THE NIAGARA RIVER
UPSTREAM/DOWNSTREAM PROGRAM
1986/87 - 2004/05

CONCENTRATIONS, LOADS, and TRENDS

by

R.B. Hill and P. Klawunn

Environment Canada
Water Quality Monitoring & Surveillance - Ontario

Locator # WQMS10-003
Contribution # 10-253

TABLE OF CONTENTS

TABLE OF CONTENTS iii

LIST OF TABLES v
LIST OF FIGURES v
LIST OF APPENDICES vii

EXECUTIVE SUMMARY 1

1.0 INTRODUCTION 3

2.0 THE UPSTREAM/DOWNSTREAM PROGRAM 4
  2.1 Overview 4
  2.2 Target Analytes 5

3.0 STATISTICAL METHODS AND DATA CALCULATIONS 7
  3.1 Calculation Of Mean Annual Concentrations/Loads Maximum Likelihood Estimation (MLE) Method 7
  3.2 Calculation Of Trends: The LIFEREG Model 7

4.0 RESULTS AND DISCUSSION 8
  4.1 Exceedences 12
  4.2 Trends 16
    4.2.1. Long Term Concentrations (1986/87 - 2004/05) 19
    4.2.2 Long Term Loadings (1986/87 - 2004/05) 21
    4.2.3 Recent Concentrations (1996/97 - 2004/05) 23
    4.2.4 Recent Loadings (1996/97 - 2004/05) 25
  4.3 Sources 27
  4.4 Modified Source Analysis 31

5.0 SUMMARY 34

6.0 ACKNOWLEDGEMENTS 40

REFERENCES 41

LIST OF TABLES

Table 1. Chemicals Analysed in the Niagara River Upstream/Downstream Program (1986/87 - 2004/05)

Table 2. Phase Distributions For Selected Niagara River Chemicals

Table 3a. Comparison of Upper 90% CI Concentrations with Most Stringent Agency Water Quality Criteria at FE

Table 3b. Comparison of Upper 90% CI Concentrations with Most Stringent Agency Water Quality Criteria at NOTL

Table 4. Trends in Niagara River Contaminant Concentrations and Loadings, 1986/87-2004/05

Table 5. Trends in Niagara River Contaminant Concentrations and Loadings, 1996/97-2004/05

Table 6. Statistically Significant MLE Ratios for Niagara River Contaminants

Table 7. Statistically Significant MLE Ratios for Niagara River Contaminants (Modified Confidence Interval)

Table 8. Status/Trend Summary for FE Concentrations

Table 9. Status/Trend Summary for NOTL Concentrations

Table 10. Status/Trend Summary for FE Loadings

Table 11. Status/Trend Summary for NOTL Loadings

LIST OF FIGURES

Figure 1. Niagara River Upstream/Downstream Program Sampling Locations

Figure 2: Niagara River Mean Annual Discharge (1986/87 - 2004/05)

Figure 3: Niagara River Suspended Particulate Matter Concentration

Figure 4: Recombined Whole Water MLE Dieldrin Concentrations (1986/87 - 2004/05)

LIST OF APPENDICES

(*NOTE: All appendices compiled as a separate document*)

Appendix A: Niagara River Protocol Changes - 1986/87 - 2004/05

Appendix B: Annual Mean Concentrations/Loads (and Associated 90% Confidence Limits) for the Upstream/Downstream Program Chemicals at FE Calculated Using the MLE

Appendix C: Annual Mean Concentrations/Loads (and Associated 90% Confidence Limits) for the Upstream/Downstream Program Chemicals at NOTL Calculated Using the MLE

Appendix D: Time Series Plots of the Concentrations of Upstream/Downstream Program Chemicals Showing Significant Trends Over the Period, 1986/87 - 2004/05

Appendix E: Time Series Plots of the Concentrations of Upstream/Downstream Program Chemicals Showing Significant Trends Over the Period, 1996/97 - 2004/05

Appendix F: Niagara River Downstream/Upstream Ratios

Appendix G: Niagara River Downstream/Upstream Ratios (Modified Confidence Interval)

Appendix H: Acronym Dictionary

EXECUTIVE SUMMARY

Contaminant data collected by the Niagara River Upstream/Downstream Program were analyzed to determine annual mean concentrations and loads, guideline exceedences, potential sources and trends over both the 1986/87-2004/05 and 1996/97-2004/05 time periods. For the analysis, consistent methods were used for calculating:

- *annual* mean concentrations and loads using the Maximum Likelihood Estimation method; and,
- changes/trends in the concentrations and loads using a statistical model and implemented using the SAS LIFEREG procedure.

Chemicals were divided into classes (eg. chlorobenzenes, organochlorine pesticides, etc.) and discussed under these headings.

A comparison of the recombined whole water concentrations for those chemicals having water quality criteria, to the strictest agency criteria indicated that a number of the chemicals still exceeded their criteria. This represents a possible threat to aquatic life and the real or potential impairment of beneficial uses.

Concentrations/loads calculated by the LIFEREG MODEL were used to determine the change between base years (usually 1986/87 and 1996/97) and 2004/05. These results were then used to calculate an index of change over the two periods. Although the pattern of change was different for different chemicals, the results showed that most of the chemicals for which a trend was discernible exhibited a significant decrease over the nineteen-year period, but that this trend may be leveling off for many of the chemicals in more recent years. The trend for several chemicals, particularly some PAHs, trace metals, and neutral herbicides, actually increased while other chemicals exhibited no significant change/trend.

The data showed that contaminant concentrations and, more particularly, loadings, are strongly influenced by both phase distribution and soluble particulate matter concentration. In addition, data analysis in this report indicates that Niagara River sources continue to provide inputs for a number of compounds such as the chlorobenzenes and industrial by-products while the principal source of others appear to be upstream or Great Lakes basin-wide.

Finally, while considerable progress has been made in reducing the concentrations of toxic contaminants in the Niagara River, much work is left to be done.

1.0 INTRODUCTION

The Niagara River, responsible for more than 85% of the total tributary inflow to Lake Ontario (Eadie and Robertson 1976) and about 50% of all incoming fine grained sediment (Kemp and Harper 1976), has a significant influence on the lake. Because of this influence, Environment Canada established a monitoring station in 1975 at the mouth of the Niagara River at Niagara-on-the-Lake (NOTL) to estimate the annual chemical loads and changes/trends in these loads from the river to Lake Ontario. Love Canal, and the publication of numerous reports on the magnitude of the hazardous waste site problem on the U.S. side of the river in the late ‘70s, further heightened Environment Canada’s concern about the input of chemicals to the river and, subsequently, to Lake Ontario. A second station was established at the head of the Niagara River at Fort Erie (FE) in October, 1983 to estimate the loads of chemicals to the river from Lake Erie. The “differential load”, obtained by subtracting the loads of chemicals measured at FE from those measured at NOTL, provided an estimate of the chemical load entering the river from Niagara River sources.

This Upstream/Downstream Program, as it became known, was a key component of the Niagara River Long Term Monitoring Plan recommended by the Niagara River Toxics Committee (NRTC 1984). It was formally incorporated into the Niagara River “Declaration of Intent” signed by the Four Parties - Environment Canada, the United States Environmental Protection Agency (Region II), the Ontario Ministry of the Environment, and New York State Department of Environmental Conservation - in February, 1987. Thus, what had begun as an Environment Canada initiative became a component of the Niagara River Toxics Management Plan (NRTMP).

The overall goal of the NRTMP is to achieve significant reductions of toxic chemical pollutants in the Niagara River and the purpose of the Upstream/Downstream Program, in both its original and NRTMP contexts, has been to report on concentrations, loadings and trends of contaminants in the river, specifically in relation to implemented control measures.

In 1996, the Four Parties reaffirmed their commitment to the NRTMP with the signing of the “Letter of Support” which identified new measurable milestones including:

- Maintain downward trends in concentrations of chemicals that exceed U.S. or Canadian water and sediment criteria, that cause fish consumption advisories, and that are detected in sediment cores.
- Achieve downstream concentrations that are statistically equivalent to those upstream.
- Maintain downward trends in concentrations of chemicals that are associated with particular sources, so that remediation program success can be demonstrated

While the NRTMP has primarily focused on 18 “Priority Toxics”, the Niagara River Upstream/Downstream Program reports on a much larger suite of compounds made up of organics, trace metals, nutrients, and major ions in both the dissolved and particulate phase. This report summarizes the Upstream/Downstream Program chemical data, including the 18 "Priority Toxics", collected between 1986/87 and 2004/05. In addition, the report also summarizes these same data over the shorter 1996/97 to 2004/05 time period in order to compare and contrast both long-term and more "recent" trends.

Ultimately, the report:

- summarizes the changes/trends in the concentrations/loads of the Upstream Downstream Program chemicals over the periods 1986/87 to 2004/05 and 1996/97 - 2004/05, at NOTL and FE stations;
- summarizes the *annual* mean concentrations and loads of the Upstream/Downstream Program chemicals for these same periods, at NOTL and FE stations;
- estimates the annual mean recombined whole water (RWW) concentrations and their 90% confidence limits at both stations, and compares the upper 90% confidence level RWW concentrations to water quality objectives;
- briefly discusses the most probable sources of the Upstream/Downstream Program chemicals;
- briefly discusses possible reasons for the observed changes; and
- briefly discusses the implications of the Upstream/Downstream Program results for Lake Ontario and the Niagara River, specifically, by comparing the annual mean whole water concentrations to water quality objectives.

It should also be emphasized that this report utilizes consistent methods for calculating the following:

- changes/trends in the concentrations and loads of Upstream/Downstream chemicals over the period of record, for both the dissolved and particulate phases, at both NOTL and FE using a statistical model developed by El-Shaarawi and Al-Ibrahim (1996) and implemented using the SAS LIFEREG procedure; and,
- *annual* mean concentrations and loads of Upstream/Downstream Program chemicals, for both dissolved and particulate phases, at both NOTL and FE using the Maximum Likelihood Estimation method (MLE; El-Shaarawi 1989).

2.0 THE UPSTREAM/DOWNSTREAM PROGRAM

2.1 Overview

The Upstream/Downstream Program measures the concentrations of chemicals in both dissolved and particulate phases in water at the head [Fort Erie (FE)] and mouth [Niagara-on-the-Lake (NOTL)] of the Niagara River (Figure 1). Program results are reported based upon Environment Canada's fiscal year which runs from April 1 to March 31. Over the eleven-year period 1986/87 -1996/97, sampling was conducted weekly while bi-weekly samples were collected between 1997/98 - 2004/05. Sampling times at the two stations are offset by approximately 15-18 hours to allow for the travel time of water between the head and mouth of the river. While this does not account for the storage and release of water from the Robert Moses and Sir Adam Beck power plant reservoirs, it does better approximate the river's hydrodynamic regime. Large-volume, 24-hour time-integrated dissolved phase and particulate phase water samples for organic contaminants are collected using a submersible pump, intake line, and Westfalia centrifuge assembly while grab samples for whole water trace metal analyses are collected from the intake line.

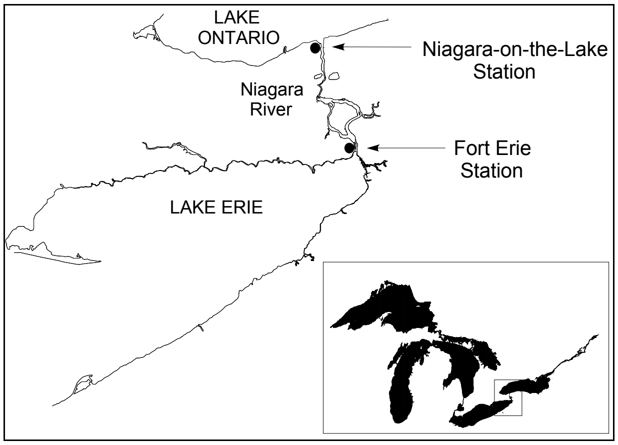


Figure 1. Niagara River Upstream/Downstream Sampling Locations

Daily flow data are obtained from the Co-ordinating Committee on Great Lakes Basin Hydraulic and Hydrologic Data. Loads for both the dissolved and suspended particulate phases are calculated using the chemical concentrations, river flows and suspended particulate matter (SPM) concentrations.

Sampling procedures, analytical methodologies, and quality assurance/control for the Upstream/Downstream Program have been documented thoroughly (NRAP 1992; NRSP 1995; Data Interpretation Group 1997; Data Interpretation Group 1999, NRAP 2000, NRSP 2003, SOP 06-6001; Hill & Klawunn (2009)). These protocols, developed and agreed to by the Four Parties, include the requirement for regular audits of Environment Canada field and laboratory operations. The purpose of the audits is to ensure that the protocols are being followed by Environment Canada's field and laboratory staff. The program was designed, and has been operated, by a single agency (Environment Canada) ensuring the consistency of field and laboratory work and data management. Four Party audits were conducted in 1988, 1991, 1993, 1997, 2000, and most recently in 2005. In each case, the audit teams concluded that the procedures generally adhered to those described in the sampling and analytical protocol documents and should, therefore, result in the generation of data of acceptable quality. A summary of field and laboratory protocol changes can be found in Appendix A.

2.2 Target Analytes

The list of chemicals analysed in the Niagara River Upstream/Downstream Program has undergone changes over the 1986/87 to 2004/05 period. The reasons for these changes are outlined below. Furthermore, detection limits over this period changed as improvements were made to analytical methods and instrumentation. Despite these improvements, concentrations of many chemicals, particularly organic chemicals, measured in the Niagara River are still often below the sensitive analytical detection limits used to measure them.

In some cases, results show that certain compounds, like toxaphene, chlorophenols, and dioxins were always below the practical detection limit (PDL) in both phases and/or at both stations; consequently, their analysis was discontinued (note that Niagara River dioxins, chlorophenols, and toxaphene are still monitored through the Ontario Ministry of the Environment's Niagara River Mussel Biomonitoring Program). In other cases, the analytical method was not sufficiently sensitive (i.e. mercury in water) or there has been evidence of ongoing contamination problems during sampling and analysis (i.e. mercury and PCB in water and phthalates in water and sediment) and therefore analytical results were suspect. In the case of volatile organic compounds (VOCs), few compounds were above the PDL or exceeded water quality criteria and, perhaps more importantly, quantifying loadings and sources was very difficult due to significant losses attributed to the violent actions of water moving over Niagara Falls.

For these reasons, this report will not focus on discontinued analytes whose results, as described above, can be found in previous Upstream/Downstream reports; instead, it will concentrate on the compounds which remain in the suite currently investigated by the Niagara River Upstream/Downstream Monitoring Program (Table 1).

Table 1. Chemicals Analysed in the Niagara River Upstream/Downstream Program (1986/87 - 2004/05)

Chlorobenzenes:		
1,2-Dichlorobenzene	1,3-Dichlorobenze	1,4-Dichlorobenzen
1,2,3,4-Tetrachlorobenzene	1,2,3-Trichlorobenzene	1,2,4-Trichlorobenzene
1,3,5-Trichlorobenzene	Hexachlorobenzene	Pentachlorobenzene
Industrial By-Products:		
Hexachlorobutadiene	Hexachlorocyclopentadiene	Octachlorostryene
Neutral Herbicides:		
Atrazine	Metolachlor	
Organochlorine Pesticides and PCBs:		
Aldrin	α-Chlordane	γ-Chlordane
p,p-DDD	p,p-DDE	o,p-DDT
p,p-DDT	Dieldrin	α-Endosulfan
β-Endosulfan	Endrin	Endrin Aldehyde
α-HCH	γ-HCH	Heptachlor
Heptachlor Epoxide	Methoxychlor	Mirex
PCB (Total)	Photo-mirex	
PAHs:		
1-Methylnaphthalene	2-Methylnaphthalene	β-chloronapthalene
Acenaphthalene	Anthracene	Benz(a)anthracene
Benzo(a)pyrene	Benzo(bk)fluoranthene	Benzo(ghi)perylene
Chrysene/Triphenylene	Dibenzo(ah)anthracene	Fluoranthene
Fluorene	Indeno(123cd)pyrene	Naphthalene
Phenanthrene	Pyrene	
Trace Metals:		
Aluminum	Antimony	Arsenic
Barium	Beryllium	Cadmium
Chromium	Cobalt	Copper
Iron	Lead	Lithium
Manganese	Mercury	Molybdenum
Nickel	Selenium	Silver
Strontium	Vanadium	Zinc

3.0 STATISTICAL METHODS AND DATA CALCULATIONS

3.1 Calculation Of Mean Annual Concentrations/Loads Maximum Likelihood Estimation (MLE) Method

Originally, the Upstream/Downstream Program reported estimates of the annual mean concentrations and loads with their 90% confidence limits based upon the Maximum Likelihood Estimation method (MLE) (El-Shaarawi 1989) for chemicals having at least 3 “trace” values; however, as detection limits improved, a revised MLE method requiring at least 3 or more values above the PDL (Kuntz & Klawunn (2005) and Hill & Klawunn (2009)) was adopted by the Program. MLE results for this report are based upon the revised method.

For the purposes of this report, data was categorized as follows:

- “measured” (i.e., values above the practical detection limit);
- “trace” (i.e., values below the practical detection limit, but still quantified);
- “censored” (i.e., values below the practical detection limit, and not quantified); and,
- missing values (due to instrument failure or other reasons).

In addition, this report uses the paired contaminant concentration and SPM concentration for each individual sample (rather than the annual means) along with annual mean discharge to calculate the annual mean particulate phase loads as outlined in recent Upstream/Downstream Program reports (Kuntz & Klawunn, 2005; Hill & Klawunn, 2009) which provides a more accurate concentration and loading estimate.

3.2 Calculation Of Trends: The LIFEREG Model

To determine trends over time with known confidence for measured chemicals, a statistical procedure was developed that dealt with “censored” and missing data, auto-correlation and seasonality, as well as changing analytical limits of detection (El-Shaarawi and Al-Ibrahim 1996). A detailed description of the model was provided in the previous Niagara River Upstream/Downstream trend report (Williams et al., 2000); however, in essence, the model assesses the significance of the components: seasonality, trend, and unstructured variability (i.e. errors) which contribute to data variability. The model then determines whether a trend is present, whether the trend is statistically significant, and the shape of the trend.

The model was run individually on each of the chemicals, in each phase (whole water for metals), at both stations, for both the 1986/87 - 2004/05 and 1996/97 - 2004/05 periods. Contaminant concentrations, SPM concentrations and river flow were always included as covariates.

It is important to note that the model’s reported percent change between the base year (1986/87 for most chemicals in the “long term” analysis and 1996/97 for the “recent”) and 2004/05 was based on the *annual means estimated by the model* (i.e., the central tendencies of the model) running it over the entire period of record for which data were available. As a result, these means are not directly comparable to, nor will they be the same as, the means calculated for each year individually using the MLE method and reported in the Niagara River Upstream/Downstream Monitoring Program Final Reports (Appendices B & C).

4.0 RESULTS AND DISCUSSION

In 1986, the Four Parties signed the “Declaration Of Intent” with the goal of significantly reducing toxic chemical pollutants from point and non-point sources to the Niagara River taking into account applicable water quality and drinking water standards. Approximately 10 years later, the Four Parties signed the “Letter of Support” with the goals of maintaining downward trends in toxic chemical concentrations and achieving downstream concentrations that are statistically equivalent to those upstream. In both cases, the Upstream/Downstream Program was identified as one of the primary means of determining toxic chemical concentrations and loadings, evaluating reductions, and reporting progress. Given the original goals and objectives of both the “Declaration Of Intent” and “Letter Of Support”, it seems most appropriate to discuss the monitoring results in the contexts of “Exceedences” of guidelines, “Trends”, and “Sources”.

Before presenting the results a few points should be emphasized. First, as previously stated, reported percent changes in the long and short term trends are based on the *annual means estimated by the model*; consequently, they are not directly comparable to, nor will they be the same as, the means calculated for each year individually using the MLE method.

Secondly, the percent change in the long and short term trends applies to each station independently and provides no information on the magnitude of the change at either station in absolute terms. For example, concentrations at FE may change from 0.1 to 0.05 ng/L, and those at NOTL from 10 to 5 ng/L. Both represent a 50% decrease, but they are vastly different in absolute terms. A 50% decrease at FE, therefore, does not necessarily translate into a 50% decrease at NOTL (although it may contribute to the overall decrease). That is, comparing the percent change at the two stations is rather meaningless without some indication of what the starting points were at each station.

