Division Control No. ECD-73

This copy is to provide information
prior to publication.

THE WELLAND CANAL, WELLAND RIVER AND TWELVE MILE CREEK AREA. INDUSTRIAL DISCHARGES WITH POTENTIAL IMPACT ON LAKE ONTARIO

M.E. Comba and K.L.E. Kaiser

NWRI Contribution No. 86-36

Environmental Contaminants Division
National Water Research Institute
Canada Centre for Inland Waters
Burlington, Ontario, Canada L7R 4A6

. Environment Canada

THE WELLAND CANAL, WELLAND RIVER AND TWELVE MILE CREEK AREA. INDUSTRIAL DISCHARGES WITH POTENTIAL IMPACT ON LAKE ONTARIO

Environmental Contaminants Division,
National Water Research Institute,
Burlington, Ontario, L7R 4A6 (Canada)

M.E. Comba and K.L.E. Kaiser*

*Author to whom correspondence should be addressed

TABLE OF CONTENTS

This National Water Research Institute contribution is a compilation of research data reflecting the activities of the Environmental Contaminants Division. Material in this report may eventually appear in published form and prior right to publication is reserved. Enquiries concerning the contents of this report should be addressed to the authors.

EXECUTIVE SUMMARY

The Welland Canal, Welland River and Twelve Mile Creek Area. Industrial discharges with potential impact on Lake Ontario.

M.E. Comba and K.L.E. Kaiser

Publication: National Water Research Institute Report

Summary:

The assessment of loadings of toxic and persistent contaminants to Lake Ontario has focused on the Niagara River. This report addresses contaminants entering the lake indirectly via the Welland River (a tributary of the Niagara River) and directly via the Welland Canal and the Twelve Mile Creek, all of which are located in the Niagara Peninsula and which receive substantial loadings of various effluents from both urban and industrial sources in that region.

Canadian sources account for 11% of the total load of priority pollutants discharged by municipal and industrial facilities to the Niagara River. Discharges to the Welland Canal and Twelve Mile Creek were not accounted for in assessment of loadings to Lake Ontario from the Niagara River (Niagara River Toxics Committee, 1984), as these tributaries are not part of the Niagara River drainage basin. The definition and subsequent management of toxic chemicals in the Lake Ontario basin will require an assessment of contaminant sources within the basin in addition to those located on the Niagara River.

Preliminary assessment of waters receiving these discharges indicates loadings of potentially hazardous organic materials. We estimate that of the total extractable organic burden entering Lake Ontario from these sources, only ten per cent can be accounted for by the currently measured priority organic pollutants. The remaining 90 per cent is composed primarily of alkylated benzenes, benzaldehydes and heterocyclic compounds. The potential biological impact of these compounds on Lake Ontario is unknown; however, localized impacts on biota within these tributaries have been observed. Finally, we estimate that organic contaminants in over 50 per cent of Canadian industrial and municipal discharges to interconnecting channels in the central Niagara peninsula are presently excluded from the assessment of loadings to Lake Ontario.

RÉSUMÉ À L'INTENTION DE LA DIRECTION

Le canal Welland, la rivière Welland et le ruisseau Twelve Mile : déversement industriels et leurs incidences potentielles sur le lac Ontario

Publication: Rapport de l'Institut national de recherche sur les eau

Résumé

L'évaluation des charges de contaminants toxiques et persistants dans le lac Ontario s'est limitée à la rivière Niagara. Dans ce rapport, on traite des contaminants pénétrant dans le lac par le canal Welland, la rivière Welland et le ruisseau Twelve Mile, qui sont tous situées dans la péninsule de Niagara et reçoivent des charges substantielles de divers effluents : ces derniers proviennent des charges substantielles de divers effluents : ces derniers proviennent de sources urbaines et industrielles qui se trouvent dans cette région.

Les déversements municipaux et industriels dans la rivière Niagara proviennent de sources canadiennes dans une proportion de 11%. Dans l'évaluation régionale des charges apportées par ses tributaires au lac Ontario, on ne tient pas comte des introductions de contaminants dans le canal Welland et le ruisseau Twelve Mile

(Niagara River Toxics Committee, 1984) puisque les tributaires en question ne font pas partie du bassin hydrographique de la rivière Niagara. La caracterisation et la gestion subséquente des produits toxiques dans le bassin du lac Ontario requireront une évaluation des sources des contaminants dans le bassin même autant que de celles situées aux abords de la rivière Niagara.

