.153	0.211	ins. data			0.052	0.030	0.091	9.34	7.44	11.7
1988	0.911	0.723	1.15	17.1	11.2	26.2	0.269	0.242	0.297	8.97	7.08	11.4	0.047	0.041	0.055	6.81	5.58	8.30
1989	3.23	2.76	3.79	11.9	9.54	14.9	0.352	0.287	0.433	6.67	5.18	8.58	0.067	0.055	0.081	3.93	3.10	4.97
1990	2.94	2.15	4.01	ins. data			0.205	0.168	0.251	ins. data			0.083	0.028	0.241	2.17	1.45	3.25
1991	1.52	1.18	1.96	ins. data			0.143	0.139	0.148	ins. data			0.088	0.061	0.127	3.32	2.27	4.86
1992	1.82	1.54	2.14	ins. data			0.314	0.249	0.396	5.84	3.02	11.3	0.062	0.055	0.070	2.55	2.07	3.14
1993	1.41	1.27	1.57	ins. data			0.291	0.224	0.379	ins. data			0.053	0.042	0.067	1.65	0.76	3.58
1994	0.918	0.820	1.03	8.66	7.30	10.3	0.116	0.101	0.135	4.28	3.71	4.93	0.074	0.059	0.093	2.85	2.24	3.62
1995	0.624	0.564	0.690	8.39	7.90	8.90	0.300	0.176	0.511	4.94	4.21	5.81	0.061	0.047	0.080	3.92	2.99	5.13
1996	0.754	0.634	0.896	5.30	5.04	5.57	0.411	0.224	0.753	5.47	4.34	6.91	0.026	0.017	0.040	2.78	2.03	3.79
1997	0.824	0.599	1.13	7.25	6.25	8.41	ins. data			7.32	5.64	9.52	0.061	0.047	0.080	7.14	5.31	9.59
1998	0.625	0.520	0.751	4.27	3.78	4.81	0.212	0.159	0.282	3.57	2.71	4.72	0.052	0.046	0.058	3.36	2.62	4.32
1999	1.55	1.38	1.74	8.41	7.52	9.41	0.302	0.231	0.396	5.54	4.64	6.62	0.077	0.062	0.095	3.17	2.32	4.33

CI Confidence Interval  
ins. data insufficient data  
N.A. Not Available

# Chlorobenzene

1,2,4-Trichlorobenzene							Pentachlorobenzene						Hexachlorobenzene					
Mean	dissolved			particulate			dissolved			particulate			dissolved			particulate		
	ng/L (n)	Lower 90% CI	Upper 90% CI	ng/g (n)	Lower 90% CI	Upper 90% CI	ng/L (n)	Lower 90% CI	Upper 90% CI	ng/g (n)	Lower 90% CI	Upper 90% CI	ng/L (n)	Lower 90% CI	Upper 90% CI	ng/g (n)	Lower 90% CI	Upper 90% CI
<b>Pt. Edward</b>																		
1987	0.077	0.068	0.087	ins. data			0.022	0.017	0.027	ins. data			0.031	0.025	0.040	0.871	0.764	0.992
1988	0.115	0.095	0.139	ins. data			0.013	0.011	0.016	ins. data			0.022	0.019	0.025	ins. data		
1989	0.104	0.062	0.172	ins. data			0.010	0.010	0.010	ins. data			0.023	0.019	0.028	ins. data		
1990	0.122	0.094	0.159	ins. data			0.012	0.011	0.014	ins. data			0.026	0.024	0.029	ins. data		
1991	0.144	0.111	0.188	ins. data			0.024	0.021	0.027	ins. data			0.021	0.019	0.024	1.33	1.13	1.6
1992	0.110	0.086	0.140	ins. data			0.014	0.012	0.017	ins. data			0.021	0.017	0.026	2.53	2.02	3.1
1993	0.074	0.062	0.087	ins. data			0.020	0.016	0.026	ins. data			0.028	0.024	0.032	3.87	1.89	7.9
1994	0.034	0.028	0.041	3.40	2.02	5.74	0.022	0.017	0.029	ins. data			0.021	0.018	0.025	1.16	0.954	1.4
1995	0.066	0.047	0.093	1.56	1.27	1.91	0.024	0.022	0.026	1.00	0.72	1.39	0.015	0.013	0.019	1.18	0.923	1.5
1996	0.023	0.019	0.027	1.11	1.02	1.21	0.016	0.013	0.020	ins. data			0.022	0.018	0.026	0.897	0.779	1.0
1997	0.033	0.025	0.044	0.927	0.808	1.06	0.013	0.011	0.015	0.41	0.33	0.50	0.011	0.010	0.013	0.939	0.762	1.2
1998	0.021	0.019	0.023	0.503	0.404	0.626	0.010	0.010	0.011	0.19	0.17	0.23	0.012	0.011	0.013	0.514	0.418	0.63
1999	0.030	0.023	0.039	0.596	0.468	0.759	0.012	0.011	0.014	0.25	0.20	0.31	0.017	0.015	0.020	0.483	0.456	0.51
<b>Port Lambton</b>																		
Mean																		
1987	0.080	0.067	0.096	3.68	3.07	4.43	0.043	0.032	0.059	10.55	8.16	13.63	0.064	0.047	0.087	116	69.9	194
1988	0.090	0.064	0.125	3.22	2.48	4.18	0.032	0.026	0.040	10.01	7.44	13.47	0.071	0.058	0.087	73.1	57.5	93.1
1989	0.186	0.123	0.281	2.22	1.90	2.59	0.036	0.031	0.043	5.24	4.02	6.82	0.074	0.063	0.088	54.8	38.7	77.6
1990	0.132	0.102	0.171	2.15	1.91	2.42	0.029	0.025	0.034	5.05	3.62	7.05	0.059	0.047	0.073	39.5	26.8	58.4
1991	0.150	0.106	0.211	2.14	1.55	2.96	0.039	0.034	0.045	6.04	4.43	8.24	0.054	0.047	0.061	61.7	42.5	89.5
1992	0.102	0.082	0.126	2.79	2.18	3.57	0.034	0.029	0.041	3.54	2.68	4.69	0.043	0.039	0.048	23.0	14.7	35.9
1993	0.058	0.048	0.071	2.00	1.97	2.03	0.029	0.026	0.032	3.34	2.10	5.32	0.036	0.031	0.041	27.3	14.0	53.3
1994	0.034	0.026	0.043	1.96	1.62	2.38	0.030	0.027	0.034	3.54	2.94	4.26	0.044	0.034	0.057	33.7	21.4	53.1
1995	0.061	0.044	0.084	1.84	1.67	2.04	0.030	0.027	0.033	4.01	3.09	5.20	0.036	0.029	0.044	31.5	22.4	44.3
1996	0.022	0.019	0.025	1.44	1.24	1.67	0.037	0.030	0.045	4.14	3.07	5.59	0.052	0.042	0.064	37.6	25.2	56.2
1997	0.023	0.021	0.025	2.57	2.04	3.24	0.024	0.021	0.028	3.80	3.11	4.63	0.037	0.029	0.046	21.0	16.2	27.2
1998	0.021	0.019	0.024	1.43	1.17	1.75	0.016	0.014	0.018	2.17	1.66	2.85	0.020	0.018	0.023	17.7	12.8	24.4
1999	0.031	0.026	0.036	1.22	1.04	1.44	0.020	0.018	0.022	2.06	1.57	2.70	0.048	0.035	0.065	21.2	12.6	35.7