Thirdly, because the Niagara River Program examines concentrations and loadings in both the dissolved and particulate phases, it becomes apparent that some compounds partition disproportionately in one phase versus the other. This is primarily due to the water partition coefficient of each individual compound, which is a measure of the compound’s physical/chemical properties, including solubility. Table 2 shows the mean phase distribution for each of the Niagara River compounds based upon data from 1986/87 to 2004/05.

Table 2. Phase Distribution For Selected Niagara River Chemicals

Chemical	FE			NOTL	
	% Dissolved	% Particulate		% Dissolved	% Particulate
Chlorobenzenes					
1,2-Dichlorobenzene	99	1		98	2
1,3-Dichlorobenzene	99	1		98	2
1,4-Dichlorobenzene	98	2		96	4
1,2,3,4-Tetrachlorobenzene	100	0		92	8
1,2,3-Trichlorobenzene	100	0		96	4
1,2,4-Trichlorobenzene	97	3		94	6
1,3,5-Trichlorobenzene	98	2		94	6
Hexachlorobenzene	81	19		50	50
Pentachlorobenzene	93	7		79	21
Industrial By-products					
Hexachlorobutadiene	60	40		84	16
Hexachlorocyclopentadiene	100	0		84	16
Octachlorostyrene	*n/a*	*n/a*		12	88
Neutral Herbicides					
Atrazine	100	0		100	0
Metolachlor	94	6		94	6
OC Pesticides & PCBs					
Aldrin	0	100		0	100
α-Chlordane	44	56		53	47
γ-Chlordane	59	41		69	31
p,p-DDD	51	49		71	29
p,p-DDE	37	63		46	54
o,p-DDT	26	74		30	70
p,p-DDT	24	76		17	83
Dieldrin	96	4		95	5
Endrin	98	2		97	3
Endrin Aldehyde	0	100		*n/a*	*n/a*
α-Endosulfan	98	2		94	6
β-Endosulfan	66	34		73	27
α-HCH	100	0		99	1
γ-HCH	100	0		99	1
Heptachlor	*n/a*	*n/a*		0	100
Heptachlor Epoxide	99	1		99	1
Mirex	0	100		0	100
Methoxychlor	17	83		22	78
*PCB (Total)***	0	100		0	100
Photomirex	*n/a*	*n/a*		*n/a*	*n/a*

Table 2 (cont.). Phase Distribution For Selected Niagara River Chemicals

Chemical	FE			NOTL	
	% Dissolved	% Particulate		% Dissolved	% Particulate
PAHs					
1-Methylnaphthalene	91	9		87	13
2-Methylnaphthalene	93	7		89	11
Acenaphthylene	84	16		74	26
Anthracene	26	74		42	58
Benz(a)anthracene	12	88		12	88
Benzo(a)pyrene	10	90		10	90
Benzo(bk)fluoranthene	11	89		9	91
Benzo(g,h,i)perylene	11	89		11	89
Chrysene/Triphenylene	21	79		18	82
Dibenzo(a,h)anthracene	4	96		16	84
Fluoranthene	36	64		34	66
Fluorene	87	13		83	17
Indeno(1,2,3-cd)pyrene	11	89		12	88
Naphthalene	59	41		56	44
Phenanthrene	64	36		64	36
Pyrene	26	74		35	65

** Trace metal samples are analysed in whole water*

*** PCB and Mercury values based on sediment contribution only (field blank studies indicate majority of dissolved phase concentration is due to background contamination)*

While Table 2 indicates that some compounds come close to an even split between phases (or even an approximate 60/40 split), most tend to partition disproportionately in one phase or the other. In fact, many Niagara River compounds show phase distribution ratios of 70/30 or higher and several are only found in one phase. Atrazine, for example, is only found in the dissolved phase while Mirex is only found in the particulate phase. As a result, the bulk of the Discussion section will focus on the predominant phase for each compound. In the case of trace metals, samples are collected and analysed as “whole water” (with the exception of Mercury); therefore, results and discussion will be presented accordingly. As mentioned, concerns over contaminant issues in dissolved phase Mercury mean that only particulate phase results will be discussed for this compound.

Given the partitioning tendencies for various compounds, it’s important to understand the flow and suspended sediment regime of the Niagara River. This is particularly true for particulate phase loadings which are dependent on both the SPM concentrations and the flow; however, low dissolved phase concentrations can also have a significant impact on loadings due to the high volume of Niagara River flow. Figure 2 illustrates both the magnitude and consistency of the Niagara River discharge over the 1986/87 – 2004/05 time period. Interestingly, SPM concentrations have undergone a notable decline during this time (Figure 3) which should, intuitively, lead to a corresponding decline in contaminant concentrations, particularly for those found predominately in the particulate phase; however, results in this report illustrate that this is not always true as there are cases where contaminant concentrations have increased over the period of record.

Finally, some mention should be made of how well the upstream and downstream stations represent actual conditions in the river. Investigations conclude that samples collected at the Fort Erie station are representative of the water in eastern Lake Erie and that effluent from Smoke Creek and the Buffalo River do not mix with water in the upper part of the Niagara River (Ad Hoc Group on Physical Limnology and Hydraulics 1989;Williams et al 2003); however, there is some evidence that the upstream station may be influenced by sources on the Canadian side of the Niagara River upstream and close to the FE station (Williams et al, 2000).

Figure 2. Niagara River Mean Annual Discharge (1986/87 - 2004/05)

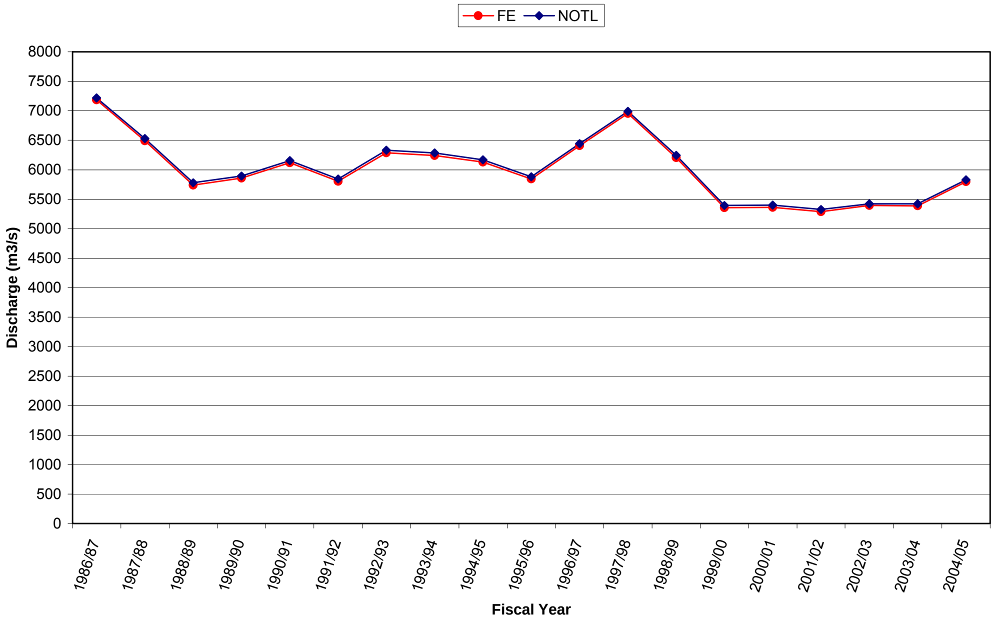
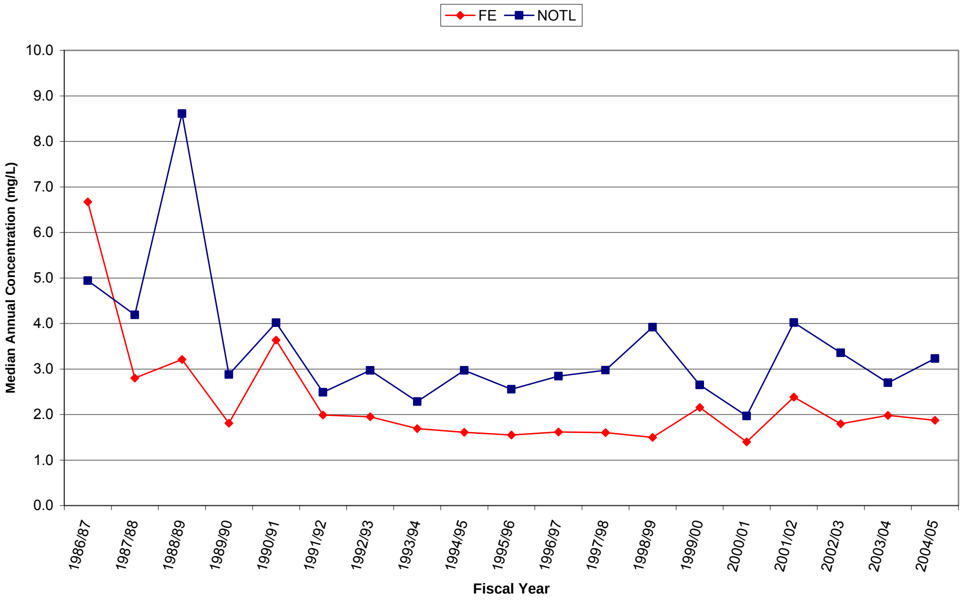


Figure 3. Niagara River Suspended Particulate Matter Concentration



Downstream, a study funded by Environment Canada (Green/Seastar, 1988) indicated that the distribution of contaminants in the Niagara River at Niagara-on-the-Lake is homogeneous and significant mixing of the Niagara River as it passes over the falls and through the rapids and whirlpools eliminate any of the nearshore effects observed at the upstream station. It should be noted however, that, while there have not been any definitive source inputs identified along the lower reach of the river, any contaminant inputs downstream of the rapids would not be well mixed and would tend to flow along the shoreline from which they were released.

4.1 Exceedences

In order to help the Four Parties meet the “Letter of Support” goal of achieving “ambient water quality that will protect human health, aquatic life, and wildlife”, the Niagara River Upstream/Downstream Monitoring Program is a key component used to identify toxic chemical concentrations that exceed water quality guidelines.

The annual mean concentrations and loads for each chemical in both the dissolved and particulate phases calculated using the MLE have been summarized for NOTL and FE under separate cover in Appendices B and C, respectively. The particulate phase concentrations are given both as weight of contaminant per weight of particulate and equivalent water concentration (EWC), the latter of which were calculated by multiplying the particulate phase concentration of the contaminant by the water column SPM concentration. The EWC is needed to calculate the recombined whole water (RWW) concentrations (i.e., dissolved + particulate phase) which can then be compared with water quality criteria and used to determine annual mean total loads.

For the purpose of this report, the upper 90% confidence interval for recombined whole water concentrations (dissolved plus particulate phases) were compared to the current most stringent agency criterion (Tables 3a and 3b) and exceedences were indicated by bold highlighted numbers. Using the upper 90% confidence interval is a more conservative approach to assess criteria exceedences than using the mean.

The current “most stringent agency criterion” cited in Tables 3a and 3b were taken from the following sources:

1. Canadian Council of Ministers of the Environment (CCME). “CEQG Online”. Canadian Environmental Quality Guidelines. 2009. CCME. July 14, 2009. < http://ceqg-rcqe.ccme.ca/>.

2. IJC: (1) Specific Objectives. Annex 1 of the Great Lakes Water Quality Agreement of 1978, as amended 1987.

3. NY State: Division of Water Technical and Operational Guidance Series (1.1.1), June 1998. New York State Department of Environmental Conservation, Albany, NY.

4. Ontario MOE: (1) Water Management Policies, Guidelines, Provincial Water Quality Objectives. July 1994.

5. U.S. EPA: National Recommended Water Quality Criteria. Office of Science and Technology, Washington, DC. May 21, 1999.

Table 3a. Comparison of Upper 90% CI Concentrations with Most Stringent Agency Water Quality Criteria at FE