L'évaluation préliminaire des eaux réceptrices indique l'existence de charges significatives de produits organique potentiellement dangereux. Nous estimons approximativement que l'on peut seulement justifier dix pour cent du total de la charge organique extracible introduite dans le lac Ontario à partir de ces sources par les principaux polluants organiques actuellement mesurés. L'autre 90% des polluants organique consiste pour le plupart de benzènes alkyées, de benzadéhydes, et de composés phénoliques et héterocycliques. On ne connaît pas l'impact biologique potentiel de ce mélange sur le lac Ontario; cependant, on a observé des effets localisés sur les organismes à l'intérieure du bassin. Finalement, nous jugeons que jusqu'ici on a exclu de toute évaluation des incidences sur la qualité des eaux du lac Ontario, au moins 50% des rejets, industriels et urbains, effectués dans des chenaux interreliés du sud de la région de Niagara.

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Industrial and municipal effluents in the central Niagara peninsula of Ontario contribute contaminant loadings to Lake Ontario by discharging to the interconnecting channels of this region. As shown in Figure 1, two principal waterways connect Lake Erie to Lake Ontario: the Niagara River and the Welland Canal System. For clarity, it is useful to consider - apart from the Niagara River - three waterways; namely, (i) the Welland River which combines with hydro race water from the upper Niagara River that re-enters the Niagara River at the Sir Adam Beck electrical power generating station in Queenston, Ontario; (ii) the Welland Canal which flows from Port Colborne on Lake Erie to Port Weller on Lake Ontario; and (iii) Twelve Mile Creek which diverts water from the upper Welland Canal to the DeCew Falls electrical power generating station and drains to Lake Ontario at Port Dalhousie. Canadian sources account for 11% of the total loading of priority pollutants to Lake Ontario (NRTC, 1984), arising from point source discharges of approximately 200,000 m^3 a day to the Welland-Niagara River (i) watershed (Table 1), while similar discharges to Lake Ontario via the Welland Canal (ii) and Twelve Mile Creek (iii) total 400,000 m^3 daily (Table 1). Consequently, 65% of the point source discharges within the central Niagara peninsula of Ontario are excluded from the assessment of contaminant loadings to Lake Ontario. Contaminant parameters as detailed in the organic priority pollutants schedule (NRTC, 1984) which include such compounds

Table 1. Major municipal and industrial discharges to Lake Ontario through interconnecting channels in the central Niagara Peninsula, 1978 and 1984.

Sub Area	Flow[1] in 1978 10^3 $m^3.day^{-1}$	Flow[2] in 1984 10^3 $m^3.day^{-1}$
Niagara River/Welland River		
Niagara Falls WPCP	40.9	57.3
Atlas Steel	36.0	7.2
Welland WPCP	34.2	39.9
Cyanamid, Welland	24.9	25.1
Norton Company	19.6	9.8
Canadian Carborundum (Sohio Minerals)	15.9	14.1
Cyanamid, Niagara Falls	13.6	39.3
Ford	2.7	2.7
Stelco Tube	1.3	0.08
Wabasso	0.9	[d]
B.F. Goodrich	0.8	2.0
McMaster Avenue Sewer	[d]	12.3
Total (a)	190.8 (35%)	209.8 (35%)
Welland Canal		
McKinnon Industries (GM Plant Two)	110.6	120.9
Port Weller STP	35.1	36.5
Stelco Page Hersey	10.5	11.9
Union Carbide	6.2	[d]
Total (b)	164.4	169.3
Twelve Mile Creek		
Ontario Paper	128.8	119.0
Port Dalhousie WPCP	32.9	32.6
Fraser (formerly Abitibi)	24.5	25.3
Beaver Wood Fibre	19.1	14.7
Domtar Fine Papers	10.1	9.9
Kimberly Clark	9.9	8.3
Port Colborn WPCP	9.5	14.2
Exolon	9.1	[d]
Domtar Construction	.27	0.77
Hayes Dana	.09	[d]
General Motors (GM Plant One)	8.6	[d]
Total (c)	252.8	224.7
Sum b and c	398.6 (65%)	394.0 (65%)

[1] Data compiled from IJC, 1979.
[2] Data compiled from NRTC (1984), COR (1985), and COR (1986).
[d] No values reported.