CI  
ins. data  
N.A.

<b>Pt. Edward</b>	<b>PCBs particulate</b>		
Mean	ng/g (n)	Lower 90%	Upper 90% CI
1988	97.981	71.214	134.809
1989	ins. Data		
1990	203.153	168.886	244.373
1991	52.244	28.45	95.94
1992	80.611	52.753	123.181
1993	ins. Data		
1994	ins. Data		
1995	43.245	36.579	51.125
1996	ins. Data		
1997	ins. Data		
1998	37.885	33.885	42.356
1999	35.018	31.855	38.495
<b>Port Lambton</b>			
Mean			
1987	44.005	36.861	52.533
1988	60.361	47.642	76.476
1989	78.135	53.877	113.317
1990	95.515	72.793	125.33
1991	79.034	32.006	195.16
1992	56.196	48.983	64.471
1993	49.328	43.059	56.511
1994	39.189	35.486	43.278
1995	ins. Data		
1996	ins. Data		
1997	ins. Data		
1998	40.118	37.674	42.721
1999	45.896	42.359	49.728
Det. Limit	10		

CI	Confidence Interval
ins. Data	Insufficient Data
N.A.	Not Available

# Organochlorine Pesticides

Pt. Edward	$\alpha$ -Hexachlorocyclohexane						$\gamma$ -Hexachlorocyclohexane					
	dissolved			particulate			dissolved			particulate		
	Mean ng/L (n)	Lower 90% CI	Upper 90% CI	ng/g (n)	Lower 90% CI	Upper 90% CI	ng/L (n)	Lower 90% CI	Upper 90% CI	ng/g (n)	Lower 90% CI	Upper 90% CI
1987	2.973	2.525	3.501	1.507	1.379	1.648	0.413	0.373	0.457	ins. Data		
1988	2.833	2.482	3.233	ins. Data			0.411	0.379	0.446	ins. Data		
1989	2.560	2.507	2.615	ins. Data			0.407	0.375	0.441	ins. Data		
1990	1.270	1.183	1.363	ins. Data			0.326	0.297	0.357	ins. Data		
1991	1.066	0.995	1.141	ins. Data			0.277	0.262	0.293	ins. Data		
1992	1.026	0.964	1.091	ins. Data			0.287	0.272	0.302	ins. Data		
1993	0.779	0.717	0.846	ins. Data			0.264	0.246	0.283	ins. Data		
1994	0.727	0.704	0.751	ins. Data			0.226	0.191	0.268	ins. Data		
1995	0.541	0.477	0.612	ins. Data			0.192	0.170	0.218	ins. Data		
1996	0.550	0.522	0.580	2.514	1.932	3.271	0.243	0.210	0.280	ins. Data		
1997	0.544	0.423	0.699	2.804	1.753	4.484	0.238	0.201	0.280	1.907	1.559	2.333
1998	0.357	0.328	0.388	1.253	0.761	2.061	0.177	0.162	0.192	ins. Data		
1999	0.261	0.241	0.282	0.447	0.325	0.615	0.162	0.133	0.198	0.922	0.481	1.767
<b>Port Lambton</b>												
Mean												
1987	2.886	2.685	3.102	1.435	1.247	1.651	0.445	0.415	0.477	ins. Data		
1988	2.993	2.733	3.278	1.354	1.224	1.498	0.465	0.438	0.492	ins. Data		
1989	1.764	1.588	1.960	ins. Data			0.425	0.404	0.446	ins. Data		
1990	1.378	1.182	1.607	ins. Data			0.352	0.299	0.415	ins. Data		
1991	1.000	0.923	1.083	ins. Data			0.276	0.254	0.301	ins. Data		
1992	0.957	0.913	1.002	ins. Data			0.295	0.282	0.308	1.559	1.361	1.786
1993	0.732	0.683	0.783	ins. Data			0.274	0.256	0.293	ins. Data		
1994	0.634	0.594	0.678	0.275	0.244	0.309	0.266	0.238	0.297	ins. Data		
1995	0.557	0.504	0.616	ins. Data			0.228	0.203	0.257	ins. Data		
1996	0.548	0.515	0.583	ins. Data			0.259	0.234	0.287	ins. Data		
1997	0.495	0.399	0.614	0.792	0.641	0.979	0.234	0.201	0.273	1.197	0.759	1.890
1998	0.324	0.262	0.400	0.599	0.441	0.813	0.171	0.149	0.196	0.159	0.134	0.189
1999	0.228	0.207	0.252	0.390	0.297	0.512	0.152	0.138	0.168	0.429	0.359	0.513