				Upper 90% Confidence Interval Concentration																		
	Criteria	Units	Agency	86-87	87-88	88-89	89-90	90-91	91-92	92-93	93-94	94-95	95-96	96-97	97-98	98-99	99-00	00-01	01-02	02-03	03-04	04-05
CHLOROBENZENES																						
1,2-Dichlorobenzene	3000	ng/L	NYSDEC	0.6428	0.4241	0.4111	0.5869	0.3931	0.2324	0.3414	0.4223	0.2808	0.1745	0.2469	0.4519	0.2163	0.2076					
1,3-Dichlorobenzene	2500	ng/L	MOE	0.2559	0.3000	0.2932		0.2272		0.2689					0.2349	0.1228	0.4929					
1,4-Dichlorobenzene	4000	ng/L	MOE	1.0751	1.1200	1.2900	1.7951	1.2032	1.1811	1.1001	1.0689	0.9094	0.6351	0.6921	0.6736	0.4854	0.7792	0.7058	0.4422	0.3209	0.2475	
1,2,3-Trichlorobenzene	900	ng/L	MOE	0.0453	0.0563	0.0453	0.0436	0.0370	0.0297	0.0279	0.0475	0.0192	0.0119	0.0264	0.0274	0.0101	0.0147	0.0140	0.0118	0.0064	0.0102	0.0162
1,2,4-Trichlorobenzene	500	ng/L	MOE	0.5237	0.3129	0.1662	0.1476	0.1862	0.1185	0.1011	0.1347	0.0652	0.0696	0.0463	0.0480	0.0482	0.0648	0.0570	0.0258	0.0184	0.0267	0.0266
1,3,5-Trichlorobenzene	650	ng/L	MOE	0.0277								0.0125			0.0169	0.0134	0.0109	0.0086				
1,2,3,4-Tetrachlorobenzene	100	ng/L	MOE	0.0254	0.0334	0.0304	0.0280	0.0245		0.0201	0.0368	0.0159	0.0182		0.0259	0.0129	0.0123	0.0115	0.0066	0.0051	0.0052	0.0050
Hexachlorobenzene	0.03	ng/L	NYSDEC	**0.0455**	**0.0390**	**0.0307**	**0.0310**	**0.0371**	0.0291	**0.0309**	**0.0335**	0.0239	0.0221	0.0197	0.0211	0.0185	0.0237	0.0234	0.0193	0.0132	0.0139	0.0149
Pentachlorobenzene	30	ng/L	MOE	0.0269	0.0271	0.0169	0.0219	0.0193	0.0200	0.0217	0.0389	0.0175	0.0136	0.0166	0.0217	0.0227	0.0195	0.0228	0.0187	0.0071	0.0095	0.0093
INDUSTRIAL BY-PRODUCTS																						
Hexachlorobutadiene	10	ng/L	NYSDEC	0.0278	0.0124		0.0793	0.0462	0.0008					0.0009	0.0009				0.0021			
Hexachlorocyclopentadiene	450	ng/L	NYSDEC																		0.0034	0.0030
Octachlorostryene	0.006	ng/L	NYSDEC																			
NEUTRAL HERBICIDES																						
Atrazine	1800	ng/L	CCME				221.1120	49.7910	79.4120	58.8780	72.7600	76.3680	61.3920	56.8740	68.9210	110.3300	51.4591	58.2356	52.6850	52.8754	53.7910	71.0492
Metolachlor	3000	ng/L	MOE			1.4001	11.4234	24.4080	27.9464	18.5740	20.4094	22.7215	21.8205	23.6982	30.8495	41.5069	14.7378	19.3461	12.9059	11.9311	13.8266	15.0775
ORGANOCHLORINE PESTICIDES & PCBs																						
Aldrin	2	ng/L	NYSDEC								0.0021											
α-HCH	2	ng/L	NYSDEC	**2.7257**	**2.7500**	**2.2569**	1.5830	1.4031	1.0092	0.9871	0.7774	0.5895	0.5681	0.5109	0.4872	0.4038	0.1466	0.1470	0.1386	0.0968	0.1043	0.1196
γ-HCH	8	ng/L	NYSDEC	0.6851	0.8290	0.7283	0.6515	0.7237	0.5195	0.4789	0.4556	0.4503	0.3391	0.3336	0.3710	0.3894	0.1645	0.1836	0.2059	0.1513	0.1321	0.1450
α-Chlordane				0.0681	0.0379	0.0045	0.0706	0.0434		0.0605	0.0342	0.0352	0.0019	0.0063	0.0215	0.0163		0.0104	0.0044	0.0016	0.0020	0.0022
γ-Chlordane				0.0217	0.0014		0.0237	0.0214	0.0174	0.0034	0.0024	0.0151		0.0027	0.0057	0.0016		0.0076	0.0061	0.0051	0.0068	0.0068
Total Chlordane	0.02	ng/L	NYSDEC	**0.0898**	**0.0392**	0.0045	**0.0943**	**0.0648**	0.0174	**0.0639**	**0.0365**	**0.0503**	0.0019	0.0089	**0.0272**	0.0179		0.0180	0.0106	0.0067	0.0088	0.0089
o,p-DDT				0.0472	0.0495		0.1800	0.0086	0.0081		0.0037	0.0309	0.0046	0.0091	0.0433	0.0283		0.0029	0.0043	0.0011		0.0014
p,p-DDD	0.08	ng/L	NYSDEC	**0.2217**	**0.3007**	**0.1897**	**0.2054**	**0.1840**	**0.1511**	**0.1843**	**0.1453**	**0.1269**	**0.1295**	**0.1435**	**0.3016**	**0.0805**	0.0615	0.0589	0.0576	0.0351	0.0167	0.0515
p,p-DDE	0.007	ng/L	NYSDEC	**0.4569**	**0.2910**	**0.1227**	**0.1109**	**0.1216**	**0.1320**	**0.1332**	**0.0966**	**0.0939**	**0.1016**	**0.1400**	**0.2112**	**0.0920**	**0.0608**	**0.0957**	**0.0580**	**0.0361**	**0.0364**	**0.0535**
p,p-DDT	0.01	ng/L	NYSDEC	**0.3179**	**0.0935**	**0.0325**	**0.7008**	**0.1242**	**0.1298**	**0.1054**	**0.0902**	**0.0233**	**0.0258**	**0.0956**	**0.0847**	**0.0241**	**0.0193**	**0.0754**	**0.0265**	**0.0108**	**0.0199**	**0.0181**
Total DDT	0.01	ng/L	NYSDEC	***1.0438***	***0.7347***	***0.3448***	***1.1971***	***0.4384***	***0.4211***	***0.4228***	***0.3358***	***0.2750***	***0.2614***	***0.3883***	***0.6408***	***0.2248***	***0.1416***	***0.2329***	***0.1465***	***0.0831***	***0.0730***	***0.1244***
Dieldrin	0.0006	ng/L	NYSDEC	**0.3678**	**0.3533**	**0.3214**	**0.3213**	**0.3049**	**0.2598**	**0.2316**	**0.2145**	**0.1936**	**0.1626**	**0.1518**	**0.1768**	**0.1339**	**0.1100**	**0.1305**	**0.1254**	**0.1045**	**0.0963**	**0.0959**
α-Endosulfan				0.0300	0.0357	0.0388	0.0444	0.0382	0.0459	0.0450	0.0333	0.0272	0.0279	0.0240	0.0307	0.0191		0.0179	0.0227	0.0134	0.0154	0.0150
β-Endosulfan					0.0027	0.0040	0.0400	0.0362		0.0348	0.0327	0.0425		0.0349		0.0022		0.0026	0.0095	0.0082	0.0116	
Total Endosulfan	9	ng/L	NYSDEC	*0.0300*	*0.0384*	*0.0428*	*0.0844*	*0.0744*	*0.0459*	*0.0798*	*0.0660*	*0.0697*	*0.0279*	*0.0590*	*0.0307*	*0.0212*	*0.0000*	*0.0205*	*0.0322*	*0.0217*	*0.0270*	*0.0150*
Endrin	2	ng/L	NYSDEC	0.0637	0.0483	0.0222	0.0245									0.0257		0.0100				
Endrin Aldehyde												0.0009										
Heptachlor	0.2	ng/L	NYSDEC																			
Heptachlor Epoxide	0.3	ng/L	NYSDEC	0.1351	0.1244	0.1428	0.1500	0.1268	0.1169	0.0905	0.0895	0.0889	0.0594	0.0511	0.0749	0.0525	0.0387	0.0448	0.0489	0.0335	0.0306	0.0329
Methoxychlor	30	ng/L	NYSDEC		0.1527			0.0322		0.0127					0.0200			0.0210				
Mirex	0.001	ng/L	NYSDEC												**0.0016**							
Photomirex																						
PCB (Total)	0.001	ng/L	NYSDEC	**3.1819**	**2.2293**	**2.1585**	**1.7981**	**1.8544**	**1.7765**	**1.6251**	**1.3255**	**1.4129**	**1.1839**	**0.8137**	**0.9879**	**0.2175**	**0.1252**	**0.2793**	**0.2568**	**0.1719**	**0.2970**	**0.1899**
PAHs																						
1-Methylnaphthalene	2000	ng/L	MOE					1.2448	0.8477	1.1894	1.0285	1.2666	0.6872	0.5506	0.6359	0.6244	0.5672	1.0042	0.4470	0.4083	0.7469	0.6060
2-Methylnaphthalene	4700	ng/L	NYSDEC					0.9755	1.1609	1.5823	1.3796	2.2015	1.1770	0.8735	1.2534	1.1304	0.9272	0.9386	0.7390	0.6572	0.8364	0.7807
2-Betachloronaphthalene	1000	ng/L	NYSDEC																			
Acenaphthylene								0.2497	0.2453	0.2563	0.2159	0.2518	0.2006	0.2059	0.1609	0.1704	0.1826	0.2460	0.1684	0.1272	0.1641	0.1484
Anthracene	3800	ng/L	NYSDEC					0.2658	0.1965	0.2269	0.0675	0.4229	0.1494	0.1406	0.2540	0.2167	0.1945	0.5682	0.2663	0.2480	0.3231	0.2819
Benz(a)anthracene	2	ng/L	NYSDEC	**2.1148**	1.5813	**2.0377**	1.0824	1.9195	1.0139	0.9654	0.4065	1.1333	0.8313	0.8166	0.8118	0.4819	0.5832	1.9342	0.9499	0.4112	0.9128	0.9478
Benzo(a)pyrene	1.2	ng/L	NYSDEC		0.4990	**1.2784**	0.4269	0.7658	0.6728	1.0842	0.4573	1.0568	0.9162	0.9478	0.8093	0.6290	0.7744	**2.6426**	1.1680	0.3943	1.0139	0.9620
Benzo(bk)fluoranthene	2	ng/L	NYSDEC	1.7946	**2.7313**	**2.9641**	1.3312	**2.3975**	1.7389	**2.3940**	1.2532	**2.3478**	1.9516	1.3587	**2.0227**	1.5548	1.8825	**6.0598**	**2.4170**	0.9314	**2.2510**	**2.2204**
Benzo(g,h,i)perylene	0.02	ng/L	MOE					**0.3429**	**0.3473**	**0.7792**	**0.3467**	**0.7663**	**0.7403**	**0.9224**	**0.6419**	**0.7309**	**0.6746**	**2.5605**	**0.8874**	**0.4028**	**1.0003**	**0.6558**
Chrysene/Triphenylene	2	ng/L	NYSDEC	**2.9093**	**2.0548**	**2.2813**	1.1239	1.6617	1.1156	1.4385	0.6739	1.6221	1.3218	1.3455	0.9625	0.8301	0.9637	**2.6473**	1.3743	0.6589	1.1553	1.1000
Dibenzo(a,h)anthracene	2	ng/L	MOE							0.1952		0.0801		0.1239	0.0995	0.0697	0.0471	1.0653	0.1480	0.0737	0.1800	0.1525
Fluoranthene	50000	ng/L	NYSDEC	3.4087	1.9537	3.7246	1.6501	2.6663	2.1792	3.2375	1.7603	3.6587	3.0652	2.9299	2.5206	2.0842	2.2425	9.0420	3.0123	1.6417	3.1654	2.8802
Fluorene	540	ng/L	NYSDEC					0.8885	0.5745	0.8050	0.6925	0.9946	0.6766	0.5343	0.5304	0.4970	0.5757	0.8275	0.5543	0.5597	0.6446	0.7673
Indeno(1,2,3-cd)pyrene	2	ng/L	NYSDEC					0.3768	0.3654	0.8066	0.2876	0.7625	0.6436	0.9509	0.8311	0.7980	1.0230	**4.0995**	0.9445	0.4295	0.9793	0.8054
Naphthalene	10000	ng/L	NYSDEC					2.8236	3.3027	3.0536	2.3529	4.6512	1.9975	1.9010			0.0679	0.4905	1.4598	0.0418	0.1438	0.0768
Phenanthrene	5000	ng/L	NYSDEC					3.9930	3.1041	2.7275	1.9185	3.3149	2.6779	2.5760	2.3741	2.0729	1.8525	5.2944	2.3151	1.6042	2.8148	3.0830
Pyrene	4600	ng/L	NYSDEC	2.7681	1.6542	2.5606	1.0465	1.4875	1.2573	2.0709	1.0420	2.6753	2.0392	2.1815	1.8944	1.6025	1.3609	3.8978	2.1665	1.0478	2.4938	1.9100
TRACE METALS																						
Aluminum	75	ug/L	MOE	**384.1600**	**306.6700**	**707.7200**	**215.5200**	**296.3700**	**545.0800**	**227.0000**	**223.9100**	**383.9700**	**228.4200**	**155.6400**	**154.0900**	**567.9500**	**382.6400**	**580.0500**	**636.8910**	**160.0720**	**217.8660**	**137.2340**
Antimony	3	ug/L	NYSDEC	0.2243	0.2068	0.3346	0.2791	0.1839	0.2024	0.2940	0.2126	0.2260	0.2630	0.2643	0.2756	0.1787	0.1772	0.2348	0.1722	0.1752	0.1793	0.1574
Arsenic	5	ug/L	MOE	0.6331	0.5597	0.7259	0.6229	0.6640	0.6739	0.6504	0.6720	0.7770	0.7338	0.6514	0.6188	0.5700	0.5930	0.6161	0.5630	0.6070	1.5033	0.9810
Barium	1000	ug/L	NYSDEC												21.3300	22.9270	24.2880	24.4520	25.2318	26.0004	25.0423	24.0026
Beryllium	1100	ug/L	MOE														0.0440	0.0260	0.0182	0.0089	0.0094	0.0069
Cadmium	0.2	ug/L	IJC	0.1201	0.1032	0.1806	0.1253	0.1331	0.1622	0.0929	0.0846	0.1556	0.0800	0.1129	0.0998	0.1266	0.1107	0.0230	0.0199	0.0211	0.0269	0.0191
Chromium	50	ug/L	IJC	0.8262	0.6008	1.1380	0.5036	0.8022	0.9734	0.5319	0.4565	0.7109	1.5342	1.1075	0.3346	0.8204	0.7714	2.1963	0.7571	0.3200	0.4184	0.2923
Cobalt	5	ug/L	NYSDEC	0.4103	0.2888	0.4561	0.3035	0.3988	0.4720	0.2021	0.1923	0.3274	0.2289	0.5670	0.1866	0.3782	0.3078	0.2711	0.3701	0.1228	0.2192	0.1083
Copper	10.5	ug/L	NYSDEC	1.7375	1.3595	1.9648	1.4112	1.9802	1.9150	1.3619	1.4221	2.0025	1.4937	1.3572	1.2577	1.8680	1.6875	1.5852	1.6656	1.3275	1.2363	1.2220
Iron	300	ug/L	MOE												266.2900	**989.8000**	**645.5700**	**712.8400**	**736.8110**	246.1400	**592.8090**	216.5370
Lead	2.5	ug/L	USEPA	2.0540	1.8213	3.0088	0.9747	1.1304	1.9633	0.4327	0.3923	1.4694	0.6826	0.6638	0.6345	1.4934	1.4278	0.7089	0.7821	0.3598	0.3651	0.3546
Lithium															2.4071	2.6059	2.4245	2.2956	2.3765	2.0255	2.1722	2.1385
Manganese	300	ug/L	NYSDEC												8.9760	29.7600	25.3960	23.1730	24.2736	8.5164	11.4634	7.8505
Mercury	1.3	ng/L	USEPA	1.16743	0.69960	0.95500	0.46777	0.64952	0.64344	0.51128	0.37334	0.61891	0.62148	0.46244	0.47150	0.43770	0.81543	1.24641	1.25937	0.30625	0.0007	0.0004
Molybdenum	10	ug/L	MOE												1.1065	1.1303	1.8649	1.2430	1.2920	1.4568	1.4224	1.3547
Nickel	25	ug/L	MOE	1.9791	1.5735	2.3723	1.2309	1.7934	1.8281	1.1367	1.1261	1.6383	1.2131	1.3190	1.0065	1.5705	1.5362	1.4340	1.9429	1.1510	1.1653	1.1079
Selenium	4.6	ug/L	NYSDEC	0.1878	0.1440	0.2300	0.2028	0.1917	0.2605	0.1970	0.1942	0.1473	0.1982	0.2170	0.2371	0.2258	0.2165	0.2247	0.1747	0.1718	0.2200	0.1997
Silver	3.2	ug/L	USEPA															0.2089	0.0034		0.0034	0.0036
Strontium															148.8100	149.8600	153.2200	165.4000	164.8790	173.4930	166.6520	172.6230
Vanadium	14	ug/L	NYSDEC												0.4871	1.0159	0.9345	0.8717	0.9060	0.5055	0.5359	0.5036
Zinc	20	ug/L	MOE	3.6072	3.3099	6.6364	2.4015	3.4162	6.0719	2.6562	1.9609	4.8214	2.1522	2.5236	1.7915	5.3429	4.4940	2.8453	3.5388	2.1305	2.3821	1.3067

bold highlighted values represent Water Quality Criteria exceedences
blank fields = not measured or not detected

*NOTES:

- Trace metal results represent “Whole Water” concentrations while the Water Quality Criteria for Metals are based on the dissolved phase (with the exception of mercury)
- Aluminum criteria is based upon “clay-free” samples; however, trace metal samples were not filtered and; therefore may contain clay particles
- PCB and Mercury values based on sediment contribution only (field blank studies indicate majority of dissolved phase concentration is due to background contamination)
- Naphthalene values based on sediment contribution only due to poor and variable recovery of the analyte in the dissolved phase

Table 3b. Comparison of Upper 90% CI Concentrations with Most Stringent Agency Water Quality Criteria at NOTL

				Upper 90% Confidence Interval Concentration																		
	Criteria	Units	Agency	86-87	87-88	88-89	89-90	90-91	91-92	92-93	93-94	94-95	95-96	96-97	97-98	98-99	99-00	00-01	01-02	02-03	03-04	04-05
CHLOROBENZENES																						
1,2-Dichlorobenzene	3000	ng/L	NYSDEC	2.4066	2.7498	2.8652	2.5048	2.9319	1.5208	0.8980	1.0684	1.2383	0.6456	0.5916	0.5342	0.5504	0.8501	0.9650	0.4328	0.3846	0.3303	0.3279
1,3-Dichlorobenzene	2500	ng/L	MOE	1.6439	1.4699	0.6207	0.8102	0.9064	0.7289	0.5999	0.5005	0.6225	0.4564	0.3606	0.6519	0.3862	0.7873	0.5911	0.3418	0.3400	0.3248	0.2982
1,4-Dichlorobenzene	4000	ng/L	MOE	3.2471	3.2897	2.4747	3.5209	3.8108	2.9956	2.2386	1.9563	1.9610	1.4353	1.2929	1.6579	1.0496	1.8673	2.2812	1.5797	1.3183	1.3969	1.1174
1,2,3-Trichlorobenzene	900	ng/L	MOE	0.3985	0.4601	0.3798	0.4793	0.6082	0.4109	0.3000	0.1867	0.2672	0.1701	0.1369	0.1685	0.1257	0.2019	0.1598	0.0937	0.0730	0.0580	0.1006
1,2,4-Trichlorobenzene	500	ng/L	MOE	1.9000	1.7649	1.3743	1.6152	2.0109	1.4403	1.1144	0.7428	0.9138	0.6894	0.5126	0.5491	0.4947	0.8517	0.6665	0.4011	0.3033	0.2620	0.2744
1,3,5-Trichlorobenzene	650	ng/L	MOE	0.1766	0.1457	0.0688	0.0927	0.1058	0.1021	0.0822	0.0756	0.0937	0.0744	0.0574	0.1054	0.0768	0.1061	0.0782	0.0564	0.0460	0.0599	0.0445
1,2,3,4-Tetrachlorobenzene	100	ng/L	MOE	1.1648	1.0489	0.6305	0.8617	1.0120	0.7820	0.7315	0.4334	0.6045	0.4442	0.2822	0.3143	0.3131	0.4009	0.3305	0.2167	0.1652	0.1642	0.2546
Hexachlorobenzene	0.03	ng/L	NYSDEC	**0.2795**	**0.2360**	**0.1540**	**0.2126**	**0.1626**	**0.1298**	**0.1089**	**0.0827**	**0.1222**	**0.0757**	**0.0719**	**0.1104**	**0.0846**	**0.0905**	**0.0612**	**0.0676**	**0.0436**	**0.0388**	**0.0651**
Pentachlorobenzene	30	ng/L	MOE	0.4175	0.3452	0.1629	0.2003	0.2292	0.1978	0.1952	0.1347	0.1777	0.1324	0.1039	0.1363	0.1237	0.1205	0.1072	0.0961	0.0639	0.0553	0.0891
INDUSTRIAL BY-PRODUCTS																						
Hexachlorobutadiene	10	ng/L	NYSDEC	0.1567	0.1503	0.1098	0.2212	0.1860	0.1144	0.0964	0.2187	0.0691	0.0555	0.0517	0.0787	0.0652	0.0587	0.0434	0.0421	0.0351	0.0441	0.0585
Hexachlorocyclopentadiene	450	ng/L	NYSDEC				0.0790	0.8188	1.1544	0.0323	0.0332	0.0137	0.0154	0.0016	0.0292	0.0040	0.0962	0.0188	0.0411		0.0050	0.0237
Octachlorostryene	0.006	ng/L	NYSDEC			**0.0172**	**0.0710**	**0.0475**	**0.0087**	0.0044	0.0025	**0.0065**	0.0034		0.0047	**0.0213**	0.0054	0.0018	0.0027	0.0016	0.0016	0.0047
NEUTRAL HERBICIDES																						
Atrazine	1800	ng/L	CCME				212.348	52.918	78.622	54.655	64.239	73.904	64.953	55.939	71.441	65.355	57.844	61.851	46.474	52.277	59.811	71.967
Metolachlor	3000	ng/L	MOE			1.783	12.709	47.056	29.072	17.977	20.065	22.702	22.705	21.208	28.590	24.622	17.035	21.892	11.510	12.224	14.708	16.165
ORGANOCHLORINE PESTICIDES & PCBs																						
Aldrin	2	ng/L	NYSDEC														0.0034	0.0017				
α-HCH	2	ng/L	NYSDEC	**2.6448**	**2.9112**	**2.5705**	1.8203	1.5148	1.1792	1.2611	0.8811	0.7698	0.7220	0.5669	0.6271	0.5528	0.2039	0.1942	0.1952	0.1392	0.1409	0.1455
γ-HCH	8	ng/L	NYSDEC	0.6938	0.7619	0.6491	0.6777	0.6072	0.4934	0.5221	0.4763	0.4691	0.3989	0.3630	0.4478	0.4005	0.2005	0.2165	0.2508	0.1798	0.1554	0.1360
α-Chlordane				0.0328	0.0469	0.0107	0.1075	0.0355	0.0028	0.0787	0.0498	0.0609	0.0582	0.0417	0.0390	0.0245		0.0026	0.0111	0.0054	0.0045	0.0052
γ-Chlordane				0.0287	0.0300	0.0178	0.0244	0.0262	0.0221	0.0180	0.0029	0.0245	0.0123	0.0092	0.0110	0.0046		0.0052	0.0114	0.0078	0.0089	0.0064
Total Chlordane	0.02	ng/L	NYSDEC	**0.0616**	**0.0769**	**0.0285**	**0.1319**	**0.0616**	**0.0249**	**0.0967**	**0.0527**	**0.0854**	**0.0705**	**0.0509**	**0.0500**	**0.0291**	0.0000	0.0078	**0.0225**	0.0132	0.0134	0.0116
o,p-DDT				0.0235	0.0077						0.0362	0.0081	0.0085	0.0153	0.0691	0.0231	0.0029	0.0026				0.0045
p,p-DDD	0.08	ng/L	NYSDEC	0.0787	**0.1135**	0.0514	**0.0850**	**0.1120**	0.0732	**0.0833**	0.0708	0.0749	**0.0967**	0.0430	0.0655	0.0509	0.0175	0.0307	0.0570	0.0335	0.0380	0.0147
p,p-DDE	0.007	ng/L	NYSDEC	**0.0886**	**0.0893**	**0.0889**	**0.0708**	**0.0902**	**0.0817**	**0.0745**	**0.0418**	**0.0671**	**0.0628**	**0.1144**	**0.0926**	**0.0555**	**0.0382**	**0.0270**	**0.0416**	**0.0245**	**0.0322**	**0.0507**
p,p-DDT	0.01	ng/L	NYSDEC	**0.0958**	**0.0417**	**0.0645**	**0.0493**	**0.0445**	**0.1321**	**0.0722**	**0.0730**	**0.0134**	**0.0170**	**0.0455**	**0.0834**	**0.0212**	**0.0376**	**0.0103**	**0.0216**	0.0093	**0.0116**	**0.0219**
Total DDT	0.01	ng/L	NYSDEC	**0.2630**	**0.2445**	**0.2048**	**0.2051**	**0.2468**	**0.2870**	**0.2300**	**0.1856**	**0.1555**	**0.1764**	**0.2029**	**0.2415**	**0.1276**	**0.0933**	**0.0680**	**0.1202**	**0.0673**	**0.0818**	**0.0873**
Dieldrin	0.0006	ng/L	NYSDEC	**0.3655**	**0.3667**	**0.3207**	**0.3277**	**0.2933**	**0.2795**	**0.2285**	**0.2161**	**0.2063**	**0.1776**	**0.1617**	**0.2281**	**0.1661**	**0.1000**	**0.1200**	**0.1364**	**0.1177**	**0.1112**	**0.1114**
α-Endosulfan				0.0445	0.0731	0.0432	0.0672	0.0538	0.0581	0.0712	0.0363	0.0501	0.0545	0.0273	0.0687	0.0252	0.0298	0.0287	0.0395	0.0206	0.0207	0.0208
β-Endosulfan				0.0468	0.0084	0.0240	0.0507	0.0494	0.0239	0.0462	0.0407	0.0494	0.0447	0.0405	0.0121	0.0196	0.0170	0.0115	0.0213	0.0138	0.0167	0.0151
Total Endosulfan	9	ng/L	NYSDEC	0.0913	0.0815	0.0673	0.1179	0.1033	0.0820	0.1174	0.0770	0.0995	0.0993	0.0678	0.0808	0.0449	0.0468	0.0402	0.0607	0.0344	0.0375	0.0359
Endrin	2	ng/L	NYSDEC	0.0667	0.0757				0.0254							0.0389	0.0000	0.0176				
Endrin Aldehyde																						
Heptachlor	0.2	ng/L	NYSDEC														0.0018					
Heptachlor Epoxide	0.3	ng/L	NYSDEC	0.1497	0.1351	0.1427	0.1556	0.1151	0.1226	0.0984	0.0951	0.0966	0.0652	0.0563	0.0766	0.0607	0.0307	0.0366	0.0488	0.0417	0.0416	0.0430
Methoxychlor	30	ng/L	NYSDEC	0.1289	0.1664	0.0374		0.0217		0.0264		0.0291		0.0362								
Mirex	0.001	ng/L	NYSDEC	**0.0162**	**0.0188**	**0.0218**	**0.0089**	**0.0124**	**0.0135**	**0.0075**	**0.0056**	**0.0087**	**0.0042**	**0.0075**	**0.0101**	**0.0268**	**0.0148**	**0.0072**	**0.0112**	**0.0039**	**0.0032**	**0.0069**
Photomirex																						
PCB (Total)	0.001	ng/L	NYSDEC	**2.9972**	**2.7677**	**3.2215**	**3.1934**	**2.0030**	**1.8345**	**1.9812**	**1.3116**	**1.2976**	**1.2007**	**0.9481**	**1.2857**	**0.0268**	**0.6045**	**0.3161**	**0.6479**	**0.5515**	**0.5040**	**0.4912**
PAHs																						
1-Methylnaphthalene	2000	ng/L	MOE					1.4266	1.2672	1.3573	1.2170	1.0393	0.9356	0.6630	0.7064	1.0178	0.7053	0.5341	0.6252	0.6898	0.8300	0.5928
2-Methylnaphthalene	4700	ng/L	NYSDEC					1.6969	1.6098	1.7669	1.6058	1.6485	1.5868	1.0774	1.2231	1.6785	0.9757	0.8151	1.0214	0.9386	1.1062	0.8101
2-Betachloronaphthalene	1000	ng/L	NYSDEC																			
Acenaphthylene								0.4730	0.3792	0.3129	0.2795	0.3286	0.2643	0.3607	0.2566	0.4470	0.2901	0.1970	0.4250	0.3464	0.3233	0.2594
Anthracene	3800	ng/L	NYSDEC					1.1283	2.2812	0.4595	0.3175	1.0612	1.8194	0.5377	0.7478	0.7644	0.7525	0.4603	0.7863	0.8001	0.7380	0.5915
Benz(a)anthracene	2	ng/L	NYSDEC	**2.5603**	**3.0410**	**4.4465**	**2.0244**	**2.9959**	1.9027	1.8620	0.8563	1.9887	1.5974	1.9599	1.9315	**2.2448**	1.3614	1.3228	**2.3032**	**2.0763**	1.8961	1.9597
Benzo(a)pyrene	1.2	ng/L	NYSDEC	**1.8754**	0.9406	**3.5841**	1.1089	**1.4624**	**1.3377**	**1.8322**	0.9723	**1.8559**	**1.6042**	**2.3828**	**2.2023**	**2.6460**	**1.7273**	**1.8591**	**2.5956**	**1.8920**	**1.9537**	**2.2718**
Benzo(bk)fluoranthene	2	ng/L	NYSDEC	**3.9310**	**4.8890**	**7.1420**	**2.8930**	**4.3790**	**3.6300**	**3.7800**	**2.3720**	**3.9910**	**3.6200**	**3.3640**	**6.3703**	**6.0749**	**3.8558**	**4.4888**	**4.5696**	**3.9863**	**4.1559**	**5.1074**
Benzo(g,h,i)perylene	0.02	ng/L	MOE					**1.1186**	**0.6405**	**1.0203**	**0.7227**	**1.4228**	**1.3336**	**2.0748**	**2.2244**	**2.6988**	**1.3627**	**1.4496**	**1.8765**	**1.6357**	**1.6181**	**1.6395**
Chrysene/Triphenylene	2	ng/L	NYSDEC	**3.7362**	**3.6517**	**5.0618**	**2.0153**	**2.9788**	1.8490	**2.6597**	1.4802	**2.9428**	**2.6116**	**3.0763**	**3.0389**	**3.2195**	1.9868	1.7813	**2.7463**	**2.4462**	**2.2169**	**2.6812**
Dibenzo(a,h)anthracene	2	ng/L	MOE							0.2773		0.3962	0.3716	0.3591	0.3761	0.3190	0.7879	0.3458	0.4214	0.4134	0.3257	0.3826
Fluoranthene	50000	ng/L	NYSDEC	4.5083	4.1981	8.5709	3.2353	4.5990	4.0073	4.9695	3.1907	6.0597	5.3853	6.1354	6.1978	6.7542	4.3792	3.7263	5.6909	5.2444	5.7100	5.3598
Fluorene	540	ng/L	NYSDEC					1.2878	1.0376	0.9185	0.9555	1.5069	1.1018	0.8479	0.8004	1.0479	0.8244	0.6854	0.9201	0.9329	1.0159	0.9046
Indeno(1,2,3-cd)pyrene	2	ng/L	NYSDEC					1.1040	0.4834	0.9470	0.7898	1.3882	1.4516	**2.0974**	**2.3474**	**2.4273**	1.8342	**2.1239**	**2.0572**	1.8154	1.6264	1.8923
Naphthalene	10000	ng/L	NYSDEC					4.1859	3.5024	3.2887	3.3157	2.9579	2.8773	2.0544			0.1394	0.1183	1.8378	0.2289	0.3340	0.2926
Phenanthrene	5000	ng/L	NYSDEC					5.6216	13.2443	3.9050	3.4886	6.2789	4.9040	5.1040	5.1734	6.0110	3.7047	3.3477	4.2657	4.0988	5.0183	4.9740
Pyrene	4600	ng/L	NYSDEC	4.2334	3.5322	7.1193	2.5544	3.2841	3.1683	3.7548	2.6685	5.4401	4.6681	4.9732	5.2145	5.6198	3.4641	2.9030	4.8284	5.2603	4.8385	4.5803
TRACE METALS																						
Aluminum	75	ug/L	MOE	**589.4000**	**415.7300**	**567.0900**	**418.9400**	**677.5800**	**438.6900**	**356.2200**	**250.2400**	**368.4200**	**327.5200**	**396.6400**	**302.6500**	**350.8600**	**720.6900**	**923.4700**	**360.9390**	**210.7550**	**562.4000**	**352.2060**
Antimony	3	ug/L	NYSDEC	0.2415	0.2248	0.3484	0.2786	0.1745	0.2163	0.2708	0.2066	0.2189	0.2677	0.2475	0.2063	0.1617	0.1894	0.2999	0.1658	0.1791	0.6425	0.1696
Arsenic	5	ug/L	MOE	0.8328	0.6498	0.8342	0.8183	0.7778	0.8226	0.6795	0.6993	0.8213	0.8628	0.7015	0.6837	0.5804	0.6065	0.6126	0.5841	0.6153	1.6766	1.1611
Barium	1000	ug/L	NYSDEC												22.2110	24.2270	24.0560	25.7590	24.7470	25.7163	27.3821	26.3377
Beryllium	1100	ug/L	MOE													0.0384		0.0511	0.0145	0.0138	0.0216	0.0229
Cadmium	0.2	ug/L	IJC	0.1693	0.1162	0.1665	0.1687	0.1828	0.1378	0.1073	0.0918	0.1213	0.1071	0.0903	0.0999	0.1177	0.1371	0.0331	0.0200	0.0244	0.0333	0.0377
Chromium	50	ug/L	IJC	1.2914	1.0493	1.2534	0.9995	1.1758	0.9779	0.7543	0.6281	0.8536	1.0598	1.8613	0.5476	1.2649	0.7427	3.3064	0.7545	0.5014	1.1354	0.7170
Cobalt	5	ug/L	NYSDEC	0.6513	0.4514	0.4012	0.4910	0.5310	0.4029	0.3242	0.2212	0.3131	0.3203	0.6012	0.2730	0.3346	0.3571	0.6398	0.2681	0.1964	0.2424	0.3055
Copper	10.5	ug/L	NYSDEC	1.9782	1.5487	1.7616	1.7453	2.0887	1.7525	1.6657	1.4764	1.9586	1.8990	1.6799	1.5110	1.8341	1.7533	2.0062	1.6001	1.5348	1.5716	1.8407
Iron	300	ug/L	MOE												**557.8200**	**655.7600**	**2561.8900**	**1548.5200**	**514.1900**	**389.6530**	**538.9650**	**668.9890**
Lead	2.5	ug/L	USEPA	**2.5380**	2.1273	1.9198	1.4571	1.7994	0.8423	0.6631	0.4213	0.8712	0.8250	0.7686	0.7844	0.8244	0.9109	1.3817	0.6290	0.5241	0.7461	0.7924
Lithium															2.7708	2.6525	3.1650	2.8331	2.4001	2.3159	2.6542	2.7247
Manganese	300	ug/L	NYSDEC												15.8700	16.3940	32.5790	42.2200	15.9814	13.3691	16.9324	21.9734
Mercury	1.3	ng/L	USEPA	1.0000	**1.3000**	**1.5000**	1.0000	1.1000	0.9000	0.8000	0.7000	**1.4000**	0.9000	0.8000	0.7318	0.9532	0.6800	0.6170	**1.6020**	0.8400	1.0230	0.6950
Molybdenum	10	ug/L	MOE												1.1228	1.1381	1.7682	1.2415	1.3374	1.4682	1.4452	1.3580
Nickel	25	ug/L	MOE	2.2757	1.8878	2.0919	1.6279	1.8800	1.4454	1.4283	1.1337	1.5361	1.5544	1.4139	1.2262	1.5483	1.5685	2.2064	1.5273	1.3915	1.5527	1.6963
Selenium	4.6	ug/L	NYSDEC	0.1793	0.1332	0.2345	0.1960	0.2046	0.2673	0.1982	0.1951	0.1604	0.2179	0.2257	0.2490	0.2113	0.2389	0.2233	0.1677	0.1643	0.2147	0.1829
Silver	3.2	ug/L	USEPA																0.0045	0.0031	0.0127	0.0108
Strontium															148.3800	147.6200	151.4100	165.1100	162.5610	171.7820	174.3240	171.8760
Vanadium	14	ug/L	NYSDEC												0.7099	0.8299	0.8619	1.1686	0.7923	0.6066	0.7605	0.8991
Zinc	20	ug/L	MOE	5.6046	4.6611	6.4393	4.2226	5.5356	4.0944	3.7567	2.3377	4.4059	3.3132	3.7209	4.1153	4.0577	4.2248	5.6672	3.0365	3.1973	2.9219	4.0558