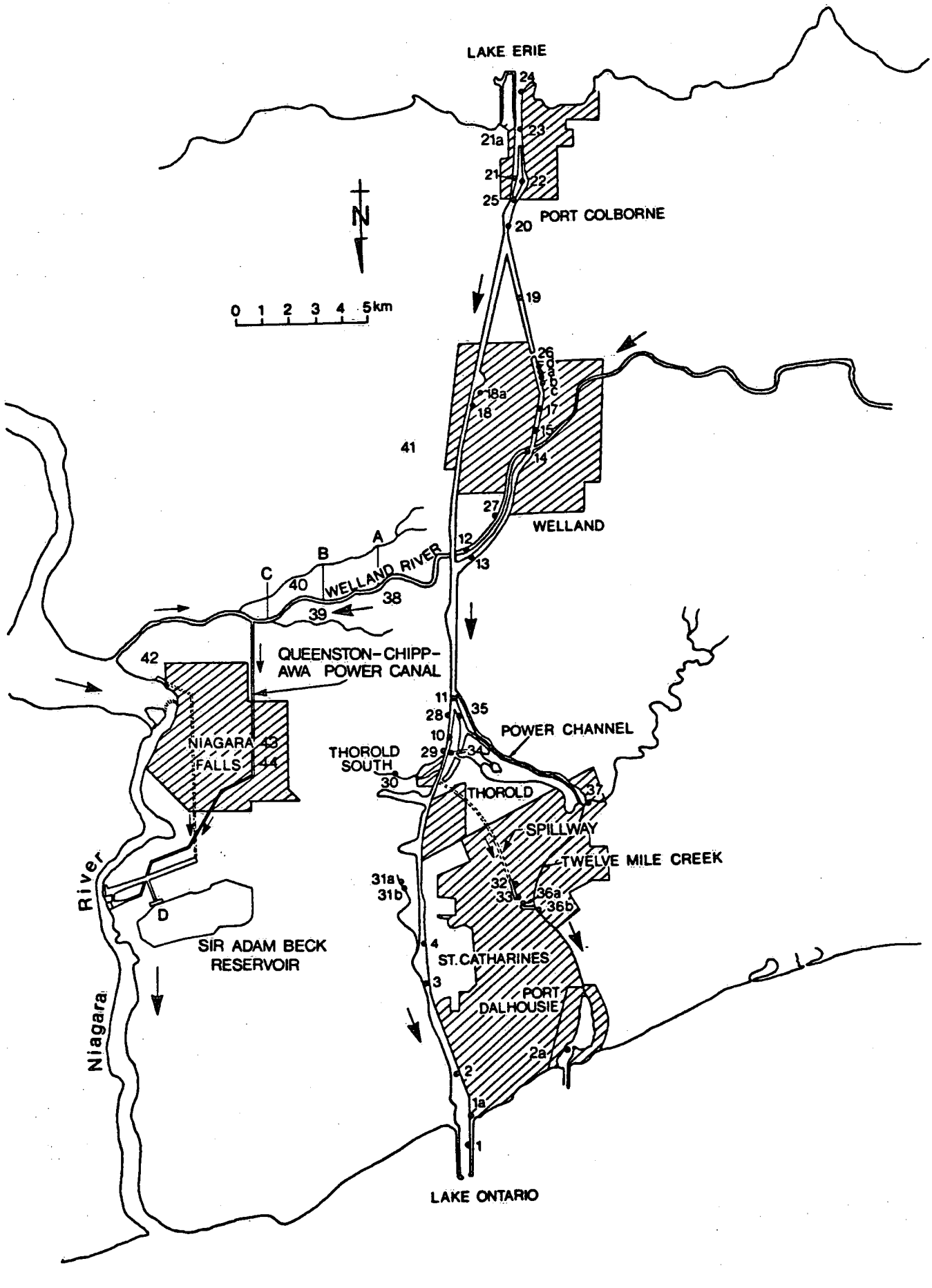


FIGURE 1. Map of the study area with sampling stations

as chlorinated insecticides and polynuclear aromatic hydrocarbons are less typical for the industries in this area. We feel that these compounds were measured primarily because of the analytical capabilities in place and current practices to restrict contaminant programmes to the "priority pollutant" list. Industries in the central Niagara peninsula are mainly orientated to the production of paper and wood products, fertilizers, amino intermediates, rubber, textiles, plastics and steel processing. Discharges of effluents from these industries are significant in volume and contain contaminants of undefined nature that may produce undesirable effects on the water quality of the receiving water.