CI Confidence Interval  
ins. Data insufficient data  
N.A. Not Available

# Organochlorine Pesticides

Pt. Edward	Dieldrin						Heptachlor Epoxide					
	dissolved			particulate			dissolved			particulate		
	ng/L (n)	Lower 90% CI	Upper 90% CI	ng/g (n)	Lower 90% CI	Upper 90% CI	ng/L (n)	Lower 90% CI	Upper 90% CI	ng/g (n)	Lower 90% CI	Upper 90% CI
Mean												
1987	0.207	0.184	0.231	2.368	1.927	2.911	0.099	0.087	0.113	ins. Data		
1988	0.210	0.189	0.233	10.871	8.987	13.150	0.109	0.097	0.122	5.991	4.804	7.470
1989	0.213	0.195	0.234	22.217	12.398	39.814	0.187	0.175	0.199	2.596	1.487	4.535
1990	0.205	0.188	0.224	7.792	6.539	9.285	0.109	0.100	0.119	ins. Data		
1991	0.197	0.188	0.206	9.004	6.224	13.026	0.113	0.106	0.121	1.974	1.421	2.743
1992	0.171	0.163	0.178	10.753	7.353	15.725	0.090	0.084	0.097	ins. Data		
1993	0.175	0.170	0.180	7.825	5.084	12.044	0.079	0.074	0.083	ins. Data		
1994	0.148	0.141	0.156	3.580	2.328	5.503	0.064	0.060	0.068	2.658	2.339	3.021
1995	0.129	0.112	0.148	2.037	1.759	2.360	0.059	0.053	0.066	ins. Data		
1996	0.125	0.118	0.132	2.551	2.191	2.969	0.050	0.040	0.062	ins. Data		
1997	0.109	0.097	0.122	1.245	1.073	1.443	0.034	0.027	0.042	ins. Data		
1998	0.099	0.093	0.105	1.793	1.434	2.242	0.040	0.035	0.047	0.517	0.353	0.757
1999	0.105	0.095	0.115	2.923	1.612	5.300	0.028	0.024	0.032	0.536	0.459	0.627
Port Lambton												
Mean												
1987	0.212	0.196	0.229	2.977	2.718	3.262	0.101	0.093	0.109	ins. Data		
1988	0.206	0.177	0.239	2.551	2.164	3.006	0.116	0.104	0.129	1.041	0.862	1.257
1989	0.206	0.198	0.215	3.052	2.240	4.157	0.130	0.112	0.149	ins. Data		
1990	0.210	0.179	0.247	1.689	1.451	1.965	0.110	0.093	0.129	ins. Data		
1991	0.174	0.161	0.187	1.772	1.434	2.188	0.100	0.092	0.108	1.359	1.163	1.588
1992	0.150	0.143	0.157	2.328	1.940	2.793	0.076	0.072	0.081	1.080	0.924	1.263
1993	0.156	0.146	0.165	1.935	1.506	2.486	0.073	0.068	0.077	ins. Data		
1994	0.139	0.129	0.150	1.021	0.881	1.183	0.062	0.056	0.068	ins. Data		
1995	0.130	0.120	0.142	0.907	0.783	1.051	0.067	0.055	0.081	ins. Data		
1996	0.132	0.125	0.140	1.134	0.914	1.407	0.051	0.043	0.060	ins. Data		
1997	0.110	0.099	0.121	1.127	0.929	1.367	0.033	0.027	0.042	0.332	0.242	0.456
1998	0.103	0.095	0.112	1.061	0.870	1.294	0.031	0.025	0.038	ins. Data		
1999	0.110	0.095	0.128	ins. Data			0.095	0.058	0.154	ins. Data		

CI

ins. Data

N.A.