bold highlighted values represent Water Quality Criteria exceedences
blank fields = not measured or not detected

*NOTES:

- Trace metal results represent “Whole Water” concentrations while the Water Quality Criteria for Metals are based on the dissolved phase (with the exception of mercury)
- Aluminum criteria is based upon “clay-free” samples; however, trace metal samples were not filtered and; therefore may contain clay particles
- PCB and Mercury values based on sediment contribution only (field blank studies indicate majority of dissolved phase concentration is due to background contamination)
- Naphthalene values based on sediment contribution only due to poor and variable recovery of the analyte in the dissolved phase

Note that the concentration and loading values for Mercury differ from previous reports. In the past, whole water concentrations were reported; however, more recent reports (Kuntz & Klawunn, 2005 and Hill & Klawunn, 2009) have focused solely on the particulate phase due to concerns over both the sensitivity of the analytical method and possible contamination of the dissolved phase sample. In order to facilitate comparisons, historical data were re-evaluated using the current method based solely on the particulate phase contribution.

It should also be noted that current analytical methodology does not distinguish between the two PAH compounds Chrysene and Triphenylene, nor the two isomers Benzo(b)- and Benzo(k)fluoranthene; therefore, results are reported as Chrysene/Triphenylene and Benzo(b/k)fluoranthene. The criteria are applicable to Chrysene alone (i.e., there is no criterion for Triphenylene), and to Benzo(b)- and Benzo(k)fluoranthene alone but, in keeping with past practice, use of the upper 90% confidence interval provides a conservative measure of exceedence which we are comfortable identifying due to the magnitude by which these values exceed the respective criteria.

Also, we suspect that Chrysene is the contaminant that is being measured in the Niagara River (as opposed to Triphenylene), given its potential sources. Chrysene is a ubiquitous environmental contaminant that occurs as a product of the incomplete combustion of organic compounds. Anthropogenic sources of Chrysene include gasoline, diesel and aircraft turbine exhausts; coal combustion and gasification; emissions from coke ovens, wood burning stoves, and waste incineration; and various industrial processes such as iron, aluminum, and steel production. Chrysene is also a constituent of coal, oil, and their distillates, such as coal tar, and creosote. Triphenylene, on the other hand, is a minor constituent of gasoline and, while it is often found as a by product of industrial emissions, its concentration levels are relatively low unless measured directly downstream from a point source (Niagara River Secretariat; 2007).

At first glance, the results in Tables 3a and 3b look quite similar. With the exception of Octachlorostyrene, Lead, and Mercury at Niagara-on-the-Lake, the same 18 compounds (Hexachlorobenzene, α-HCH, Total Chlordane, p,p-DDD, p,p-DDE, p,p-DDT, Total DDT, Dieldrin, Mirex, PCBs, Benz(a)anthracene, Benzo(a)pyrene, Benzo(bk)fluoranthene, Benzo(ghi)perylene, Chrysene/Triphenylene, Indeno(123cd)pyrene, Aluminum, and Iron) exceed strictest agency criteria at both Fort Erie and NOTL and the stations share some of the few compounds that exceed their water quality criteria every year including p,p-DDE, Total DDT, Dieldrin, PCB, and Aluminum. Finally, neither station reports any exceedence for compounds in the neutral herbicides class.

Closer inspection, however, reveals some important differences between the upstream and downstream stations. For example, Hexachlorobenzene, Mirex, and Benzo(bk)fluoranthene exceed strictest agency criteria for the entire period of record at NOTL but only for periods at FE implying that sources for these compounds continue to exist along the Niagara River.

In more general terms, there were notably more exceedences in Chlorobenzenes, PAHs, and Industrial By-Products from 1986/87 to 2004/05 at NOTL while the Fort Erie station had fewer annual exceedences. In addition, Fort Erie has experienced a larger reduction in the number of exceedences over the 19-year period relative to NOTL and, aside from the DDT metabolites, the magnitudes of the exceedences are generally lower than those at NOTL.

In the case of DDT and its metabolites; however, the exceedences were consistently larger at Fort Erie in all but 5 cases (p,p-DDT in 1988/89, 1991/92, 1999/00, 2004/05, and Total DDT in 2003/04). In this case, investigations suggest a local DDT source in sediments just upstream and close to the FE station (Williams et al, 2000) which may account for higher concentrations and exceedences at this location.

In looking at the upper 90% confidence interval data, it was interesting to note the dramatic shift in 2000/01 PAH concentrations at the FE station. MLE concentrations rose uniformly across this entire class and, while exceedences may have only occurred in 5 of the 17 compounds, most saw their concentrations double, triple, and, in the case of Dibenzo(ah)anthracene, actually increase by more than 20 times the 1999/2000 values. During the same time period, MLE concentrations at NOTL remained relatively unchanged. Some preliminary investigations into this anomaly have been undertaken and, while the bi-weekly samples show that the annual MLEs were driven up by exceptionally high values in May through August of 2000, a full explanation has yet to be developed.

It should also be pointed out that while aluminum exceeds the strictest agency criteria at FE and NOTL for the entire period of record, this may be due, in part, to the fact that the guideline is based upon a “clay-free” sample which does not reflect the current Niagara River analytical method which uses whole water samples for trace metals.

4.2 Trends

In addition to identifying water quality criteria exceedences, the Niagara River Upstream/Downstream Monitoring program is used to examine trends in the concentration and loading of toxic compounds which can provide useful information on contaminant sources to the river and the success of control measures and other management actions.

Table 4 shows the “long term” percent change in the annual mean concentrations and loads of all chemicals, in both phases, at both stations, between the base year 1986/87 (varies for some compounds) and end year (2004/05) as *generated by the model*. Table 5 shows the same for the “recent” 1996/97 to 2004/05 time period. A dashed line in Table 4 and Table 5 indicates that the chemical either had too few data to run the model (less than three “measured” or “trace” data points in each year over the entire period of record), or insufficient data for us to have confidence in the model output (eg., mostly “trace” values). A positive number indicates a significant increase, and a negative number a significant decrease, in the model estimates of annual mean concentrations/loads while “NS” signifies no significant change in the model estimates over the respective periods of record.

In producing the output for Table 4 and Table 5, the model also generated time series plots (i.e., trends) of the dissolved and suspended particulate phase concentrations of all the Upstream/Downstream Program chemicals for both NOTL and FE which have been compiled in Appendix D for 1986/87 – 2004/05 and Appendix E for 1996/97 – 2004/05.

Table 4. Trends in Niagara River Contaminant Concentrations and Loadings, 1986/87-2004/05

			FE					NOTL			
			% change [ ]		% change (load)			% change [ ]		% change (load)	
		Period	Dissolved	Particulate	Dissolved	Particulate		Dissolved	Particulate	Dissolved	Particulate
CHLOROBENZENES											
	1,2-Dichlorobenzene	86-05	-84.41	--	-87.42	--		-80.31	-63.77	-84.10	-79.64
	1,3-Dichlorobenze	86-05	-32.21	--	-45.31	--		-76.51	NS	-81.04	NS
	1,4-Dichlorobenzen	86-05	-76.14	--	-80.75	--		-65.49	-26.70	-72.13	-58.82
	1,2,3-Trichlorobenzene	86-05	-85.00	--	-87.90	--		-86.44	-69.59	-89.05	-82.92
	1,2,4-Trichlorobenzene	86-05	-93.61	-83.34	-94.84	-95.74		-85.30	-69.59	-88.13	-82.92
	1,3,5-Trichlorobenzene	86-05	--	--	--	--		-64.68	-36.14	-71.48	-64.12
	1,2,3,4-Tetrachlorobenzene	86-05	-84.30	--	-87.33	--		-82.17	-84.37	-85.60	-91.22
	Hexachlorobenzene	86-05	-60.19	-54.82	-67.88	-88.45		-76.69	-69.91	-81.18	-83.10
	Pentachlorobenzene	86-05	-50.48	-44.37	-60.04	-85.77		-75.17	-79.46	-79.95	-88.46
INDUSTRIAL BY-PRODUCTS											
	Hexachlorobutadiene	86-05	--	--	--	--		-78.95	-80.76	-83.00	-89.19
	Hexachlorocyclopentadiene	89-05	--	--	--	--		--	-75.16	--	-71.18
	Octachlorostryene	89-05	--	--	--	--		--	-93.71	--	-92.71
NEUTRAL HERBICIDES											
	Atrazine	89-05	NS	--	NS	--		-7.95	--	-8.95	--
	Metolachlor	89-05	27.56	--	26.20	--		5.93	--	4.79	--
ORGANOCHLORINE PESTICIDES & PCBs											
	Aldrin	86-05	--	--	--	--		--	--	--	--
	α-HCH	86-05	-97.16	--	-97.71	--		-96.07	-87.18	-96.82	-92.80
	γ-HCH	87-05	-83.49	--	-85.26	--		-80.95	--	-82.99	--
	α-Chlordane	86-05	-80.67	-58.96	-84.40	-89.51		-78.52	-48.87	-82.66	-71.27
	γ-Chlordane	86-05	-76.07	--	-80.69	--		-77.25	--	-81.63	--
	op-DDT	86-05	--	-84.68	--	-96.08		--	-75.04	--	-85.98
	pp-DDD	86-05	-75.52	-70.71	-80.25	-92.51		-75.99	-59.86	-80.61	-77.45
	pp-DDE	86-05	-76.68	-66.73	-81.19	-91.49		-69.60	-51.04	-75.45	-72.49
	pp-DDT	86-05	--	-76.52	--	-94.00		--	-72.39	--	-84.49
	Dieldrin	86-05	-75.38	-72.91	-80.14	-93.07		-72.93	-76.48	-78.14	-86.78
	α-Endosulfan	86-05	-59.89	--	-67.64	--		-65.25	--	-71.94	--
	β-Endosulfan	86-05	--	--	--	--		-74.79	-76.19	-79.64	-86.62
	Endrin	86-05	--	--	--	--		--	--	--	--
	Endrin Aldehyde	86-05	--	--	--	--		--	--	--	--
	Heptachlor	86-05	--	--	--	--		--	--	--	--
	Heptachlor Epoxide	86-05	-79.84	--	-83.74	--		-79.29	--	-83.28	--
	Methoxychlor	86-05	--	--	--	--		--	--	--	--
	Mirex	86-05	--	--	--	--		--	-56.64	--	-75.64
	PCBs - Arachlor	86-98	--	-61.38	--	-85.65		--	-77.37	--	-86.00
	Photo-mirex	86-05	--	--	--	--		--	--	--	--
PAHs											
	1-Methylnaphthalene	89-05	-58.67	-35.24	-59.11	-49.74		-65.96	-44.86	-66.32	-36.04
	2-Methylnaphthalene	89-05	-27.69	NS	-28.45	NS		-42.64	NS	-43.26	NS
	2-Beta Chloronapthalene	89-05	--	--	--	--		--	--	--	--
	Acenaphthalene	89-05	-59.66	--	-60.09	--		-58.56	--	-59.01	--
	Anthracene	89-05	NS	-35.31	NS	-49.80		NS	-27.91	NS	-16.38
	Benz(a)anthracene	86-05	-78.32	-24.85	-82.51	-80.78		-41.75	NS	-52.96	NS
	Benzo(a)pyrene	86-05	-75.22	110.43	-80.01	-46.18		NS	85.29	NS	4.11
	Benzo(bk)fluoranthene	86-05	-56.02	83.63	-64.52	-53.04		-16.79	54.77	-32.81	-13.04
	Benzo(g,h,i)perylene	89-05	-50.12	114.46	-50.65	66.43		-34.30	254.36	-35.00	311.04
	Chrysene/Triphenylene	86-05	-64.96	NS	-71.73	NS		-34.96	NS	-47.48	NS
	Dibenzo(a,h)anthracene	89-05	--	--	--	--		--	--	--	--
	Fluoranthene	86-05	102.11	89.23	63.07	-51.60		144.14	73.33	97.14	-2.62
	Fluorene	89-05	NS	-44.36	NS	-56.82		-19.86	NS	-20.73	NS
	Indeno(1,2,3-cd)pyrene	89-05	-58.88	170.22	-59.31	109.70		NS	363.38	NS	437.51
	Naphthalene	92-05	--	NS	--	NS		--	41.86	--	26.79
	Phenanthrene	89-05	NS	-21.58	NS	-39.14		33.33	NS	31.89	NS
	Pyrene	86-05	38.24	104.16	11.54	-47.79		149.98	64.94	101.86	-7.33