Topography and Hydrology

The Niagara peninsula has experienced drastic changes during recorded history. In particular, since the War of 1812, economic development along both shores of the Niagara River and in the associated hinterlands has resulted in significant changes of the local topography and the hydrology of this region. The desire for shipping lanes between Lake Ontario and Lake Erie brought on the first Welland Canal in 1829, which has since seen several stages of major alterations, accompanied by large changes in the hydraulic regime. In addition, the large scale use of Niagara River water for hydro-electric power generation has given rise to the construction of surface and subterranean water conduits and large water reservoirs

with associated changes in the levels and flows of smaller rivers in the area, such as the Welland River. Over this period of approximately 150 years, numerous canals, spillways, conduits, and syphons have been built, abandoned, cut off, re-used for different purposes, connected and disconnected, resulting in a very complex and almost unintelligible system of natural and man-made features. Moreover, continued industrial and municipal developments, including the installation of waste water treatment plants, particularly in the greater St. Catharines area, introduce further changes to the system, some of which are not yet reflected in the latest topographical maps available. Therefore, some of the observations presented in this report may have become obsolete in terms of concentrations and loadings mentioned.

Lake Ontario Contamination Problem

The Welland Canal is an important waterway for commercial shipping of goods within the Great Lakes region and beyond. It is administered by the St. Lawrence Seaway Authority, a Crown Corporation of Canada. The degradation of the water quality in the Lake Ontario/ Niagara River/Lake Erie part of the Great Lakes prompted research studies into the origin, consequence and abatement of the observed pollution problem (Burns, 1976). As these phosphate-induced problems began to be resolved, research interests shifted towards the every increasing variety and amount of xenobiotic chemicals entering the

environment. The finding of mirex in Lake Ontario fish (Kaiser, 1974) and numerous other contaminants in the water, sediments and biota of the lakes prompted detailed investigations of the Niagara River problem (Allan et al, 1983; NRTC, 1984).

The results presented here provide additional information on various samples from the Welland River, Welland Canal, and Twelve Mile Creek which were taken over several years. They represent investigations, both with respect to the Niagara River contamination problem as well as other research projects using accessible local sites where analytical methodologies and techniques could be developed and tested. For example, the extremely sensitive headspace analysis of water samples for volatile halocarbons, such as perchloroethylene (PERC), was developed and applied first to samples from the Welland and Niagara Falls area (Comba and Kaiser, 1983).

EXPERIMENTAL

Background

Sampling in the lower Welland River commenced in July 1980 in a cooperative effort with Dr. M. Dickman, Brock University, St. Catharines, Ontario. Goals of the study were to determine the types

and levels of contaminants entering this Niagara River tributary from both point and non-point sources. Parts of the results have previously been published (Dickman et al., 1983; Dickman and Steele, 1986; Kaiser and Comba, 1983). Water, sediment and fish samples were collected at several sites within the river to determine what materials were present and their possible relationships with contaminant levels observed in the biota. Later, in the spring of 1981, fish were collected from the reservoir at the Sir Adam Beck generating station and also water and sediment samples were taken for comparison with the upstream sites. In the fall of 1981, as part of the Niagara River Toxics Program, water samples throughout the Niagara River and at 100 stations in Lake Ontario were analyzed for volatile halocarbons (Kaiser et al., 1983).

In the fall of 1982, Lake Ontario was sampled again for volatile halocarbons (Kaiser and Comba, unpublished results) and a sampling program for these compounds was conducted off the mouth of the Niagara River (Comba and Kaiser, 1984). As a result of these measurements, sampling was initiated during the winter of 1983 in the other two interconnecting channels; the Welland Canal and Twelve Mile Creek and also in the upper Welland River. Bulk water samples were collected in the spring of 1983 at sites identified previously by volatile halocarbon levels as receiving industrial or municipal effluents. Many of these sites were resampled in the winter of 1984 to reconfirm the earlier investigations and to collaborate with Dr. K. Lum, ECD, NWRI on an assessment of trace metals.