# Organochlorine Pesticides

Pt. Edward		p,p'-DDE					
Mean	ng/L (n)	dissolved		particulate			
		Lower 90% CI	Upper 90% CI	ng/g (n)	Lower 90% CI	Upper 90% CI	
1987	0.060	0.049	0.072	1.400	1.313	1.491	
1988	ins. Data			8.320	7.075	9.782	
1989	ins. Data			ins. Data			
1990	ins. Data			4.541	4.162	4.955	
1991	0.039	0.033	0.046	3.874	3.304	4.542	
1992	ins. Data			4.052	3.558	4.616	
1993	ins. Data			ins. Data			
1994	ins. Data			2.896	2.226	3.769	
1995	ins. Data			2.422	1.975	2.969	
1996	0.040	0.035	0.046	2.828	2.471	3.237	
1997	0.029	0.023	0.035	2.652	2.143	3.282	
1998	0.032	0.028	0.036	1.590	1.358	1.862	
1999	0.020	0.016	0.025	1.165	1.006	1.348	
Port Lambton							
Mean							
1987	ins. Data			2.155	1.885	2.464	
1988	ins. Data			2.690	2.366	3.057	
1989	ins. Data			2.424	2.099	2.799	
1990	ins. Data			1.973	1.770	2.198	
1991	0.033	0.028	0.038	1.745	1.486	2.049	
1992	ins. Data			2.140	2.086	2.195	
1993	0.051	0.046	0.058	ins. Data			
1994	ins. Data			1.139	1.020	1.271	
1995	ins. Data			1.269	1.093	1.472	
1996	ins. Data			1.801	1.574	2.061	
1997	0.029	0.025	0.033	1.908	1.677	2.172	
1998	0.020	0.020	0.020	0.938	0.862	1.021	
1999	0.016	0.014	0.019	0.890	0.826	0.958	

CI

ins. Data

N.A.

# **Polyaromatic Hydrocarbons**

Pt. Edward	1-Methyl Naphthalene						2-Methyl Naphthalene						
	dissolved			particulate			dissolved			particulate			
	Mean	ng/L (n)	Lower 90% CI	Upper 90% CI	ng/g (n)	Lower 90% CI	Upper 90% CI	ng/L (n)	Lower 90% CI	Upper 90% CI	ng/g (n)	Lower 90% CI	Upper 90% CI
	1987	0.836	0.564	1.237	26.912	19.468	37.203	0.976	0.738	1.290	ins. Data	27.514	59.892
	1988	0.507	0.386	0.666	ins. Data			0.720	0.488	1.064	ins. Data		
	1989	0.284	0.224	0.358	ins. Data			0.497	0.404	0.611	ins. Data		
	1990	0.375	0.213	0.662	ins. Data			0.472	0.147	1.512	ins. Data		
	1991	0.167	0.137	0.202	ins. Data			0.242	0.198	0.296	ins. Data		
	1992	0.456	0.370	0.562	9.056	8.752	9.372	0.629	0.468	0.847	7.743	6.388	9.386
	1993	0.467	0.366	0.597	ins. Data			0.825	0.559	1.217	11.338	7.932	16.206
	1994	0.172	0.124	0.238	ins. Data			0.331	0.254	0.431	ins. Data		
	1995	0.400	0.333	0.482	ins. Data			0.595	0.469	0.756	ins. Data		
	1996	0.190	0.159	0.228	14.059	12.219	16.175	0.336	0.241	0.468	14.059	12.219	16.175
	1997	0.563	0.371	0.856	18.062	16.653	19.589	1.014	0.572	1.798	18.062	16.653	19.589
	1998	0.260	0.200	0.336	16.324	15.029	17.732	0.394	0.252	0.616	16.324	15.029	17.732
	1999	0.450	0.314	0.647	12.181	11.042	13.439	0.704	0.501	0.989	12.181	11.042	13.439
Port Lambton	Mean												
	1987	0.543	0.463	0.637	61.185	44.182	84.733	0.816	0.701	0.951	124.221	80.196	192.415
	1988	0.339	0.283	0.406	28.600	24.039	34.026	0.467	0.375	0.583	36.947	31.106	43.884
	1989	0.287	0.237	0.346	22.999	17.162	30.820	0.379	0.306	0.469	31.371	23.651	41.610
	1990	ins. Data			8.896	4.828	16.390	ins. Data			14.050	8.777	22.490
	1991	0.135	0.111	0.165	9.132	6.332	13.171	0.177	0.144	0.217	10.774	7.515	15.448
	1992	0.430	0.353	0.524	8.728	6.299	12.095	0.461	0.346	0.614	11.894	8.021	17.636
	1993	0.291	0.228	0.372	9.866	7.689	12.660	0.448	0.365	0.551	12.598	9.160	17.326
	1994	0.232	0.221	0.243	ins. Data			0.346	0.280	0.429	27.667	7.437	102.923
	1995	ins. Data			ins. Data			0.353	0.334	0.374	11.447	8.487	15.439
	1996	0.125	0.104	0.151	19.362	15.608	24.019	0.163	0.126	0.212	20.584	16.797	25.224
	1997	0.111	0.076	0.161	29.237	25.528	33.486	0.144	0.103	0.200	29.237	25.528	33.486
	1998	0.135	0.102	0.178	30.634	22.520	41.672	0.085	0.070	0.104	30.634	22.520	41.672
1999	0.369	0.207	0.656	21.688	18.820	24.994	0.508	0.292	0.884	21.688	18.820	24.994	