TRACE METALS							
			FE			NOTL	
			% change [ ]	% change (load)		% change [ ]	% change (load)
		Period	Whole Water	Whole Water		Whole Water	Whole Water
	Aluminum	86-05	-60.77	-68.35		-61.10	-68.59
	Antimony	86-05	-23.23	-38.06		-32.60	-45.57
	Arsenic	86-03	NS	NS		-31.74	-48.68
	Barium	86-05	2.08	-17.64		NS	NS
	Beryllium	86-05	NS	NS		NS	NS
	Cadmium	86-05	-84.85	-87.96		-86.29	-89.17
	Chromium	86-05	-58.11	-66.20		-65.73	-72.33
	Cobalt	86-05	NS	NS		NS	NS
	Copper	86-05	NS	NS		NS	NS
	Iron	86-05	NS	NS		-61.17	-68.65
	Lead	86-05	NS	NS		NS	NS
	Lithium	86-05	NS	NS		-30.28	-43.70
	Manganese	86-05	NS	NS		-55.63	-64.17
	Mercury*	86-05	-4.77	-75.65		-7.32	-47.93
	Molybdenum	86-05	28.13	3.38		32.74	7.18
	Nickel	86-05	NS	NS		-32.07	-45.75
	Selenium	86-05	15.71	-6.64		NS	NS
	Silver	86-05	--	--		--	--
	Strontium	86-05	NS	NS		NS	NS
	Vanadium	86-05	-27.50	-41.50		NS	NS
	Zinc	86-05	NS	NS		-54.31	-63.11

NS = no statistically significant trend
-- = insufficient data to generate trend

Table 5. Trends in Niagara River Contaminant Concentrations and Loadings, 1996/97-2004/05

		FE				NOTL			
		% change []		% change (load)		% change []		% change (load)	
	Period	Dissolved	Particulate	Dissolved	Particulate	Dissolved	Particulate	Dissolved	Particulate
CHLOROBENZENES									
1,2-Dichlorobenzene	96-05	-82.49	--	-84.16	--	-52.18	NS	-56.73	NS
1,3-Dichlorobenzene	96-05	0.37	--	-66.55	--	-28.80	-63.10	-35.56	-70.71
1,4-Dichlorobenzene	96-05	-76.58	--	-78.82	--	-31.96	-28.40	-38.42	-43.17
1,2,3-Trichlorobenzene	96-05	NS	--	NS	--	-64.68	NS	-68.04	NS
1,2,4-Trichlorobenzene	96-05	-57.65	-15.94	-61.69	-46.80	-59.67	-27.24	-63.50	-42.25
1,3,5-Trichlorobenzene	96-05	--	--	--	--	-34.39	-43.29	-40.63	-54.99
1,2,3,4-Tetrachlorobenzene	96-05	-71.06	NS	-73.82	NS	-50.09	-55.25	-54.83	-64.48
Hexachlorobenzene	96-05	-26.05	NS	-33.10	NS	-36.17	-59.37	-42.24	-67.75
Pentachlorobenzene	96-05	-55.95	-42.18	-60.15	-63.41	-43.62	-57.58	-48.98	-66.33
INDUSTRIAL BY-PRODUCTS									
Hexachlorobutadiene	96-05	--	--	--	--	-32.59	-66.75	-39.00	-73.61
Hexachlorocyclopentadiene	96-05	--	--	--	--	NS	-91.28	NS	-93.07
Octachlorostryene	96-05	--	--	--	--	--	NS	--	NS
NEUTRAL HERBICIDES									
Atrazine	96-05	NS	--	NS	--	15.39	--	4.43	--
Metolachlor	96-05	-32.29	--	-38.74	--	-31.03	--	-37.58	--
ORGANOCHLORINE PESTICIDES & PCBs									
Aldrin	96-05	--	--	--	--	--	--	--	--
α-HCH	96-05	-78.34	--	-80.40	--	-77.50	-75.64	-79.63	-80.66
γ-HCH	96-05	-57.42	--	-61.48	--	-63.53	--	-67.00	--
α-Chlordane	96-05	-42.52	NS	-48.00	NS	-62.64	NS	-66.19	NS
γ-Chlordane	96-05	--	-74.86	--	-84.09	--	-58.14	--	-66.77
op-DDT	96-05	--	-83.57	--	-89.60	--	-69.10	--	-75.47
pp-DDD	96-05	-49.01	-73.19	-53.87	-83.03	-28.85	-18.52	-35.61	-35.33
pp-DDE	96-05	-70.08	-70.69	-72.93	-81.45	-65.66	-34.31	-68.92	-47.86
pp-DDT	96-05	--	NS	--	NS	--	NS	--	NS
Dieldrin	96-05	-32.28	NS	-38.74	NS	-27.41	NS	-34.31	NS
α-Endosulfan	96-05	NS	--	NS	--	NS	--	NS	--
β-Endosulfan	96-05	--	--	--	--	-35.89	-58.05	-41.99	-66.71
Endrin	96-05	--	--	--	--	--	--	--	--
Endrin Aldehyde	96-05	--	--	--	--	--	--	--	--
Heptachlor	96-05	--	--	--	--	--	--	--	--
Heptachlor Epoxide	96-05	-34.02	--	-40.31	--	NS	--	NS	--
Methoxychlor	96-05	--	--	--	--	--	--	--	--
Mirex	96-05	--	--	--	--	--	-57.51	--	-66.27
PCBs - Congener	98-05	--	21.92	--	-12.88	--	NS	--	NS
Photo-mirex	96-05	--	--	--	--	--	--	--	--
PAHs									
1-Methylnaphthalene	96-05	NS	30.57	NS	-17.36	-24.36	16.40	-31.55	-7.61
2-Methylnaphthalene	96-05	NS	28.78	NS	-18.50	-29.27	28.92	-35.99	2.33
2-Beta Chloronapthalene	96-05	--	--	--	--	--	--	--	--
Acenaphthalene	96-05	NS	NS	NS	NS	NS	NS	NS	NS
Anthracene	96-05	--	NS	--	NS	--	14.81	--	-8.87
Benz(a)anthracene	96-05	10.17	NS	-0.34	NS	89.44	34.74	71.44	6.96
Benzo(a)pyrene	96-05	17.10	NS	5.93	NS	22.69	22.06	11.03	-3.12
Benzo(bk)fluoranthene	96-05	33.00	50.48	20.32	-4.76	57.04	64.18	42.12	30.31
Benzo(g,h,i)perylene	96-05	-71.14	NS	-73.89	NS	-64.18	22.54	-67.59	-2.73
Chrysene/Triphenylene	96-05	NS	NS	NS	NS	NS	NS	NS	NS
Dibenzo(a,h)anthracene	96-05	--	NS	--	NS	--	59.87	--	26.90
Fluoranthene	96-05	3.38	NS	-6.48	NS	NS	19.45	NS	-5.19
Fluorene	96-05	31.08	NS	18.58	NS	NS	21.06	NS	-3.90
Indeno(1,2,3-cd)pyrene	96-05	-75.16	NS	-77.53	NS	-57.86	27.60	-61.87	1.28
Naphthalene	96-05	--	NS	--	NS	--	43.43	--	13.85
Phenanthrene	96-05	17.28	NS	6.10	NS	NS	17.61	NS	-6.64
Pyrene	96-05	NS	45.91	NS	-7.65	NS	32.17	NS	4.91

TRACE METALS

		FE		NOTL	
		% change []	% change (load)	% change []	% change (load)
	Period	Whole Water	Whole Water	Whole Water	Whole Water
Aluminum	96-05	NS	NS	NS	NS
Antimony	96-05	NS	NS	NS	NS
Arsenic	96-03	29.70	9.17	8.31	-8.83
Barium	96-05	16.40	5.31	NS	NS
Beryllium	96-05	NS	NS	NS	NS
Cadmium	96-05	-68.34	-71.23	-64.60	-67.16
Chromium	96-05	NS	NS	NS	NS
Cobalt	96-05	-65.69	-68.96	-48.18	-53.11
Copper	96-05	NS	NS	NS	NS
Iron	96-05	NS	NS	NS	NS
Lead	96-05	NS	NS	NS	NS
Lithium	96-05	NS	NS	NS	NS
Manganese	96-05	NS	NS	NS	NS
Mercury	96-05	-4.76	-39.72	0.50	-20.23
Molybdenum	96-05	60.97	1.88	NS	NS
Nickel	96-05	NS	NS	NS	NS
Selenium	96-05	NS	NS	NS	NS
Silver	96-05	--	--	--	--
Strontium	96-05	19.24	7.87	NS	NS
Vanadium	96-05	NS	NS	NS	NS
Zinc	96-05	NS	NS	NS	NS

NS = no statistically significant trend
-- = insufficient data to generate trend

4.2.1. Long Term Concentrations (1986/87 - 2004/05)

In general, Table 4 shows that most of the organic Upstream/Downstream analytes exhibit a long term downward trend in both dissolved and particulate phase concentrations.

At Fort Erie, statistically significant reductions in dissolved phase dominant compounds ranged from 32.21% in 1,3-Dichlorobenzene to 97.16% in α-HCH. Concentrations in particulate phase dominant compounds underwent declines ranging from 24.85% in Benz(a)anthracene to 84.68% in the DDT metabolite o,p-DDT.

At Niagara-on-the-Lake, concentration reductions in dissolved phase dominant compounds ranged from 7.95% in Atrazine to 96.07% in α-HCH. For particulate phase dominant compounds, the downward trends ranged from 56.64% in Mirex to as much as 93.71% in the industrial by-product Octachlorostyrene.

Similarly, both stations also experienced reductions in some trace metal concentrations over the 1996-2005 time period. Mercury concentrations at Fort Erie represent the smallest decline at 4.7% and Cadmium concentrations at Niagara-on-the-Lake represent the largest at 86.29%.

Despite the general downward trend in chemical concentrations in the Niagara River, results also indicate that there are compounds which have undergone a statistically significant increase in concentrations over the 19-year period between 1986/87 and 2004/05; however, these upward trends were only observed in compounds from the neutral herbicide, trace metal, and PAH classes and will be discussed in more detail on the following pages under their respective class headings.

Chlorobenzenes

Long term downward trends are observed in all Chlorobenzenes with the exception of 1,3,5-Trichlorobenzene at FE where there was insufficient data to produce a trend. Reductions are fairly consistent between both stations and range from 50.48% in Pentachlorobenzene to 93.61% in 1,2,4-Trichlorobenzene. For most compounds, reductions were slightly more pronounced at the upstream station; however, NOTL experienced larger declines in Pentachlorobenzene and Hexachlorobenzene. In the case of the latter, it is interesting to note that the data shows phase distribution shifts from 80% dissolved phase at Fort Erie to a 50% dissolved phase at NOTL. A similar shift in phase distribution occurs with Pentachlorobenzene and, while the specific causes for these changes has not been fully investigated, there is the possibility that they are related to increased inputs of hexa and penta chlorobenzene contaminated sediment along the reach of the river.

Organochlorine Pesticides and PCBs

Interpretation of the organochlorine pesticide and PCB class is complicated by the broader range and variation of phase distributions between both compounds and stations. It should also be pointed out that the trend model was only run between 1986/97 and 1997/98 for PCBs due to a change in analytical protocol. As outlined in the “Niagara River Upstream/Downstream Monitoring Program Final Report 1999/00 & 2000/01”, the change from an Aroclor based method to a congener specific method for the analysis of total PCBs make it impossible to directly compare PCB data from the method used prior to April 1998 to those results after this date. In addition, only the sediment phase PCB data was considered due to concerns of contamination of the dissolved phase data.

Regardless of phase distribution, virtually all of the compounds reported significant downward trends of at least 50%; several had downward trends of greater than 75% (the greatest reduction was observed in α-HCH which decreased by approximately 97% at both FE and NOTL), and the magnitude of these trends appear to be fairly consistent between the upstream and downstream stations for all compounds within this class. Interestingly, it should be pointed out that the only compounds that didn't have downward trends had "insufficient data" to generate a trend at all. Approximately 9 of 20 OC compounds had "insufficient data" in their dominant phase(s) indicating that the concentrations and, more importantly, the frequencies of detection were not of notable concern.

Industrial By-Products

In the industrial by-product class, significant downward trends were only observed at the NOTL site where Hexachlorobutadiene concentrations declined by approximately 79% and Octachlorostyrene concentrations fell by almost 94% between 1986/87 and 2004/05 in their predominant phases. There was insufficient data to calculate Hexachlorocyclopentadiene dissolved phase trends at NOTL and for all three compounds at Fort Erie.

Neutral Herbicides

Of the two neutral herbicides measured in the Niagara River, only Metolachlor showed an upward trend over the 1986/87 - 2004/05 time period when it increased by approximately 27% at Fort Erie and 6% at Niagara-on-the-Lake. Conversely, Atrazine concentrations did not show any significant trend at the upstream site and declined by 7.95% at NOTL.

Trace Metals

For trace metals, the increases at Fort Erie ranged from 2.08% for Barium to 28.13% for Molybdenum, the latter of which also had the only significant upward trace metal trend at NOTL where it increased by 32.74%. Only one other compound, Selenium, exhibited an upward trend and, like Barium, its increase was only significant at the Fort Erie site.

PAHs

Of all the compound classes, the PAH group has the largest number of significant upward trends and the largest magnitude of increases. At Fort Erie, concentrations for 6 of the 17 PAHs increased by 83.63% to 170.22% (Benzo(bk)fluoranthene and Indeno(123cd)pyrene respectively) while NOTL had 5 PAHs increase from 64.94% (Pyrene) to 363.38% (Indeno(123cd)pyrene). With exception of fluoranthene, phenanthrene, and pyrene, upward trends are only observed in those PAH compounds which tend to partition into the particulate phase. Of the three exceptions, phenanthrene is typically found predominantly in the dissolved phase whereas only 30-35% of fluoranthene and pyrene are found in the dissolved phase. The reason for these increases are not fully understood at this point; however, work by Howell et al. (1996) suggest zebra and quagga mussel colonization may lead to greater adsorption of contaminants onto sediments due to the mussels' impacts on sediment grain size distributions. Evidence also suggests that the Niagara region may be influenced by increases in urbanization (Van Metre et al., 2000), vehicular traffic at border crossings (Beningo, 2006), and the use of coal for power and steel production (Simcik and

Offenberg, 2006). Other dissolved phase PAHs either saw concentration declines, no significant trends, or had insufficient data to evaluate. In general, it appears that PAH compounds with an upward trend are increasing by a greater magnitude at NOTL than FE and that PAH compounds with a downward trend show greater declines at the downstream (NOTL) site.

4.2.2 Long Term Loadings (1986/87 - 2004/05)

In general, decreases in contaminant concentration should, typically, result in a decreased load and *vice versa*. Table 4 demonstrates that this is true for most of the Niagara River compounds; in fact, there is almost a 1:1 correlation between dissolved phase concentration and loading trends at FE and NOTL. In the particulate phase, loading trends also tend to follow the same general direction as their associated particulate phase concentrations; however, the magnitudes of loading trends appear to be larger for downward trends and smaller for upward trends. For example, a 61.38% decline in particulate phase concentrations of PCBs at FE has a corresponding drop of 85.65% in particulate phase loadings while a 114.46% increase in particulate phase Benzo(ghi)perylene concentrations at FE corresponds to a 66.43% increase in particulate phase loadings. For a few particulate phase compounds, loadings actually decreased where their weight of contaminant per weight of particulate (ng/g) concentrations increased. In all these cases, the reduced magnitude of the loading trends is due primarily to the fact that SPM concentrations in the Niagara River decreased by as much as 72% over the 1986/87 to 2004/05 period (Fig. 3).

Trace Metals

Despite the few upward trends in trace metal concentrations, only Molybdenum showed an upward trend (3.38% at FE and 7.18% at NOTL) in trace metal loadings. While several compounds in this class did not exhibit a significant trend in either direction, most trace metal loadings fell by 45% or more. The smallest loading declines were reported for Selenium (down 6.64% at Fort Erie) which had an upward trend in long term concentrations. Interestingly, Barium loadings were reduced by more than 17% at FE despite its marginal (~2%) long term concentration increase. Cadmium experienced the largest reduction in loadings dropping 87.96% at Fort Erie and 89.17% at Niagara-on-the-Lake. Vanadium and Mercury loadings also underwent relatively large declines at Fort Erie; however, corresponding reductions in NOTL loadings were smaller or not statistically significant, a characteristic influenced by the general decline in suspended sediment concentration highlighted earlier in this report.

Neutral Herbicides

Based on our analysis, the neutral herbicides are found primarily in the dissolved phase (Table 2). As a result, they are less prone to the influence of changing suspended sediment concentrations. In the case of Metolachlor, upward trends in loadings closely mirror upward trends in concentration at FE and NOTL with the increases being somewhat larger at the upstream station (FE loadings increased by 26% while NOTL loadings increased by 5%). For atrazine, the downward trends in concentration and loading at NOTL were also very similar in magnitude (8% and 9% respectively) while there was no significant trend in either concentration or loading at FE.

Chlorobenzenes

Like the neutral herbicides, chlorobenzene compounds are found almost exclusively in the dissolved phase (Table 2); consequently, long-term loading trends tend to closely reflect long-term concentration trends. Again, all of the statistically significant loading trends are decreasing with the greatest reduction observed in 1,2,4-Trichlorobenzene at FE (94.84%) followed closely by 1,2,3-Trichlorobenzene at NOTL (89.05%). Loadings of 1,3-Dichlorobenzene at FE underwent the smallest change (45.31%) over the 1986/87 - 2004/05 time period; however, aside from that, long term loading trends were very consistent between the upstream and downstream stations. In the case of Hexachlorobenzene, which shifts from a predominately dissolved phase compound at FE to an evenly distributed dissolved and particulate phase compound at NOTL, the influence of SPM trend can be seen in the difference between the reductions in particulate phase concentration (~70%) and loading trends (83%) at the downstream (NOTL) site.

PAHs

PAH compounds vary in their phase distributions (Table 2) with lower molecular weight compounds associated more with the dissolved phase and higher molecular weight compounds with the particulate phase. The data indicates that there is some similarity between the dissolved phase compounds in this class and the neutral herbicides and chlorobenzenes because they all show a relatively consistent relationship between concentration and loading trends. For example, a 59.66% reduction in Acenaphthalene concentrations at FE results in a 60.09% reduction in loadings and a 19.86% decline in Fluorene concentration at NOTL results in a 20.73% reduction in loadings. It is interesting to note that Phenanthrene is the only predominantly dissolved phase PAH with a long term upward trend, a trend that is observed in both concentration and loading at NOTL. The remaining dissolved phase dominant PAH compounds either had insufficient data to determine a loading trend or the trends were not statistically significant.

PAH compounds with a dominant particulate phase distribution show a strong influence from the long term reduction of SPM in the Niagara River. Compounds like Anthracene and Benz(a)anthracene with a downward concentration trend exhibit an even larger downward loading trend while upward loading trends are slightly smaller for PAHs with an upward concentration trend like Benzo(a)pyrene (NOTL), Benzo(ghi)perylene, and Indeno(123cd)pyrene. In the case of Benzo(bk)fluoranthene, Benzo(a)pyrene (FE), and Fluoranthene, the influence of SPM reductions actually produces a downward trend in loadings despite an increase in overall concentrations.

In general terms, it is interesting to note that the magnitude of loading reductions for dissolved phase PAH compounds is greater at NOTL than FE while the magnitude of particulate phase loading reductions at NOTL tend to be lower. Conversely, the increases in particulate phase loadings are considerably higher at NOTL than FE and, with the exception of Benzo(a)pyrene, tend to result from considerably higher NOTL concentration increases.