Sample Collection and Preparation

Fish

Whole frozen fish samples were cut into smaller pieces and ground with an industrial Hobart grinder. Subsamples of 25 g were Soxhlet extracted for 24 hours with a 300 mL solution (50/50) of hexane-acetone. The hexane-acetone extract was reduced to a volume of 1 mL in toluene with a rotary evaporator. The toluene extract was back-extracted with three 25 mL portions of aqueous hydrochloric acid at a pH of 1.5. The toluene portion was then eluted through 10 cm of acid silica gel (30%, sulphuric acid) with 25 mL of hexane. The aqueous extract was adjusted to pH 10.5 with 0.1 M potassium carbonate and extracted twice with 50 mL portions of hexane. The hexane eluant from the acid silica gel clean-up was reduced to 1 mL toluene by rotary evaporation and fractionated on Florisil. Fractions which gave complex gas chromatograms were further partitioned on micro alumina columns with hexane (25 mL) followed by methylene chloride (25 mL). The hexane fraction from the aqueous backwash (base extractables) was analyzed without further clean-up. A schematic of this procedure is given in Fig. 2.

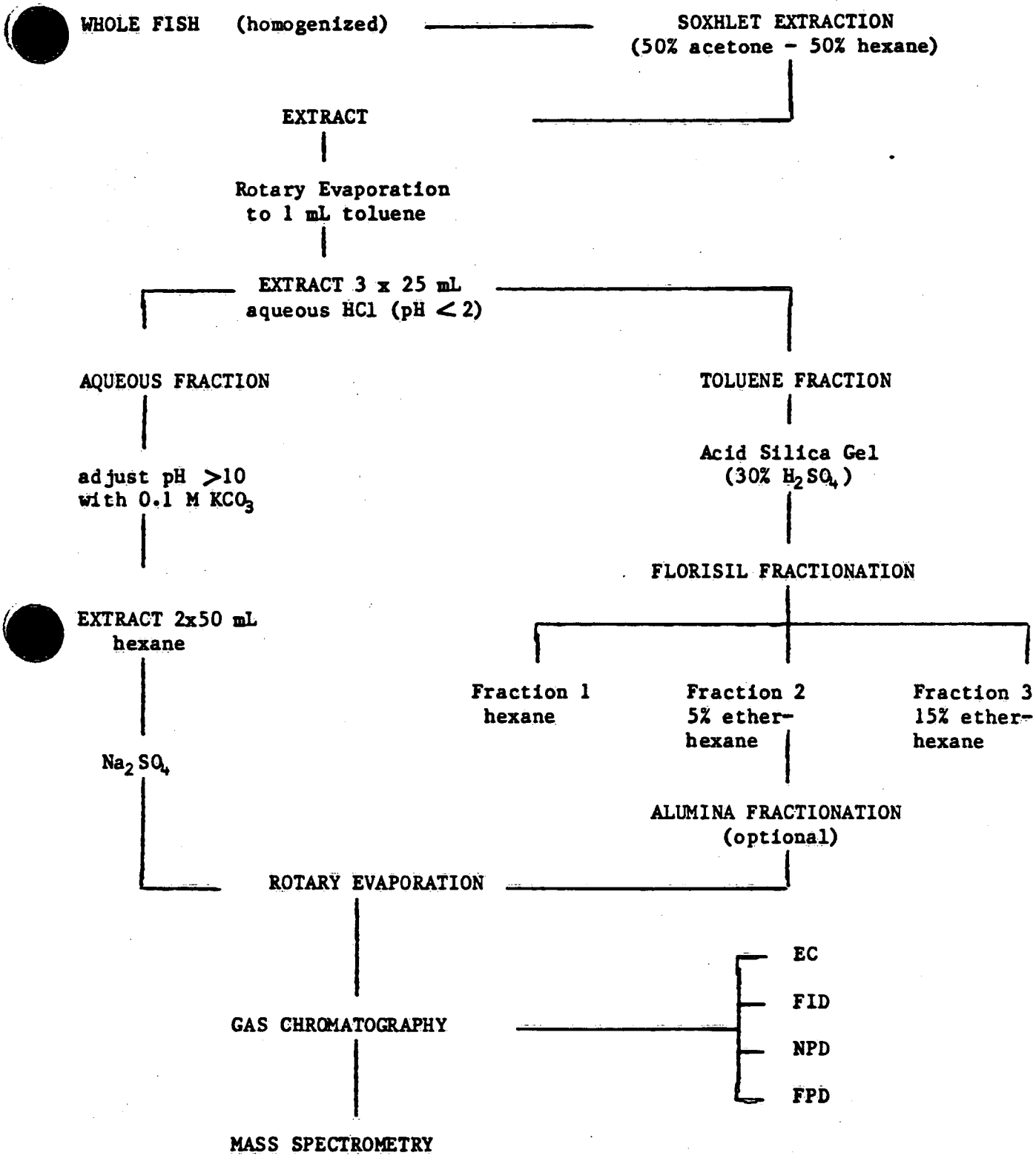


Figure 2. Extraction Scheme for Fish Samples

Sediment

Sediment samples were collected with a mini Shipek and the top 5 cm taken for analyses. Subsamples of 25 g were extracted by ultrasonification using the procedure outlined in the Analytical Methods Manual (Environment Canada, 1974). As recommended, the solvent system there (hexane-acetone) was substituted with methylene chloride, five sample duplicates were processed, one each using: (i) Sonification and (ii) Soxhlet extraction techniques with hexane-acetone as the solvent mixture. Fractionation was done on Florisil and alumina columns as described above for fish.

Water