CI Confidence Interval  
ins. Data insufficient data  
N.A. Not Available

# **Polyaromatic Hydrocarbons**

Pt. Edward	Fluorene						Phenanthrene					
	dissolved			particulate			dissolved			particulate		
	ng/L (n)	Lower 90% CI	Upper 90% CI	ng/g (n)	Lower 90% CI	Upper 90% CI	ng/L (n)	Lower 90% CI	Upper 90% CI	ng/g (n)	Lower 90% CI	Upper 90% CI
Mean												
1987	0.836	0.442	0.663	ins. Data			1.32	1.09	1.60	32.29	27.02	38.60
1988	0.507	0.433	0.565	ins. Data			2.75	0.62	12.15	76.49	70.15	83.41
1989	0.284	0.430	0.500	ins. Data			2.92	2.45	3.49	112.85	60.35	211.04
1990	0.375			ins. Data			2.02	0.14	28.92	ins. Data		
1991	0.167	0.128	0.187	ins. Data			0.46	0.26	0.83	29.01	14.30	58.85
1992	0.456	0.274	0.351	ins. Data			1.29	0.94	1.75	40.91	19.45	86.06
1993	0.467	0.310	0.442	ins. Data			2.01	1.43	2.81	92.50	49.16	174.04
1994	0.172			ins. Data			1.09	0.36	3.26	103.54	52.57	203.93
1995	0.400	0.279	1.39	47.2	19.9	112	2.31	1.34	3.96	84.77	76.77	93.60
1996	0.190			ins. Data			0.83	0.35	1.99	61.46	43.88	86.09
1997	0.563			7.32	6.39	8.38	0.98	0.67	1.42	76.75	60.24	97.79
1998	0.260			7.20	6.41	8.09	0.40	0.27	0.60	68.23	61.05	76.26
1999	0.450			5.16	4.75	5.62	1.73	1.31	2.28	55.82	49.08	63.49
<b>Port Lambton</b>												
Mean												
1987	0.543	0.348	0.647	57.6	34.1	97.3	1.59	1.31	1.92	243.75	158.39	375.13
1988	0.339	0.383	0.475	30.4	20.5	45.3	1.80	0.57	5.67	238.38	174.39	325.85
1989	0.287	0.294	0.412	22.1	13.3	36.6	1.06	0.88	1.28	127.62	96.47	168.83
1990	ins. Data			ins. Data			1.75	0.23	13.33	139.95	44.75	437.66
1991	0.135	0.129	0.151	11.3	3.28	39.1	0.52	0.25	1.07	86.20	44.50	166.97
1992	0.430	0.329	0.450	ins. Data			1.56	0.46	5.35	110.87	67.88	181.11
1993	0.291	0.276	0.330	ins. Data			1.85	1.58	2.16	76.55	66.97	87.50
1994	0.232			ins. Data			0.96	0.45	2.06	98.75	83.11	117.35
1995	ins. Data			74.6	25.2	220	3.75	0.46	30.28	80.84	67.40	96.97
1996	0.125			9.88	9.16	10.6	0.36	0.15	0.84	78.17	69.88	87.45
1997	0.111			16.3	13.8	19.3	0.39	0.27	0.57	90.79	68.53	120.29
1998	0.135			12.8	10.9	15.0	0.16	0.14	0.19	107.88	95.74	121.55
1999	0.369			10.7	9.76	11.7	1.24	0.86	1.79	99.83	88.13	113.08