Organochlorine Pesticides and PCBs

The OC pesticide and PCB group tends to exhibit similar trends to those discussed in the previous compound classes. This group is comprised of several dissolved phase dominant compounds such as the HCHs, Dieldrin, Endosulfan, and Heptachlor Epoxide which not only show consistent downward trends, but the same approximate 1:1 relationship between concentration and loading. Again, the only dissolved phase compounds that don't show a downward trend are the compounds with insufficient data. In fact, regardless of phase distribution, the only OC compounds that don't show a downward trend are the compounds with insufficient data.

For the particulate phase dominant compounds in this class, the influence of the SPM trend increases the magnitude of the loading reductions similar to the PAH class and, again, the declines are slightly larger at FE (Figure 3). In the case of those compounds which are more evenly distributed across both phases, the downward loading trends appear to be magnified slightly in both phases and, with the exception of PCBs, the declines are once again slightly larger at the upstream (FE) station.

Industrial By-Products

The industrial by-product class presents two interesting cases, one of which is different than any other compound in the Niagara River sampling suite. All three compounds (Octachlorostyrene, Hexachlorocyclopentadiene, and Hexachlorobutadiene) have insufficient data to generate concentration and loading trends at Fort Erie and Hexchlorocyclopentadiene also has insufficient data to generate trends in its dominant dissolved phase at NOTL. Hexachlorobutadiene comes close to showing to same approximate 1:1 relationship between concentration and loading trends that has been observed in most dissolved phase compounds; however, in this case the magnitude difference between concentration and loading declines is slightly larger, perhaps due to the fact that there is a slight difference in phase distribution between FE and NOTL and the possibility that slightly more hexachlorobutadiene remains bound to sediments. More interesting still is the fact that the magnitude of the downward trend in particulate phase Octachlorostyrene loadings is virtually the same as the downward trend in particulate phase concentration. In every other particulate phase compound, the long term reduction in Niagara River SPM concentration has magnified the effects of falling concentrations on loadings. It is possible that this is reflective of the fact that SPM concentrations at NOTL have not declined as much as they have at FE but, at this time, the reason for this anomaly is not fully understood and therefore warrants further investigation.

4.2.3 Recent Concentrations (1996/97 - 2004/05)

Similar to the long term concentration trends, most of the Niagara River compounds underwent a significant decrease in concentration over the 1996/97 - 2004/05 time period in both dissolved and particulate phase (Table 5). With the exception of relatively few (e.g. FE PCBs), most compounds either experienced downward concentration trends between 1996/97 - 2004/05, did not show statistically significant trend in either direction, or did not have sufficient data to generate a trend. Rates of decline varied from to 4.76% in Mercury at FE to 83.57% for the organochlorine pesticide o,p-DDT.

These results suggest that management actions have been successful in reducing the concentration of most contaminants; however, results also indicate that there are some remaining chemicals with Niagara River and/or upstream sources. As a result, a more detailed analysis is required to assess the cost/benefit of further management to track the sources of these compounds.

Organochlorine Pesticides and PCBs

Along with o,p-DDT, there are a number of compounds in the OC pesticide and PCB class with significant downward trends between 1996/97 and 2004/05. In fact, the 21.92% increase in PCB concentrations at FE is the only upward trend in this class. Concentrations of the HCHs fell approximately 58-78%, Chlordane concentrations fell by approximately 42-75%, and all of the DDT metabolite concentrations except p,p-DDT fell by approximately 28-84% (p,p-DDT did not have a significant trend at either Niagara River sampling location). Although the trends are fairly similar at both stations, it does appear that OC pesticide reductions are slightly higher at FE than NOTL and it's interesting to note that recent downward trends at FE and NOTL are smaller than the long term trends. The other interesting thing to note is that 5 compounds in this class reported non-significant trends in their dominant phase and another 9 had insufficient data to determine a trend. Again, this is considered to be a positive indication that these compounds are becoming less of an environmental concern and that management actions in banning or limiting their use have been effective.

PAHs

The PAH class also has a number of compounds showing no significant trend over the 1996/97 - 2004/05 time period, particularly at FE where 12 of the 17 analytes are designated as "NS" in their dominant phase. With the exception of 1-methylnaphthalene and 2-methylnaphthalene, the remainder of the PAH compounds all exhibit significant upward trends in their dominant phase. The largest increase is found in benzo(bk)fluoranthene at NOTL (64.18%) and the smallest increase is found in Anthracene at NOTL (14.81%). It is suspected that the reasons for recent PAH trends, particularly the increasing concentrations, are similar to those of the longer term trends described in section 4.2.1 (urbanization, vehicular traffic, coal for power and steel production, etc.). In general, the increases in PAH concentrations are higher at NOTL (with the exception of fluorene, phenanthrene, and pyrene) and the 1996/97-2004/05 trends are smaller in magnitude than those in the longer term 1986/87-2004/05 period.

Industrial By-Products

Recent changes in concentrations for the industrial by-products, like those in the PAH compound class, are notably smaller in magnitude than their associated long term trends. There is still insufficient data for all three compounds at FE; however, Octachlorostyrene no longer exhibits a statistically significant trend at NOTL and the 79% decline observed in Hexachlorobutadiene concentration between 1986/87 and 2004/05 drops to 32.59% during the 1996/97-2004/05 time period. Hexachlorocyclopentadiene does not show a significant trend in its dominant phase (dissolved) over the more recent time frame.

These results indicate that trends in the industrial by-product class appear to be leveling off which, again, implies a more detailed analysis is required to assess the cost/benefit of further management to track the sources of these compounds.

Trace Metals

Striking changes can be found in the recent trace metal concentrations as well. In addition to a slight increase in the number of compounds reporting no significant trend, there are a greater number of compounds with upward trends. Two of the three compounds that had upward trends in the long term analysis (Barium and Molybdenum) actually have steeper upward trends over the more recent time period. Along with Barium and Molybdenum, increasing trends are now observed in Arsenic, Strontium, and Mercury and several of the compounds with long term downward trends (Aluminum, Antimony, Chromium, and Vanadium) are now reporting no significant trend. It should be pointed out that the recent trend analysis for Arsenic was run from 1996/97 - 2002/03 due to the implementation of a new analytical method for this compound in 2003/04 which would not allow for a meaningful comparison with earlier data.

Neutral Herbicides

Similar to the trace metals, Atrazine and Metolachlor concentration trends change considerably when looking at the most recent 9 years of data. Compared to the long term concentration trends, the 1996/97-2004/05 trends for these two compounds change in magnitude and, more importantly, in direction. There is still no significant trend for Atrazine at FE but the long term reduction of approximately 8% at NOTL changes to an increase of more than a 15% in the more recent time period. Conversely, the long term Metolachlor increases observed at FE and NOTL become fairly consistent reductions of just over 31% between 1996/97 and 2004/05.

Chlorobenzenes

Compounds in the chlorobenzene class continue to show many of the same concentration characteristics in their recent trends as those observed in the longer term analysis. All but one of the analytes (1,3-dichlorobenzene) reporting significant trends show a reduction in concentration between 1996/97 and 2004/05 and even that single upward trend represents and increase of less than 1% over the nine-year period. Also similar to the 1986/87-2004/05 results, the magnitude of recent downward trends tend to be greater at the FE site; however, recent downward trends at the upstream location are very similar to the longer term trends while recent reductions in NOTL concentrations are notably smaller than their corresponding long term results.

4.2.4 Recent Loadings (1996/97 - 2004/05)

In most cases, the recent loading trends closely parallel the concentration trends in terms of direction and magnitude; however, the loadings generally tend to have slightly reduced upward trends and slightly increased downward trends, especially in the particulate phase dominant compounds. Out of the 72 Upstream/Downstream analytes, only 12 report significant upward trends between 1996/97 and 2004/05 and, while the increases ranged from 1.28% for Indeno(123cd)pyrene at NOTL to 30.31% for Benzo(bk)fluoranthene at NOTL, most tend to fall in the 5% - 20% range. Conversely, 37 compounds report a significant downward trend and these range from approximately 2.8% for benzo(ghi)perylene at NOTL to 89.60% for o,p-DDT at FE.

PAHs

Of the 12 compounds showing statistically significant loading increases, 7 are found in the PAH class. Interestingly, 6 of those 7 compounds (Benz(a)anthracene, Benzo(bk)fluoranthene, Dibenzo(ah)anthracene, Indeno(123cd) pyrene, Naphthalene, and Pyrene) only report upward trends at NOTL while the remaining PAH (Phenanthrene) reports an upward trend at FE alone. All 7 compounds show no significant trend at the other station except for Pyrene which actually shows a downward loading trend at FE. In addition, the magnitude of recent loading trend is greater for each of the 7 compounds except for Indeno(123cd)pyrene which reports a minor increase of only 1.28% at NOTL over the 1996/97-2004/05 span.

At the same time, the magnitude of declines in PAH compounds such as 1- and 2-methylnaphthalene and Pyrene are reduced over the 1996/97 - 2004/05 time period. In other PAHs (e.g. Anthracene and Acenaphthalene), long term reductions are replaced by non-significant trends in the recent period or, in the case of Benzo(b/k)fluoranthene, actually replaced by a recent loading increases.

Conversely, Benzo(a)pyrene and Benzo(ghi)perylene loadings at NOTL shift from long term increases to recent decreases while the long term reduction of Fluoranthene loading at the downstream station increases in magnitude.

Organochlorine Pesticides and PCBs

OC pesticides and PCBs continue to show the same general loading trends between 1996/97 and 2004/05 as they do over the longer time period. None of the compounds report a significant upward trend in loadings, 14 report either no significant trend or insufficient data to generate a trend and 12 show a significant reduction, some as high as 89.60% (o,p-DDT). The influence of SPM concentration trends is still apparent in the particulate phase compounds, particularly in the PCBs at FE where loadings fell by approximately 13% despite a 22% increase in concentration; however, the effect appears to have waned slightly, perhaps due to the fact that SPM concentrations were relatively stable over the 1996/97-2004/05 time period. At the same time, dissolved phase dominant compounds like HCH, Dieldrin, and Heptachlor Epoxide continue to show a 1:1 relationship between concentrations and loadings. It should be noted that while the general loading trends in both the 19- and 9-year periods are similar, reductions observed in the recent loading trends are notably smaller than those observed over the longer time frame.

Chlorobenzenes

The chlorobenzene compounds mirror the OC pesticide and PCB class as they exhibit the same downward trends starting with the 1996/97 base year as they did starting in 1986/87. In addition, downward trends at NOTL tend to be notably smaller in magnitude than those at FE. Exceptions to this include 1,2,3-and 1,3,5-Trichlorobenzene which report significant downward trends at NOTL when none exist at Fort Erie and Hexachlorobenzene which appears to be undergoing a more significant reduction at the downstream NOTL site relative to FE.

Industrial By-Products

Recent loading trends for compounds in the industrial by-product class are also very similar to their longer term results. All three analytes continue to have insufficient data to generate loading trends at Fort Erie and, while there is enough data for the model to run a trend for the dominant phases of Octachlorostyrene and Hexachlorocyclopentadiene at NOTL, the results indicate there is no significant trend at either site over this time period. In the case of Hexachlorobutadiene, the reduction in loading falls from 83% to 39% with the shorter time period.

Neutral Herbicides

Results for recent loading trends are relatively consistent with recent concentration trends for one of the two neutral herbicides. The 30-40% reduction in Metolachlor loadings at FE and NOTL closely mirror the concentration reductions. The interesting thing to note is that these reductions stand in stark contrast to the upward trends reported for the long term analysis of this compound. In the case of Atrazine, there is still no significant trend for either concentration or loading at FE but, more importantly, the long term reductions reported for loadings and concentrations of Atrazine at NOTL are both replaced by upward trends in the 1996/97 - 2004/05 time period.

Trace Metals

Similar to recent trends in trace metal concentrations, analysis of recent loadings show an increase in both the number of compounds with no significant trend and the number of compounds with increasing trends as well as a reduction in the magnitude of downward trends. Between 1986/87 and 2004/05, only Molybdenum had an increasing trend for loadings; however, the number increases to 4 (Arsenic, Barium, Molybdenum, and Strontium) when looking at the 1996/97-2004/05 data, all of which are found at the FE station. At the same time, the magnitude of significant long term downward trends for Cadmium and Mercury at both stations along with NOTL Arsenic is reduced and the downward trends for 10 other trace metals are no longer significant.

4.3 Sources

In addition to identifying exceedences and examining trends, the Niagara River Upstream/Downstream Program provides a means of comparing concentrations at NOTL to those measured at FE to identify chemicals with Niagara River sources. In the past, source analysis focused on differential loadings. In this report, a Recombined Whole Water (RWW) concentration ratio was calculated using the formula:

$$\frac{[MLE_{NOTL}]}{[MLE_{FE}]}$$

A statistical analysis was used to determine if there is a significant difference between NOTL and FE MLE concentrations (El-Shaarawi, pers. comm.). MLE ratios greater than one indicate a higher concentration of the analyte at the downstream (NOTL) site while ratios less than one indicate a higher concentration at the upstream site (FE). The significance of the annual MLE ratio is determined by the range of values between the upper and lower 90% confidence interval (CI). If the CI range includes unity (i.e. a value of “1”), the upstream/downstream difference is NOT considered to be significant.

Historical MLE ratios for each compound have been tabulated and recorded in Appendix F; however, Table 6 summarize this information for the most recent 5 years of downstream/upstream ratios of the annual MLE for Organic RWW and Trace Metal Whole Water (WW) concentrations respectively.

Table 6. Statistically Significant MLE Ratios for Niagara River Contaminants

	2000-2001	2001-2002	2002-2003	2003-2004	2004-2005
Chlorobenzenes					
1,2-Dichlorobenzene	NOTL	NOTL	NOTL	NOTL	NOTL
1,3-Dichlorobenzene	NOTL	NOTL	NOTL	NOTL	NOTL
1,4-Dichlorobenzene	3.646	3.533	4.331	5.791	NOTL
1,2,3,4-Tetrachlorobenzene	36.443	29.289	28.474	28.541	43.969
1,2,3-Trichlorobenzene	13.711	7.728	11.801	5.647	6.385
1,2,4-Trichlorobenzene	13.986	13.441	15.527	9.031	10.196
1,3,5-Trichlorobenzene	7.969	NOTL	NOTL	NOTL	NOTL
Hexachlorobenzene	2.882	3.454	3.249	2.791	4.279
Pentachlorobenzene	4.793	5.033	8.756	5.710	9.465
Industrial By-products					
Hexachlorobutadiene	NOTL	19.757	NOTL	NOTL	NOTL
Hexachlorocyclopentadiene	NOTL	NOTL	--	1.464	5.913
Octachlorostyrene	NOTL	NOTL	NOTL	NOTL	NOTL
Neutral Herbicides					
Atrazine	NS	0.841	NS	1.135	NS
Metolachlor	NS	0.853	1.029	1.065	1.071
OC Pesticides & PCBs					
Aldrin	--	--	--	--	--
α-Chlordane	0.838	1.540	1.837	1.149	1.259
γ-Chlordane	0.813	1.850	1.510	1.171	1.218
o,p-DDT	0.721	FE	FE	--	9.831
p,p-DDD	0.610	NS	0.925	0.908	0.688
p,p-DDE	0.335	0.708	0.651	0.895	NS
p,p-DDT	0.392	0.770	1.105	0.824	NS
Dieldrin	0.794	1.054	1.123	1.154	1.165
α-Endosulfan	1.509	1.654	1.475	1.407	1.354
β-Endosulfan	12.025	2.270	1.616	1.414	NOTL
Endrin	NOTL	--	--	--	--
Endrin Aldehyde	--	--	1.205	--	--
α-HCH	1.240	1.376	1.435	1.374	1.244
γ-HCH	1.083	1.162	1.193	1.147	0.971
Heptachlor	--	--	--	--	--
Heptachlor Epoxide	0.758	NS	1.256	1.350	1.311
Methoxychlor	FE	--	--	--	--
Mirex	NOTL	NOTL	NOTL	NOTL	NOTL
Photomirex	NOTL	--	--	--	--
PCB (Total)	1.372	2.626	3.148	1.785	2.633
PAHs					
1-Methylnaphthalene	0.853	1.370	1.624	NS	NS
2-Methylnaphthalene	NS	1.363	1.427	1.322	NS
Acenaphthylene	NS	2.487	2.684	2.024	1.749
Anthracene	0.614	2.927	3.282	2.330	2.159
Benz(a)anthracene	0.566	2.456	4.940	2.181	2.206
Benzo(a)pyrene	0.560	2.211	4.692	2.025	2.427
Benzo(bk)fluoranthene	0.587	1.937	4.171	1.936	2.353
Benzo(g,h,i)perylene	0.455	2.154	3.962	1.727	2.612
Chrysene/Triphenylene	0.578	2.027	3.632	1.999	2.507
Dibenzo(a,h)anthracene	0.543	2.926	5.681	1.810	2.486
Fluoranthene	0.618	1.909	3.133	1.869	1.886
Fluorene	NS	1.608	1.698	1.606	1.184
Indeno(1,2,3-cd)pyrene	0.412	2.217	4.154	1.803	2.494
Napthalene	0.516	1.229	5.253	2.413	3.914
Phenanthrene	0.871	1.844	2.510	1.839	1.623
Pyrene	0.700	2.274	4.699	2.080	2.479

Table 6. Statistically Significant MLE Ratios for Niagara River Contaminants

	2000-2001	2001-2002	2002-2003	2003-2004	2004-2005
Trace Metals					
Aluminum	1.716	0.622	1.301	4.722	2.504
Antimony	NS	0.975	1.023	2.852	1.075
Arsenic	NS	1.036	NS	1.507	1.168
Barium	1.034	NS	NS	1.957	1.089
Beryllium	1.501	0.841	1.526	2.192	3.219
Cadmium	1.184	NS	1.163	1.192	1.882
Chromium	NS	NS	1.540	2.399	2.366
Cobalt	1.863	0.773	1.578	NS	2.736
Copper	1.103	NS	1.150	1.568	1.468
Iron	2.161	0.758	1.574	1.919	3.007
Lead	1.790	0.844	1.442	1.948	2.222
Lithium	1.182	NS	1.140	1.255	1.251
Manganese	1.558	0.704	1.558	2.276	2.714
Mercury	1.304	1.410	1.641	1.634	1.381
Molybdenum	NS	1.035	NS	1.626	NS
Nickel	1.337	0.812	1.202	1.633	1.492
Selenium	0.773	NS	0.954	NS	0.908
Silver	FE	1.370	NOTL	3.355	2.895
Strontium	NS	0.988	0.991	3.075	NS
Vanadium	1.276	0.895	1.195	1.906	1.728
Zinc	1.558	NS	1.506	1.464	3.033

NS = non-significant ratio
FE = only detected at Fort Erie
NOTL = only detected at Niagara-on-the-Lake
-- = not detected

It is important to note that these ratios may differ slightly from those reported in the 2001/02 - 2004/05 Upstream/Downstream report. In that report, the ratios were based upon organic RWW when a compound had 3 or more measurements reported above the practical detection limit in both phases. If only one phase had 3 or more measurements above the PDL, that phase was used as the basis for the RWW concentration, loading, and MLE ratio. In this analysis, the MLE ratio is based strictly upon the "true" RWW and therefore may contain the contribution of a phase which had less than 3 measurements above the PDL (an approach that differs from the annual MLE values reported in Appendices B and C).

In 1986/87, the Upstream/Downstream program included 50 of the 72 compounds found in the current suite of analytes. Of those 50 compounds, the MLE ratio analysis indicates that 28 analytes (56%) had significant Niagara River sources and another 7 analytes (14%) had significant upstream sources. In the 2004/05 fiscal year, 49 of the 72 compounds (68%) show evidence of significant Niagara River sources while only one (p,p-DDD) shows evidence of significant upstream sources. In many cases, the ratio value has increased (indicating a more significant Niagara River source) and the number of compounds found only at the downstream station has increased slightly from 3 out of the original 50 compounds (6%) in 1986/87 to 7 out of 72 (9%) in 2004/05.

Neutral Herbicides

Examination of the MLE ratios for the two neutral herbicides shows a very small proportion are statistically significant. In the case of both Atrazine and Metolachlor, the few significant ratios that are reported are relatively small (i.e. >0.7 and <1.2) and waver between indicating Niagara River sources and upstream sources.