Bulk water samples were obtained in 30 and 16 litre quantitites during various periods of sampling. Samples were collected in precleaned glass stainless steel containers and transported to the laboratory where they were combined in large glass extractors. Sample pH was adjusted to pH 2 with concentrated hydrochloric acid and the water extracted with 3 x 500 mL of methylene chloride. The methylene chloride extracts were combined and back-extracted with 2 x 500 mL of 5% potassium hydroxide solution. The methylene chloride fraction was dried over sodium sulfate, reduced to 1 mL toluene by rotary evaporation and fractionated on Florisil, as previously described, if necessary. The aqueous layer from the

original sample (base extractables) and the aqueous layer from the methylene chloride back wash (acid extractables) were adjusted to pH 10.5 with potassium hydroxide and pH 1.5 with hydrochloric acid, respectively. The aqueous portions were extracted three times with methylene chloride, dried over sodium sulfate, reduced to 1 mL in toluene by rotary evaporation and analyzed. A general extraction scheme is given in Figure 3.

Volatile halocarbons

The sample bottles (300 mL) were filled so as to avoid any headspace and processed usually within two hours of collection. For the processing, a 100 mL aliquot of each sample was transferred to a 125 mL cylindrical separatory funnel, the funnel evacuated and placed in a water bath at 95°C for three minutes. The volatile contaminants, so purged into the funnel headspace, were then transferred to an evacuated septum-equipped 15 mL vial held in liquid nitrogen. After completion of the transfer, the vials were stored at room temperature until gas chromatographic analysis in the laboratory.

Details of the procedure to isolate the headspace samples, recoveries and subsequent analyses have been described by Comba and Kaiser (1983, 1984).