CI Confidence Interval  
ins. Data insufficient data  
N.A. Not Available



# **Polyaromatic Hydrocarbons**

Polycyclic Aromatic Hydrocarbons													
Pt. Edward		Fluoranthene						Pyrene					
Mean	ng/L (n)	dissolved		ng/g (n)	particulate		ng/L (n)	dissolved		ng/g (n)	particulate		
		Lower 90% CI	Upper 90% CI		Lower 90% CI	Upper 90% CI		Lower 90% CI	Upper 90% CI		Lower 90% CI	Upper 90% CI	
1987	0.836	0.35	1.08	51.27	38.11	68.96	1.533	1.297	1.812	33.442	26.240	42.679	
1988	0.507	1.06	1.92	175.76	140.04	220.58	0.954	0.601	1.515	115.143	109.368	121.223	
1989	0.284	0.21	0.47	188.37	93.06	381.28	0.816	0.638	1.045	144.301	78.913	263.871	
1990	0.375	0.47	0.83	70.16	48.02	102.50	ins. Data			17.357	11.698	25.754	
1991	0.167	0.93	1.52	32.82	21.29	50.58		0.316	0.231	0.433	10.851	6.680	17.626
1992	0.456	1.67	2.24	100.21	35.90	279.75	0.604	0.440	0.829	65.079	24.327	174.099	
1993	0.467	0.56	1.43	139.69	122.40	159.42	1.261	1.092	1.456	102.919	92.154	114.942	
1994	0.172	0.51	1.52	99.18	67.98	144.71	1.164	0.761	1.781	105.618	39.033	285.790	
1995	0.400	0.49	0.69	66.50	56.92	77.69	0.610	0.374	0.994	ins. Data			
1996	0.190	0.41	0.56	74.34	60.92	90.73	0.436	0.306	0.621		54.756	43.188	69.423
1997	0.563	0.43	0.66	91.95	74.30	113.79	0.443	0.298	0.660	72.136	63.921	81.408	
1998	0.260	0.91	1.68	83.11	73.24	94.30	0.816	0.550	1.212	76.628	56.796	103.384	
1999	0.450			69.57	62.20	77.82	1.206	0.840	1.731	61.060	53.176	70.113	
Port Lambton													
Mean													
1987	0.543			211.08	135.78	328.13	2.655	2.094	3.364	185.139	122.465	279.888	
1988	0.339	0.22	0.65	316.49	200.37	499.90	1.030	0.644	1.648	255.339	171.450	380.273	
1989	0.287	0.43	0.63	147.41	105.28	206.40	0.822	0.596	1.135	131.641	91.849	188.670	
1990	ins. Data	0.23	0.50	98.34	63.01	153.48	ins. Data			34.576	20.752	57.607	
1991	0.135	0.48	0.99	83.69	41.75	167.78		0.557	0.359	0.864	57.074	27.921	116.667
1992	0.430	0.67	1.40	175.49	96.52	319.08	0.819	0.609	1.102	148.425	80.316	274.290	
1993	0.291	1.49	1.91	80.50	67.11	96.58	1.359	1.200	1.539	72.756	61.185	86.514	
1994	0.232	0.37	0.64	89.95	68.90	117.44	0.825	0.574	1.187	96.042	73.326	125.797	
1995	ins. Data	0.70	2.39	66.79	54.08	82.50	1.391	0.809	2.391	33.028	14.629	74.567	
1996	0.125	0.38	0.59	68.79	59.01	80.18	0.659	0.545	0.795	66.570	57.930	76.498	
1997	0.111	0.28	0.44	90.51	81.44	100.60	0.449	0.385	0.524	87.850	79.211	97.432	
1998	0.135	0.23	0.35	97.01	84.92	110.84	0.753	0.581	0.975	97.745	85.708	111.472	
1999	0.369	0.80	1.19	95.44	76.11	119.69	1.213	1.033	1.424	69.138	61.424	77.822	

CI Confidence Interval  
ins. Data insufficient data  
N.A. Not Available

Industrial By-products												
Pt. Edward		Octachlorostyrene						Hexachlorobutadiene				
Mean	ng/L (n)	dissolved Lower 90% CI	Upper 90% CI	ng/g (n)	particulate Lower 90% CI	Upper 90% CI	ng/L (n)	dissolved Lower 90% CI	Upper 90% CI	ng/g (n)	particulate Lower 90% CI	Upper 90% CI
1987	0.023	0.018	0.028	ins. Data			0.076	0.018	0.327	ins. Data		
1988	ins. Data			ins. Data			0.015	0.013	0.018	ins. Data		
1989	ins. Data			ins. Data			ins. Data			ins. Data		
1990	ins. Data			ins. Data			ins. Data			ins. Data		
1991	ins. Data			ins. Data			0.013	0.012	0.015	ins. Data		
1992	ins. Data			ins. Data			ins. Data			ins. Data		
1993	ins. Data			ins. Data			ins. Data			ins. Data		
1994	ins. Data			ins. Data			ins. Data			ins. Data		
1995	ins. Data			ins. Data			ins. Data			ins. Data		
1996	ins. Data			ins. Data			0.233	0.033	1.63	0.520	0.385	0.702
1997	0.010	0.010	0.010	ins. Data			0.028	0.021	0.036	0.147	0.123	0.176
1998	ins. Data			ins. Data			0.023	0.015	0.033	0.185	0.149	0.230
1999	ins. Data			ins. Data			0.048	0.035	0.064	ins. Data		
Port Lambton												
Mean												
1987	ins. Data			22.8	14.9	34.9	1.213	0.415	3.55	192	81.8	451
1988	ins. Data			22.8	17.0	30.4	0.549	0.404	0.745	185	117	292
1989	ins. Data			12.6	7.54	21.2	0.779	0.399	1.52	155	42.4	569
1990	ins. Data			10.4	7.24	15.0	0.541	0.324	0.901	92.5	46.6	184
1991	ins. Data			12.0	7.76	18.5	0.362	0.297	0.441	83.5	55.9	125
1992	ins. Data			5.45	4.15	7.15	0.231	0.198	0.269	50.9	33.3	77.8
1993	ins. Data			5.48	3.31	9.06	0.253	0.209	0.307	62.9	29.9	132
1994	ins. Data			7.12	5.76	8.81	0.253	0.209	0.306	62.8	41.3	95.5
1995	ins. Data			10.5	7.08	15.5	0.298	0.230	0.385	72.2	49.4	106
1996	ins. Data			11.7	7.25	18.9	0.876	0.654	1.17	81.9	48.1	139
1997	ins. Data			12.3	8.25	18.4	0.340	0.227	0.508	43.7	37.1	51.5
1998	ins. Data			6.99	4.91	9.95	0.136	0.116	0.159	24.3	16.3	36.2
1999	ins. Data			6.44	4.21	9.85	0.116	0.108	0.126	10.8	7.983	14.7

CI      Confidence Interval  
ins. Data    insufficient data  
N.A.      Not Available