Trace Metals

Like the neutral herbicide class, many of the trace metal ratios can not be considered statistically significant because the upper and lower confidence interval contains “unity”. In addition, the ratios tend to show a relatively small difference between the upstream and downstream MLE concentrations. Exceptions include Aluminum, Beryllium, Chromium, Iron, Manganese, and Silver which all show fairly consistent ratios of 2.0 or greater - particularly in the more recent years - indicating they have Niagara River sources.

Organochlorine Pesticides and PCBs

Despite the relatively small and uniform range of significant ratios in the OC pesticide and PCB class, there are a number of compounds including Mirex, β-endosulfan, and γ-chlordane which tend to only appear at NOTL. In addition, PCB ratios tend to be above 2.5 for most of the period of record indicating MLE concentrations at the downstream station are often more than double those at the upstream station. On the other hand, compounds such as Aldrin, Endrin, Endrin Aldehyde have often only appeared at FE and the entire suite of DDT metabolites show a predominant upstream source, the latter of which is consistent with the previous discussion on local DDT sources found in section 4.1.

PAHs

The MLE ratio analysis results show that most, if not all, of the PAH compounds have significant Niagara River sources. In fact, the 2000/01 fiscal year is the only period where downstream concentrations were significantly lower than those upstream and, as mentioned in Section 4.1, there is strong evidence to suggest that the FE station was influenced by a significant local source of PAH which lead to unusually high upstream concentrations which, in turn, dramatically reduced the MLE ratios. For the rest of the 1986/87-2004/05 time period, MLE ratios for PAH compounds tend to fall within the 1.5 - 3.0 range indicating downstream concentrations are often 2 to 3 times higher than those upstream with a few PAHs having ratios as high as 5.086 (Anthracene) and 8.743 (Dibenzo(ah)anthracene).

Chlorobenzenes

Analysis of the chlorobenzene class shows nothing but significant MLE ratios, all of which range from a low of 1.3 (1,2-dichlorobenzene) to a high of 43.97 (1,2,3,4-tetrachlorobenzene). In addition, several of the chlorobenzene compounds including 1,2- and 1,3-dichlorobenzene, 1,3,5-trichlorobenzene, and 1,2,3,4-tetrachlorobenzene are often only found at NOTL. This analysis indicates that the chlorobenzene class has the most predominant Niagara River sources signature of all the compounds in the current suite of analytes.

Industrial By-Products

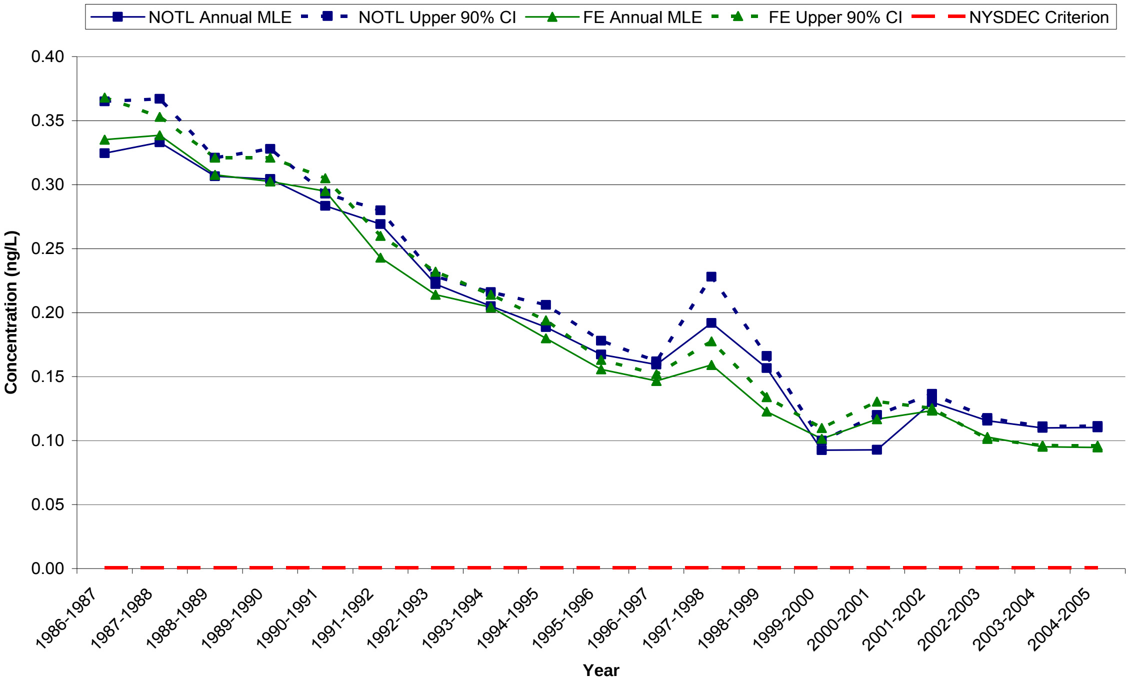
The industrial by-products class is similar to the chlorobenzenes in terms of Niagara River sources. Over most of the period of record, Octochlorostyrene, Hexachlorobutadiene, and Hexachlorocyclopentadiene have only been found at NOTL. In the two years when Hexachlorocyclopentadiene was measured at both stations (2003/04 and 2004/05), the ratios ranged from 1.464 to 5.913 and during the 7 years when Hexachlorobutadiene was measured at both stations, the ratios ranged from 3.3 to 157.64.

4.4 Modified Source Analysis

Based on the Recombined Whole Water MLE Ratio method in this report, it is clear that there continue to be Niagara River sources for many of the organic and trace metal compounds. Closer examination of this method of analysis, however, does draw attention to some anomalies in the results. For example, the significant ratios for the DDT metabolites may be misleading in terms of their suggestion of Lake Erie as a potential source since, as previously mentioned in section 4.1, investigations suggest a local DDT source in sediments. More significantly, based on this approach, Dieldrin appears to have significant Niagara River sources despite evidence that suggest this compound is ubiquitous in the Great Lakes environment (Stevens and Neilson 1989; L'Italien 1993; L'Italien 1996; Williams et al 1998a; Williams et al 1998b; Williams and Kuntz 1999; Jorgenson 2001) and that its consistent detection in air and precipitation throughout the Great Lakes basin suggests the atmosphere may be its primary route of entry into the lakes (Chan et al 1994; Hoff et al 1996; Cortes et al 1998; Hillery et al 1998).

Closer examination of Dieldrin data from the Niagara River Upstream/Downstream program (Fig. 4) shows very little difference between FE and NOTL recombined whole water concentrations; further evidence that there is not a significant Niagara River source for this compound.

Figure 4: Recombined Whole Water MLE Dieldrin Concentrations (1986/87 - 2004/05)



Using Dieldrin's upper and lower 90% confidence intervals (1.283 and 0.742 respectively) as a criteria for establishing statistical significance, the data was re-evaluated and the results were compiled in Appendix G. Looking at the most recent 5 years (Table 7), it's clear that a number of analytes would be dropped from the list of compounds with statistically significant ratios including Atrazine, Metolachlor, γ-HCH, and Lithium along with several years of Heptachlor Epoxide, Antimony, Arsenic, Copper, Nickel, Strontium, Vanadium, and, of course, Dieldrin.

Table 7. Statistically Significant MLE Ratios for Niagara River Contaminants (Modified Confidence Interval)

	2000-2001	2001-2002	2002-2003	2003-2004	2004-2005
Chlorobenzenes					
1,2-Dichlorobenzene	NOTL	NOTL	NOTL	NOTL	NOTL
1,3-Dichlorobenzene	NOTL	NOTL	NOTL	NOTL	NOTL
1,4-Dichlorobenzene	3.646	3.533	4.331	5.791	NOTL
1,2,3,4-Tetrachlorobenzene	36.443	29.289	28.474	28.541	43.969
1,2,3-Trichlorobenzene	13.711	7.728	11.801	5.647	6.385
1,2,4-Trichlorobenzene	13.986	13.441	15.527	9.031	10.196
1,3,5-Trichlorobenzene	7.969	NOTL	NOTL	NOTL	NOTL
Hexachlorobenzene	2.882	3.454	3.249	2.791	4.279
Pentachlorobenzene	4.793	5.033	8.756	5.710	9.465
Industrial By-products					
Hexachlorobutadiene	NOTL	19.757	NOTL	NOTL	NOTL
Hexachlorocyclopentadiene	NOTL	NOTL	--	1.464	5.913
Octachlorostyrene	NOTL	NOTL	NOTL	NOTL	NOTL
Neutral Herbicides					
Atrazine	NS	NS	NS	NS	NS
Metolachlor	NS	NS	NS	NS	NS
OC Pesticides & PCBs					
Aldrin	--	--	--	--	--
α-Chlordane	NS	1.540	1.837	NS	NS
γ-Chlordane	NS	1.850	1.510	NS	NS
o,p-DDT	0.721	FE	FE	--	9.831
p,p-DDD	0.610	NS	NS	NS	0.688
p,p-DDE	0.335	0.708	0.651	NS	NS
p,p-DDT	0.392	NS	NS	NS	NS
Dieldrin	NS	NS	NS	NS	NS
α-Endosulfan	1.509	1.654	1.475	1.407	1.354
β-Endosulfan	12.025	2.270	1.616	1.414	NOTL
Endrin	NOTL	--	--	--	--
Endrin Aldehyde	--	--	NS	--	--
α-HCH	NS	1.376	1.435	1.374	NS
γ-HCH	NS	NS	NS	NS	NS
Heptachlor	--	--	--	--	--
Heptachlor Epoxide	NS	NS	NS	1.350	1.311
Methoxychlor	FE	--	--	--	--
Mirex	NOTL	NOTL	NOTL	NOTL	NOTL
Photomirex	NOTL	--	--	--	--
PCB (Total)	1.372	2.626	3.148	1.785	2.633
PAHs					
1-Methylnaphthalene	NS	1.370	1.624	NS	NS
2-Methylnaphthalene	NS	1.363	1.427	1.322	NS
β-Chloronaphthalene	--	--	--	--	--
Acenaphthylene	NS	2.487	2.684	2.024	1.749
Anthracene	0.614	2.927	3.282	2.330	2.159
Benz(a)anthracene	0.566	2.456	4.940	2.181	2.206
Benzo(a)pyrene	0.560	2.211	4.692	2.025	2.427
Benzo(bk)fluoranthene	0.587	1.937	4.171	1.936	2.353
Benzo(g,h,i)perylene	0.455	2.154	3.962	1.727	2.612
Chrysene/Triphenylene	0.578	2.027	3.632	1.999	2.507
Dibenzo(a,h)anthracene	0.543	2.926	5.681	1.810	2.486
Fluoranthene	0.618	1.909	3.133	1.869	1.886
Fluorene	NS	1.608	1.698	1.606	NS
Indeno(1,2,3-cd)pyrene	0.412	2.217	4.154	1.803	2.494
Napthalene	0.516	NS	5.253	2.413	3.914
Phenanthrene	NS	1.844	2.510	1.839	1.623
Pyrene	0.700	2.274	4.699	2.080	2.479

Table 7. Statistically Significant MLE Ratios for Niagara River Contaminants (Modified Confidence Interval)

	2000-2001	2001-2002	2002-2003	2003-2004	2004-2005
Trace Metals					
Aluminum	1.716	0.622	1.301	4.722	2.504
Antimony	NS	NS	NS	2.852	NS
Arsenic	NS	NS	NS	1.507	NS
Barium	NS	NS	NS	1.957	NS
Beryllium	1.501	NS	1.526	2.192	3.219
Cadmium	NS	NS	NS	NS	1.882
Chromium	NS	NS	1.540	2.399	2.366
Cobalt	1.863	NS	1.578	NS	2.736
Copper	NS	NS	NS	1.568	1.468
Iron	2.161	NS	1.574	1.919	3.007
Lead	1.790	NS	1.442	1.948	2.222
Lithium	NS	NS	NS	NS	NS
Manganese	1.558	0.704	1.558	2.276	2.714
Mercury	1.304	1.410	1.641	1.634	1.381
Molybdenum	NS	NS	NS	1.626	NS
Nickel	1.337	NS	NS	1.633	1.492
Selenium	0.773	NS	NS	NS	NS
Silver	FE	1.370	NOTL	3.355	2.895
Strontium	NS	NS	NS	3.075	NS
Vanadium	NS	NS	NS	1.906	1.728
Zinc	1.558	NS	1.506	1.464	3.033

NS ***non-significant based on Dieldrin results***

NS = non-significant ratio

FE = only detected at Fort Erie

NOTL = only detected at Niagara-on-the-Lake

-- = not detected

While this analysis is not scientifically rigorous, it did show that a modification of the confidence interval window should be investigated as this modified approach did resolve some of the apparent anomalies within the original source analysis.

As a result, investigations are underway to determine whether or not similar statistical analysis conducted with 95% and/or 99% confidence intervals will provide a more realistic assessment of the sources for contaminants in the Niagara River.

5.0 SUMMARY

The objective of this report is to summarize contaminant data collected by the Niagara River Upstream/Downstream Monitoring program by examining annual mean concentration and loading trends, water quality guideline exceedences, and potential sources over both the 1986/87-2004/05 and 1996/97-2004/05 time periods.

In general, the results show:

- a number of chemicals from various classes still exceed their most stringent water quality criteria
- most of the chemicals for which a trend is discernible exhibited a significant decrease over the nineteen-year period, but that this trend may be leveling off for many analytes more recent years
- both long-term and recent trends for several contaminants, particularly in the PAH, trace metal, and neutral herbicide classes actually increased
- contaminant concentrations and loadings are strongly influenced by both phase distribution and soluble particulate matter concentration
- the presence of some chemicals in the river, such as the chlorobenzenes and industrial by-products, is due primarily to inputs from Niagara River sources
- the principal source of other chemicals may be upstream or Great Lakes basin-wide.

To provide a more detailed summary of the report findings, matrix tables were developed which highlight status and trends for “long-term” and “recent” contaminant concentrations and loadings at Fort Erie and Niagara-on-the-Lake (Tables 8 - 11).

The three rows of each table are based upon comparisons of the 2004/05 upper 90% confidence interval MLE concentrations and strictest agency criteria. Compounds in the top row did not exceed guidelines during the 2004/05 fiscal year; compounds in the middle row only exceeded guidelines at NOTL; and compounds in the bottom row exceeded guidelines at both NOTL and FE. It must be noted that designation of contaminants in the rows is based on a given year of data and as such may be susceptible to change, particularly in the case of those contaminants whose concentrations are close to the strictest agency criteria.

The three columns of each table are based upon trends in the predominant phase of each contaminant. The first column corresponds to compounds with downward trends; the third column to compounds with upward trends; and the middle column with those with either no significant trend or insufficient data to calculate a trend.
Each compound has been physically placed in the column representing its “long term” trend; however, they are colour-coded according to their “recent” trend. Compounds in black text have the same “long term” and “recent” trends, compounds in green have recent downward trends, compounds in red have recent upward trends, and compounds in orange have no significant recent trend.

Finally, each compound is classified according to the 2004/05 MLE ratios which provide an assessment of its potential source. Compounds with statistically significant MLE ratios greater than 1.0 are deemed to have Niagara River sources and are designated by square brackets ("[ ]"); compounds with statistically significant MLE ratios less than 1.0 are deemed to have local upstream sources (such as the DDT metabolites) and are designated by square brackets with and asterix ("[ ]*"); and compounds with non-significant MLE ratios (i.e. upper and lower confidence intervals that include "unity") are deemed to have Great Lakes basin-wide sources and are designated by curly brackets ("{ }").

Long Term Concentration Trends

The most striking messages in the long term concentration trends for FE and NOTL (Tables 8 and 9) are that:

- most of the 72 Niagara River analytes have a downward trend and are not exceeding strictest agency criteria
- PAH class makes up majority of compounds with upward trends.
- 7 of the 12 compounds that exceed strictest agency criteria exceed at both stations (i.e. they are primarily contributed from upstream sources) and, of those 7 compounds, 5 have downward trends
- only 5 compounds exceed at just NOTL and, of those, 3 have downward trends at the downstream station
- NOTL appears to have a greater number of compounds with a downward trend

Long Term Loading Trends

In general, long term loading trends (Tables 10 and 11) tend to mirror concentrations:

- most of the 72 Niagara River analytes have a downward trend and are not exceeding strictest agency criteria
- PAH class makes up majority of compounds with upward trends
- most of the compounds that exceed strictest agency criteria show downward trends
- NOTL appears to have a greater number of compounds with a downward trend.

Recent Concentration Trends

Looking at more recent concentration trends (Tables 8 and 9), the following observations can be made:

- more compounds tend to exhibit no significant trend or insufficient data to calculate one relative to long-term trends
- while more compounds exhibit upward trends relative to long-term trends, all but Benzo(a)pyrene, Benzo(b/k)fluoranthene, Benzo(ghi)perylene, and PCBs continue to fall below guidelines
- PAH and trace metals make up majority of compounds with upward trends
- NOTL continues to have slightly more compounds with a downward trend

Table 8. Status/Trend Summary for FE Concentrations

No Longer Exceed Criteria (in 04/05)	[Acenaphthalene] [Anthracene] [Benz(a)anthracene] [a-chlordane], [?-chlordane] [o,p-DDT]*, [p,p-DDD]* [1,2-dichlorobenzene] [1,3-dichlorobenzene] [1,4-dichlorobenzene] [a-endosulfan] [a-HCH], [?-HCH] [Heptachor Epoxide] {1-MethylNaphthalene} {2-MethylNaphthalene} [Pentachlorobenzene] [1,2,3,4-tetrachlorobenzene] [1,2,4-trichlorobenzene] [1,2,3-trichlorobenzene] [Antimony], [Cadmium], [Chromium] [Mercury], [Vanadium]	{Aldrin} {Atrazine} ß-chloronaphthalene [Dibenzo(ah)anthracene] [ß-endosulfan] {Endrin} {Endrin Aldehyde} [Fluorene] {Heptachlor} [Hexachlorobutadiene] [Hexachlorocyclopentadiene] {Methoxychlor} [Napthalene] [Octachlorostyrene] [Phenanthrene] {Photomirex} [1,3,5-trichlorobenzene] [Arsenic], [Beryllium], [Cobalt] [Copper], [Lead], [Lithium] [Manganese], [Nickel], [Silver] {Strontium}, [Zinc]	[Fluoranthene] [Indeno(123cd)pyrene] [Metolachlor] [Pyrene] [Barium], [Molybdenum] [Selenium]*
Exceed Criteria at NOTL (in 04/05)	[Hexachlorobenzene]	[Chrysene/Triphenylene] [Mirex] [Iron]	[Benzo(a)pyrene]
Exceed Criteria at NOTL & FE (in 04/05)	[p,p-DDE]* [p,p-DDT]* {Dieldrin} [PCBs (86-98)]** [Aluminum]		[Benzo(b/k)Fluoranthene] [Benzo(ghi)perylene]
[ ]-NR source [ ]*-Local Upstream source { }-Suspected Basin Source **-Method change	**Downward Trend (86/87-04/05)**	**No Trend (86/87-04/05)**	**Upward Trend (86/87-04/05)**

Table 9. Status/Trend Summary for NOTL Concentrations

No Longer Exceed Criteria (in 04/05)	[Acenaphthalene] [Anthracene] {Atrazine} [a-chlordane], [?-chlordane] [o,p-DDT]*, [p,p-DDD]* [1,2-dichlorobenzene] [1,3-dichlorobenzene] [1,4-dichlorobenzene] [a-endosulfan] [ß-endosulfan] [Fluorene] [a-HCH], [?-HCH] [Heptachor Epoxide] {1-MethylNaphthalene} {2-MethylNaphthalene} [Octachlorostyrene] [Pentachlorobenzene] [1,2,3,4-tetrachlorobenzene] [1,2,3-trichlorobenzene] [1,2,4-trichlorobenzene] [1,3,5-trichlorobenzene] [Antimony], [Arsenic], [Cadmium] [Chromium], [Lithium], [Manganese] [Mercury], [Nickel], [Zinc]	{Aldrin} [Benz(a)anthracene] ß-chloronaphthalene [Dibenzo(ah)anthracene] {Endrin} {Endrin Aldehyde} {Heptachlor} [Hexachlorobutadiene] [Hexachlorocyclopentadiene] {Methoxychlor} {Photomirex} [Barium], [Beryllium], [Cobalt] [Copper], [Lead], [Selenium]* [Silver], {Strontium}, [Vanadium]	[Fluoranthene] [Indeno(123cd)pyrene] [Metolachlor] [Napthalene] [Phenanthrene] [Pyrene] [Molybdenum]
Exceed Criteria at NOTL (in 04/05)	[Hexachlorobenzene] [Mirex] [Iron]	[Chrysene/Triphenylene]	[Benzo(a)pyrene]
Exceed Criteria at NOTL & FE (in 04/05)	[p,p-DDE]* [p,p-DDT]* {Dieldrin} [PCBs (86-98)]** [Aluminum]		[Benzo(b/k)Fluoranthene] [Benzo(ghi)perylene]
[ ]-NR source [ ]*-Local Upstream source { }-Suspected Basin Source **-Method change	**Downward Trend (86/87-04/05)**	**No Trend (86/87-04/05)**	**Upward Trend (86/87-04/05)**

Table 10. Status/Trend Summary for FE Loadings

No Longer Exceed Criteria (in 04/05)	**[Acenaphthalene] [Anthracene] [Benz(a)anthracene] [a-chlordane], [?-chlordane] [o,p-DDT]*, [p,p-DDD]* [1,2-dichlorobenzene] [1,3-dichlorobenzene] [1,4-dichlorobenzene] [a-endosulfan] [Fluoranthene] [a-HCH], [?-HCH] [Heptachor Epoxide] {1-MethylNaphthalene} {2-MethylNaphthalene} [Pentachlorobenzene] [Pyrene] [1,2,3,4-tetrachlorobenzene] [1,2,3-trichlorobenzene] [1,2,4-trichlorobenzene] [Antimony], [Barium], [Cadmium] [Chromium], [Mercury], [Selenium]*, [Vanadium]**	**{Aldrin} {Atrazine} ß-chloronaphthalene [Dibenzo(ah)anthracene] [ß-endosulfan] {Endrin} {Endrin Aldehyde} [Fluorene] {Heptachlor} [Hexachlorobutadiene] [Hexachlorocyclopentadiene] {Methoxychlor} [Napthalene] [Octachlorostyrene] [Phenanthrene] {Photomirex} [1,3,5-trichlorobenzene] [Arsenic], [Beryllium], [Cobalt] [Copper], [Lead], [Lithium] [Manganese], [Nickel], [Silver] {Strontium}, [Zinc]**	**[Indeno(123cd)pyrene] [Metolachlor] [Molybdenum]**
Exceed Criteria at NOTL (in 04/05)	**[Benzo(a)pyrene] [Hexachlorobenzene]**	**[Chrysene/Triphenylene] [Mirex] [Iron]**	
Exceed Criteria at NOTL & FE (in 04/05)	**[Benzo(b/k)Fluoranthene] [p,p-DDE]* [p,p-DDT]* {Dieldrin} [PCBs (86-98)]** [Aluminum]**		**[Benzo(ghi)perylene]**
[ ]-NR source [ ]*-Local Upstream source { }-Suspected Basin Source **-Method change	**Downward Trend (86/87-04/05)**	**No Trend (86/87-04/05)**	**Upward Trend (86/87-04/05)**

Table 11. Status/Trend Summary for NOTL Loadings

No Longer Exceed Criteria (in 04/05)	[Acenaphthalene] [Anthracene] {Atrazine} [a-chlordane], [?-chlordane] [o,p-DDT]*, [p,p-DDD]* [1,2-dichlorobenzene] [1,3-dichlorobenzene] [1,4-dichlorobenzene] [a-endosulfan] [ß-endosulfan] [Fluoranthene] [Fluorene] [a-HCH], [?-HCH] [Heptachor Epoxide] {1-MethylNaphthalene} {2-MethylNaphthalene} [Octachlorostyrene] [Pentachlorobenzene] [Pyrene] [1,2,3,4-tetrachlorobenzene] [1,2,3-trichlorobenzene] [1,2,4-trichlorobenzene] [1,3,5-trichlorobenzene] [Antimony], [Arsenic], [Cadmium] [Chromium], [Lithium], [Manganese] [Mercury], [Nickel], [Zinc]	{Aldrin} [Benz(a)anthracene] ß-chloronaphthalene [Dibenzo(ah)anthracene] {Endrin} {Endrin Aldehyde} {Heptachlor} [Hexachlorobutadiene] [Hexachlorocyclopentadiene] {Methoxychlor} {Photomirex} [Barium], [Beryllium], [Cobalt] [Copper], [Lead], [Selenium]* [Silver], {Strontium}, [Vanadium]	[Indeno(123cd)pyrene] [Metolachlor] [Napthalene] [Phenanthrene] [Molybdenum]
Exceed Criteria at NOTL (in 04/05)	[Hexachlorobenzene] [Mirex] [Iron]	[Chrysene/Triphenylene]	[Benzo(a)pyrene]
Exceed Criteria at NOTL & FE (in 04/05)	[Benzo(b/k)Fluoranthene] [p,p-DDE]* [p,p-DDT]* {Dieldrin} [PCBs (86-98)]** [Aluminum]		[Benzo(ghi)perylene]
[ ]-NR source [ ]*-Local Upstream source { }-Suspected Basin Source **-Method change	Downward Trend (96/97-04/05)	No Trend (96/97-04/05)	Upward Trend (96/97-04/05)

Recent Loading Trends
Looking at recent loading trends (Tables 10 and 11), the following observations can be made:

- more compounds tend to exhibit no significant trend or have insufficient data to calculate one relative to long-term trends
- trace metals make up majority of FE compounds with upward trends
- PAHs class makes up majority of NOTL compounds with upward trends
- none of the compounds exceeding criteria exhibit upward trends at FE
- NOTL appears to have greater number of compounds with downward trend

The summaries in Tables 8 - 11 not only provide a valuable assessment of the history of Niagara River water quality, but a window onto future management action as well. For those compounds in the “no longer exceeding criteria” and “downward trend” sections, there is strong reason to believe that no further management action is required.

The “good news” is that very few compounds exceed at NOTL alone which, in turn, implies that very few compounds are exceeding strictest agency guidelines primarily due to Niagara River sources. In addition, most of these compounds show downward trends in both the long and shorter term analysis. These facts alone provide evidence that existing management actions are, in fact, working.

More worrisome are those compounds which have changed trend category in the more recent time period; particularly those which have begun to show an upward trend. While some remain below strictest agency criteria, the exceedence analysis performed as part of this report has shown that many compounds are just below their respective guideline(s) and, therefore, have the potential to exceed from year to year.

Unfortunately, the contaminants that present the greatest challenge to meeting objectives are those that already exceed criteria entering the Niagara River. For these compounds, management action within the Niagara River may satisfy the objectives of the NRTMP by ensuring that downstream concentrations are equal to upstream concentrations; however, unless these compounds can be managed on a broader scale, they will continue to impact the Niagara River and downstream Lake Ontario ecosystems.

6.0 ACKNOWLEDGEMENTS

The authors express their sincere appreciation to Bruce Harrison and Mary Lou Archer for their field support, Environment Canada’s Chemistry Services Unit (Lisa Bradley, Orrin Carson, and Margaret Konefal) for their analysis of the samples, Jasmine Waltho for her Quality Assurance and support, and to Abdel El-Shaarawi and Bert Ventresca for their programming and statistical support.

REFERENCES

Ad Hoc Group on Physical Limnology and Hydraulics. 1989. The Flow and Circulation Characteristics in the Eastern Lake Erie and Upper Niagara River Area. A Report to the River Monitoring Group.

Anderson, J., A. Hayton, A. Rodriques, and L. Richman. 1991. Niagara River Biomonitoring Study, 1987. Water Resources Branch, Ontario Ministry of the Environment, Toronto, Ontario. 56p.

Chan, C.H., G. Bruce, and B. Harrison. 1994. Wet deposition of organochlorine pesticides and polychlorinated biphenyls to the Great Lakes. *J. Great Lakes Res.* 20: 546-560.

Cortes, D.R., H. Basu, C.W. Sweet, K.A. Bryce, R.A. Hoff, and R.A. Hites. Temporal Trends in Gas-Phase Concentrations of Chlorinated Pesticides at the Shores of the Great Lakes. *Environ. Sci. Technol.* 32(13):1920-1927.

Durham, R.,W., and B.G. Oliver. 1983. History of Lake Ontario contamination from the Niagara River by sediment radiodating and chlorinated hydrocarbon analysis. *J. Great Lakes Res.* 9(2):160-168.

Eadie, B.J., and A.J. Robertson. 1976. An IFYGL carbon budget for Lake Ontario. *J. Great Lakes Res.* 2:307-323.

El-Shaarawi, A.H. 1989. Inference about the mean from censored water quality data. *Wat. Resour. Res.* 25(4)685-690.

El-Shaarawi, A.H., and Al-Ibrahim. 1996. Trend Analysis and Maximum Likelihood Estimation of Niagara River Data (1986-1994). National Water Research Institute and McMaster University, Burlington, Ontario.

El-Shaarawi, A.H. 2008-2010. Personal Communication

Green/Seastar. 1988. Determination of Contaminant Concentrations Across the Niagara River Using Automatic Insitu Water Samples. Final Report, April 1988. Unsolicited proposal DSS contract No. 02SE-KW405-7-9195. David Green, Seastar Instruments Ltd., Dartmouth, N.S.

Harrison, B., B. Hill, and P. Klawunn. SOP 06-6001 - Standard Operating Procedure For The Collection Of Water And Suspended Sediment Samples At The Niagara River Monitoring Stations (Fort Erie And Niagara-On-The-Lake) By The Ontario Water Quality Monitoring And Surveillance Office (Wqms) Of Environment Canada.

Hill, B. and P. Klawunn. 2009. Niagara River Upstream/Downstream Monitoring Program Final Report 2001/02-2004/05. Environment Canada. Contribution # WQMS-09-0754.

Hillery, B.R., M.F. Simcik, I. Basu, R.M. Hoff, W.M.J. Strachan, C.H. Chan, C.W. Sweet, and R.A. Hites. 1998. Atmospheric deposition of toxic pollutants to the Great Lakes as measured by the Integrated Atmospheric Deposition Network. *Environ. Sci. Technol.* 32(15): 2216-2221.

Hoff, R.M., W.M.J. Strachan, C.W..Sweet, C.H. Chan, M. Shackleton, T.F. Bidleman, K.A. Brice, D.A. Burniston, S. Cussion, D.F. Gatz, K. Harlin, and W.H. Schroeder. 1996. Atmospheric deposition of toxic chemicals to the Great Lakes: a review of data through 1994. *Atm. Env.* 30(20): 3505-3527.

Howell, T.E., C.H. Marvin, R.W. Bilyea, P.B. Kauss and K. Sommers. 1996. Changes in the environmental conditions during Dreissena colonization of a monitoring station in eastern Lake Erie. *J. Great Lakes Res.* 22(3):744 - 756.

Inter-Agency Task Force. 1979. Inter-Agency Task Force Report on Hazardous Waste Disposal in Erie and Niagara Counties. New York , New York.

IJC: (1) Specific Objectives. Annex 1 of the Great Lakes Water Quality Agreement of 1978, as amended 1987.

Jorgenson, J. L. 2001. Aldrin and dieldrin: a review of research on their production, environmental deposition and fate, bioaccumulation, toxicology, and epidemiology in the United States. Environ. Health Perspect. 109 Suppl. 1,113-139

Kauss, P.B., and L.E. Post. 1987. Contaminant Concentrations in Bottom Sediments of the Sir Adam Beck Power Reservoir and Niagara Bar Dredgeate. Great Lakes Section, Water Resources Branch, Ontario Ministry of the Environment.

Kemp, A.L.W., and N.S. Harper. 1976. Sedimentation rates and a sedimentation budget for Lake Ontario. *J. Great Lakes Res.* 2: 324-340.

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

Kuntz, K.W., and J. Struger. 1996. Occurrence of Atrazine and Metolachlor in the Niagara River, 1989-1994. [in] Abstracts, 39th Conference on Great Lakes Research, International Association for Great Lakes Research.

Kuntz, K. and P. Klawunn. 2005. Niagara River Upstream/Downstream Monitoring Program Final Report 1999/00 & 2000/01. Environment Canada.

L'Italien, S. 1993. Organic Contaminants in the Great Lakes, 1986-1990. Environmental Quality Branch, Inland Waters Directorate-Ontario Region, Burlington, Ontario. Report No. EQB/IWD-OR/93-02/I.

L'Italien, S. 1996. Organic Contaminants in Lake Erie in 1994 and 1995: Protocols and Data Report. Ecosystem Health Division, Environmental Conservation Branch-Ontario Region, Environment Canada. Report No. EHD/ECB-OR/96-02/I.

L'Italien, S., and J. Struger 1996. Pesticide concentrations in water and suspended sediment in Lake Erie. [in] Abstracts, 39th Conference on Great Lakes Research, International Association for Great Lakes Research.

Marvin, C.H., and T.E. Howell. 1997. Contaminant burdens in sediments colonized by *Dresissena* at two nearshore sites in the lower Great Lakes. in D'Itri, E.M. [ed] Zebra Mussels and Aquatic Nuisance Species, Ann Arbor Press, Chelsea, Michigan.

Mudroch, A. 1983. Distribution of major elements and metals in sediment cores from the western basin of Lake Ontario. *J. Great Lakes Res.* 9(2):125-133.

Niagara River Secretariat; 2007; Niagara River Toxics Management Plan (NRTMP) Progress Report and Work Plan.

NRDIG. 1997. Joint Evaluation of Upstream/Downstream Niagara River Monitoring Data 1995-1996. Environment Canada, Ontario Ministry of the Environment, New York State Deparrtment of Environmental Conservation and the United States Environmental Protection Agency.

NRAP. 1992. Analytical Protocol for Monitoring Ambient Water Quality at the Niagara-on-the-Lake and Fort Erie Stations. Niagara River Analytical Protocol, a joint report of Environment Canada, United States Environmental Protection Agency, Ontario Ministry of the Environment and Energy, New York State Department of Environmental Conservation. November, 1992.

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.

NRSP. 1995. Niagara River Sampling Protocol. Joint Report of Environment Canada, the United States Protection Agency (II), New York State Department of Environmental Conservation and the Ontario Ministry of the 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.

NRTC. 1984. Report of the Niagara River Toxics Committee. Joint Report of Environment Canada, the United States Protection Agency (II), New York State Department of Environmental Conservation and the Ontario Ministry of the Environment.

NRTMP. 1999. Niagara River Toxics Management Plan. Progress Report. Niagara River Secretariat. Environment Canada, U.S. Environmental Protection Agency, Ontario Ministry of the Environment, New York State Department of Environmental Conservation. May, 1999.

NYSDEC. 1997. Follow-up Contaminant Trackdown Investigations of the Niagara River and Lake Ontario basin 1995-1996. May 1997. 55p.

NYSDEC. 1998. Contaminants in Young-of-the-Year Fish from Selected Lake Ontario Tributaries. New York State Department of Environmental Conservation, Division of Fish, Wildlife and Marine Resources, Albany, New York.

NYSDEC. 1992. Fact Sheet – Gill Creek, Niagara Falls, N.Y., Site Code 9-32-013.
NY State: Division of Water Technical and Operational Guidance Series (1.1.1), June 1998. New York State Department of Environmental Conservation, Albany, NY.

O'Connor, D.J., and J.P. Connolly. 1980. The effect of concentration of adsorbing solids on the partition coefficient. *Water Research* 14:1517-1523.

Ontario MOE: (1) Water Management Policies, Guidelines, Provincial Water Quality Objectives. July 1994.

Raven, K.G. 1991. Prioritization of US Hazardous Waste Sites Near the Niagara River. Prepared for the Great Lakes Environment Office (GLEO), Environment Canada, Toronto, Ontario.

Richards, R.P., D.B. Baker, J.W. Kramer, and D.E. Ewing. 1996. Annual loads of herbicides in Lake Erie tributaries of Michigan and Ohio. *J. Great Lakes Res.* 22(2): 414-428.

Richman, L. 1992. The Niagara River Mussel and Leech Biomonitoring Study. Great Lakes Sections, Water Resources Branch, Ontario Ministry of the Environment, Toronto, Ontario. 60p.

Richman, L. 1993. Preliminary Technical Report Summary of the 1991 Niagara River Mussel Biomonitoring Survey. Great Lakes Section, Water Resources Branch, Ontario Ministry of Environment and Energy, Toronto, Ontario. 6p.

Richman, L. 1994. Preliminary Technical Report on the Niagara River Mussel Biomonitoring Survey, 1993. Surface Water Section, Environmental Monitoring and Reporting Branch, Ontario Ministry of Environment and Energy, Toronto, Ontario. 34p.

Richman, L. 1997. Niagara River Biomonitoring Program, 1995. Surface Water Section, Environmental Monitoring and Reporting Branch, Ontario Ministry of the Environment, Toronto, Ontario. 56p.

Richman, L. 1999. Niagara River Mussel Biomonitoring Program, 1997. Water Monitoring Section, Environmental Monitoring and Reporting Branch, Ontario Ministry of Environment. ISBN-0-778-9097-6.

Richman, L. and K. Somers. 2010. Monitoring Metal and Persistent Organic Contaminant Trends Through Time Using Quagga Mussels (*Dreissena bugensis*) Collected from the Niagara River. Journal of Great Lakes Research. 36(1): 28-36.

Simcik, M.A. and J.H. Offenberg. “Polycyclic Aromatic Hydrocarbons in the Great Lakes”. *Persistant Organic Pollutants In The Great Lakes*. Edited by R.A. Hites. Vol. 5N. The Handbook Of Environmental Chemistry. 2006. pp. 307-353.

Stevens, R.J.J., and M.A. Neilson. 1989. Inter- and intra-lake distributions of trace organic contaminants in surface waters of the Great Lakes. *J. Great Lakes Res.* 15(3): 377-393.

Stewart, J., F. Estabrooks, and R. Bopp. 1996. Lake Ontario Sediment Survey: 1995 Sediment Coring Results. Bureau of Watershed Management and Research, New York State Department of Environmental Conservation (November 1996).

The National Laboratory for Environmental Testing, 2001. Protocol 09-010 Protocol for the Application of Blank Sample Residue Values to Sample Data

Thomas, R.L., J.E. Gannon, J.H. Hartig, D.J. Williams, and D.M. Whittle. 1988. Contaminants in Lake Ontario - A Case Study. In Schmidtke, N.W. [ed.] *Toxic Contamination in Large Lakes* Proceedings of a technical session of the World Conference on Large Lakes, Lewis Publishers, Chelsea, Michigan, 1988, Vol. 3:327-387.

U.S. EPA: National Recommended Water Quality Criteria. Office of Science and Technology, Washington, DC. May 21, 1999.

Van Metre, Peter C.; Barbara J. Mahler; and Edward T. Furlong., 2000, “Urban Sprawl Leaves its PAH Signature”, *Environ. Sci. Technol*., v34, p.4064-4070

Williams, D.J., K.W. Kuntz, S. L’Italien, and V. Richardson. 1998a. Lake Ontario Surveillance Program: Spatial and Temporal Trends of Selected Parameters, with Emphasis on 1992-1993 Results. Ecosystem Health Division, Environmental Conservation Branch-Ontario Region, Environment Canada. Report No. EHD/ECB-OR/98-04/I.

Williams, D.J., K.W. Kuntz, S. L’Italien, and V. Richardson. 1998b. Lake Erie Surveillance Program: Spatial and Temporal Trends of Selected Parameters, with Emphasis on 1994-1995 Results. Ecosystem Health Division, Environmental Conservation Branch-Ontario Region, Environment Canada. Report No. EHD/ECB-OR/98-05/I.

Williams, D.J., and K.W. Kuntz. 1999. Lake Superior Surveillance Program: Spatial Distribution and Temporal Trends of Selected Parameters, with Emphasis on 19961997 Results. Ecosystem Health Division, Environmental Conservation Branch-Ontario Region, Environment Canada. Report No. EHD/ECB-OR/99-01/I.

Williams, D.J., M. Neilson, J. Merriman, S. L’Italien, S. Painter, K. Kuntz, and A. El-Shaarawi. 2000. The Niagara River Upstream/Downstream Program 1986/87-1996/97. Report No. EHD/ECB-OR/00-01/I. Environment Canada, Burlington.

Williams, D.J., K. Kuntz, and E. Sverko. 2003. Seasonality in Contaminant Concentrations in the Niagara River and Lakes Erie and Ontario. *J. Great Lakes Res.* 29(4): 594-607.