## Metals

Pt. Edward	Aluminum			Barium			Cadmium			Chromium			Cobalt		
Mean (dissolved)	µg/L	n	S.D.	µg/L	n	S.D.	µg/L	n	S.D.	µg/L	n	S.D.	µg/L	n	S.D.
1988	18.76	21	10	12.73	21	0.50	<0.10	21	0.0	0.30	21	0.10	0.10	21	0.00
1989	27.33	3	21	13.77	3	0.15	<0.10	3	0.0	0.23	3	0.06	0.10	3	0.00
1990	23.08	12	16	14.28	12	0.42	<0.10	12	0.0	0.27	12	0.13	0.15	12	0.05
1991	47.29	21	42	14.74	19	0.43	<0.10	21	0.0	0.27	21	0.10	0.10	21	0.00
1992	48.80	15	31	15.04	15	0.78	<0.10	15	0.0	0.33	15	0.22	0.10	15	0.00
1993	65.75	8	54	14.24	8	0.23	<0.10	8	0.0	0.23	8	0.05	0.10	8	0.00
1994	28.09	11	28	13.89	11	0.52	<0.10	11	0.0	0.40	11	0.23	0.10	11	0.00
1995	57.60	10	57	14.41	7	0.45	<0.10	10	0.0	0.51	10	0.39	0.11	10	0.03
1996	20.23	23	24	13.96	22	0.50	<0.10	23	0.0	0.27	23	0.16	0.14	23	0.07
1997	18.14	21	14	13.69	21	0.29	<0.10	21	0.0	0.20	21	0.00	0.10	21	0.00
1998	24.52	17	31	13.90	21	0.70	<0.10	21	0.0	0.21	21	0.03	0.10	21	0.02
1999	25.41	22	44	14.25	17	0.65	<0.10	17	0.0	0.22	17	0.06	0.13	17	0.07
Port Lambton															
Mean (dissolved)															
1988	39.24	14	557	12.85	25	0.43	<0.10	25	0.00	0.36	14	0.13	0.10	25	0.00
1989	38.59	25	22	14.23	22	0.38	0.11	22	0.04	0.40	11	0.51	0.13	22	0.05
1990	31.21	22	15	14.64	14	0.66	0.10	13	0.00	0.26	22	0.09	0.13	14	0.05
1991	61.04	14	20	14.91	21	0.83	<0.10	23	0.00	0.36	14	0.24	0.12	23	0.07
1992	43.24	23	38	15.07	25	0.45	<0.10	25	0.00	0.30	23	0.20	0.10	25	0.02
1993	60.50	25	29	14.71	19	0.43	<0.10	22	0.00	0.28	25	0.14	0.10	22	0.00
1994	53.44	22	45	14.58	16	0.60	<0.10	16	0.00	0.49	22	0.12	0.11	16	0.03
1995	87.12	16	51	14.74	13	1.33	<0.10	17	0.00	0.48	16	0.32	0.13	17	0.10
1996	46.04	17	80	14.24	23	0.62	<0.10	24	0.00	0.27	17	0.18	0.15	24	0.10
1997	26.33	24	62	14.04	21	0.49	<0.10	21	0.00	0.27	24	0.28	0.11	21	0.05
1998	22.90	21	34	14.03	20	0.50	<0.10	20	0.00	0.21	21	0.03	0.14	20	0.06
1999	19.17	20	18	14.32	18	0.53	<0.10	17	0.00	0.21	20	0.02	0.15	18	0.05
Det. Limit µg/L	0.20			0.20			0.1			0.20			0.10		
p value (student t)	0.010		31	0.000						0.027			0.008		

## Metals

Pt. Edward	Copper			Iron			Lithium			Manganese			Molybdenum		
Mean (dissolved)	µg/L	n	S.D.	µg/L	n	S.D.	µg/L	n	S.D.	µg/L	n	S.D.	µg/L	n	S.D.
1988	0.94	22	0.94	24.33	20	33.97	1.10	21	0.13	0.63	21	0.31	0.45	21	0.08
1989				26.67	3	28.87	1.60	12	0.25	0.73	8	0.30	0.42	3	0.10
1990	0.73	12	0.73	16.03	12	10.45	1.83	3	0.15	0.50	7	0.14	0.42	12	0.07
1991	0.75	21	0.75	20.69	21	19.01	1.89	21	0.11	0.61	21	0.28	0.46	21	0.08
1992	0.63	15	0.63	29.67	15	31.89	1.95	15	0.16	0.71	15	0.23	0.46	15	0.07
1993	0.64	7	0.64	14.10	8	14.67	1.86	8	0.11	0.59	8	0.16	0.48	8	0.05
1994	0.64	11	0.64	16.21	11	13.08	1.91	11	0.07	0.58	11	0.22	0.48	11	0.07
1995	0.74	10	0.74	40.56	10	42.21	1.73	10	0.29	1.04	10	0.72	0.45	10	0.12
1996	0.58	23	0.58	15.89	23	18.46	1.53	23	0.23	0.67	23	0.33	0.47	23	0.09
1997	0.55	21	0.55	17.50	21	14.41	1.50	21	0.18	0.59	21	0.32	0.44	21	0.04
1998	0.60	21	0.60	23.99	21	32.30	1.48	21	0.27	0.70	21	0.49	0.52	21	0.11
1999	0.47	17	0.47	32.39	17	66.55	1.38	17	0.48	0.73	17	0.55	0.38	17	0.20
Port Lambton															
Mean (dissolved)															
1988	1.24	25	0.71	39.29	25	35.90	1.17	25	0.15	1.06	25	0.79	0.41	25	0.18
1989	0.77	22	0.29	34.95	22	27.57	1.58	22	0.14	0.87	22	0.34	0.40	22	0.08
1990	0.95	14	0.44	19.57	14	13.23	1.84	14	0.17	0.73	14	0.28	0.39	14	0.13
1991	0.78	23	0.20	28.92	23	23.20	1.99	23	0.11	0.83	23	0.32	0.42	23	0.10
1992	0.80	25	0.30	26.20	25	20.10	1.96	25	0.18	0.82	25	0.44	0.43	25	0.06
1993	0.79	22	0.18	18.35	22	13.31	1.95	22	0.10	0.78	22	0.38	0.45	22	0.06
1994	0.78	16	0.18	21.88	16	9.75	1.94	16	0.13	0.73	16	0.22	0.46	16	0.05
1995	1.28	17	1.27	27.62	17	20.00	1.87	17	0.26	1.18	17	0.76	0.41	17	0.06
1996	1.46	24	1.87	20.10	24	15.73	1.51	24	0.25	0.79	24	0.45	0.42	24	0.10
1997	0.66	21	0.25	19.55	21	13.29	1.53	21	0.20	0.70	21	0.53	0.42	21	0.06
1998	0.78	20	0.43	24.67	20	19.47	1.50	20	0.50	0.62	20	0.32	0.49	20	0.09
1999	0.52	18	0.19	20.45	18	31.58	1.25	18	0.24	0.60	18	0.38	0.40	18	0.17
Det. Limit µg/L	0.20			0.40			0.10			0.10			0.10		
p value (student t)	0.004			0.210			0.093			0.003			0.000		

## Metals

Pt. Edward Mean (dissolved)	Nickel			Lead			Strontium			Vanadium			Zinc		
	µg/L	n	S.D.	µg/L	n	S.D.	µg/L	n	S.D.	µg/L	n	S.D.	µg/L	n	S.D.
1988	0.52	21	0.16	0.29	21	0.20	93.3	21	5.70	0.20	21	0.08	0.36	21	0.2839
1989	0.30	3	0.10	0.60	3	0.26	90.0	3	0.00	0.13	3	0.06	0.68	12	0.7849
1990	0.59	12	0.28	0.31	12	0.25	92.6	12	4.21	0.23	12	0.06			
1991	0.36	21	0.13	0.26	21	0.24	98.6	21	5.73	0.24	21	0.10	0.38	21	0.3145
1992	0.43	15	0.14	0.20	15	0.00	108.5	15	8.36	0.21	15	0.05	0.45	15	0.4033
1993	0.60	8	0.38	0.21	8	0.04	99.8	8	10.14	0.26	8	0.07	0.44	8	0.2326
1994	0.52	11	0.15	0.21	11	0.03	90.8	11	1.83	0.19	11	0.03	0.68	11	0.1888
1995	0.52	10	0.15	0.27	10	0.15	90.0	10	0.00	0.31	10	0.16			
1996	0.48	23	0.14	0.25	23	0.13	90.5	23	2.11	0.27	23	0.20	0.54	23	0.9375
1997	0.42	21	0.09	0.23	21	0.07	93.1	21	4.90	0.22	21	0.06	0.34	21	0.2186
1998	0.42	21	0.10	0.22	21	0.07	97.3	21	12.21	0.22	21	0.09	0.38	21	0.2448
1999	0.47	17	0.13	0.34	17	0.18	95.9	17	3.9	0.26	17	0.14	0.37	17	0.3687
<b>Port Lambton</b> Mean (dissolved)															
1988	0.56	25	0.14	0.41	25	0.35	94.7	25	15.27	0.23	25	0.09	0.43	25	0.3964
1989	0.51	22	0.16	0.35	22	0.22	93.1	22	6.56	0.25	22	0.10	0.82	22	1.5169
1990	0.60	14	0.28	0.35	14	0.26	94.9	14	6.79	0.27	14	0.09			
1991	0.49	23	0.32	0.28	23	0.23	99.7	23	5.54	0.27	23	0.08	0.41	23	0.2029
1992	0.51	25	0.15	0.21	25	0.04	103.6	25	5.35	0.23	25	0.05	0.42	25	0.169
1993	0.62	22	0.24	0.22	22	0.06	97.9	22	9.40	0.22	22	0.06	0.74	22	0.4065
1994	0.66	16	0.21	0.20	16	0.00	91.9	16	5.32	0.24	16	0.07	0.51	16	0.1879
1995	0.69	17	0.21	0.35	17	0.18	91.7	17	3.44	0.26	17	0.10	0.75	17	0.3693
1996	0.52	24	0.16	0.29	24	0.15	92.2	24	4.27	0.26	24	0.09	0.78	24	0.551
1997	0.41	21	0.18	0.25	21	0.09	93.2	21	4.21	0.22	21	0.06			
1998	0.44	23	0.11	0.23	20	0.07	96.1	20	6.94	0.22	20	0.05	0.65	20	0.8593
1999	0.42	18	0.11	0.27	18	0.11	95.8	18	4.27	0.22	18	0.08	0.24	18	0.085
Det. Limit µg/L	0.20			0.20			0.10			0.10			0.20		
p value (student t)	0.008			0.458			0.277			0.181			0.100		