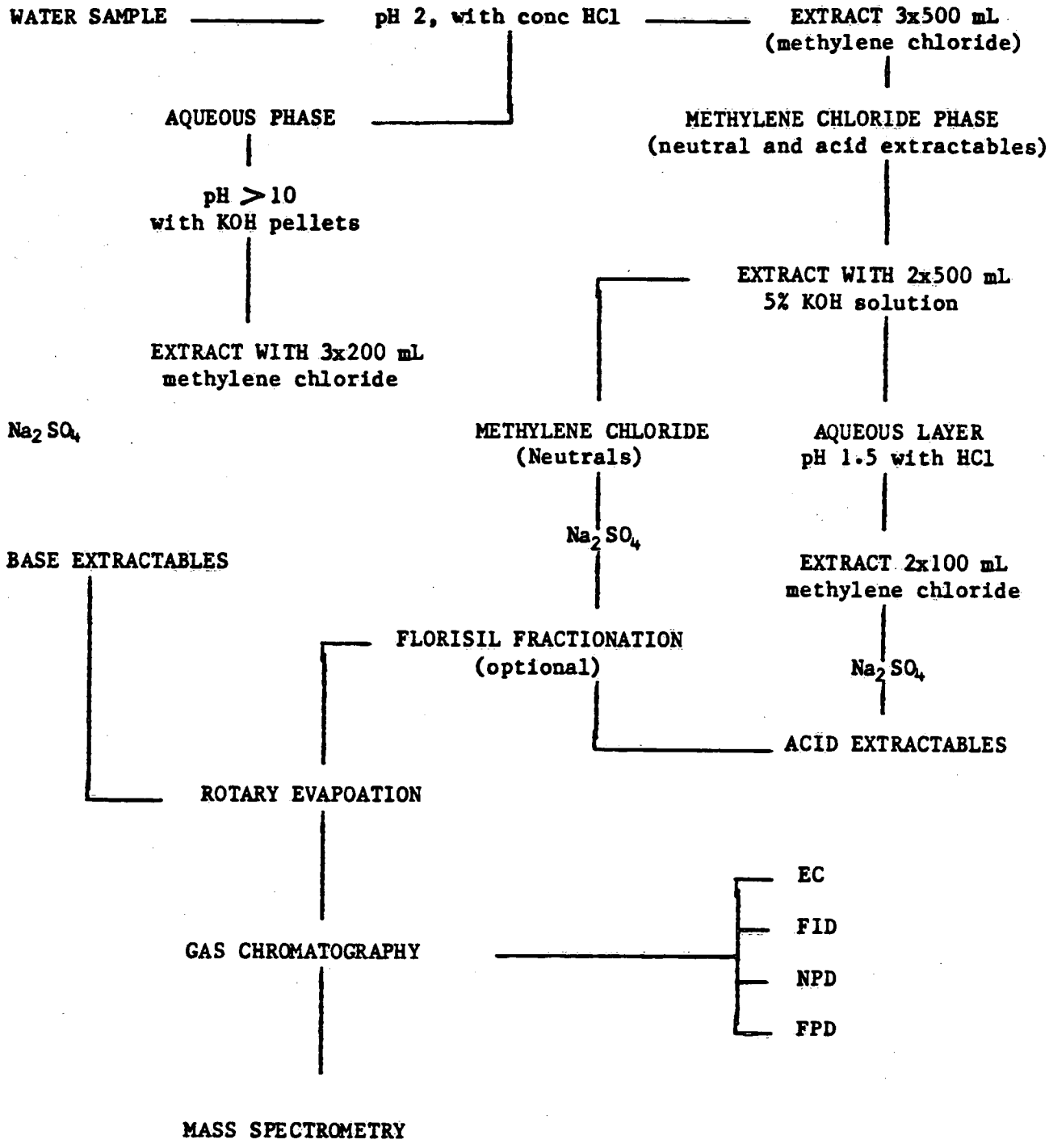


Figure 3. Extraction Scheme for Water Samples.

Chlorinated phenols

Samples were collected in 1 L precleaned glass bottles and adjusted to pH 11 with potassium hydroxide pellets. The preserved water samples were returned to the laboratory and acidified with concentrated hydrochloric acid to a pH of 1 to 2. The acidified water samples were extracted with 40 mL pesticide grade toluene by shaking in a separatory funnel. The toluene layer was removed and the aqueous layer was extracted twice with 2 x 30 mL toluene. The combined toluene extracts were then back extracted three times with 40, 30 and 30 mL of 0.1 M potassium carbonate made up with organic free water. The combined K_2CO_3 extracts were placed in a 125 mL erlenmeyer flask with a teflon lined screw cap. Ten mL of pesticide grade hexane and 1 mL of redistilled acetic anhydride were added and the tightly capped flask was shaken mechanically for one hour. The hexane layer was removed using a pasteur pipet and evaporated to an appropriate final volume in a graduated centrifuge tube with a stream of dry nitrogen after the addition of 4 mL of pesticide grade iso-octane as a keeper.

Gas Chromatography

Volatile Halocarbons

Five hundred microlitre size injections of the headspace samples were analyzed on a Hewlett Packard 5700 gas chromatograph using an electron capture detector. Split/splitless conditions were

employed with a splitless delay time of 10 seconds. Temperatures from -20°C for 2 min to 80°C at 4°C.min^{-1} were used for chromatographic separation on a 30 m x 0.25 mm OV-101 fused silica capillary column with hydrogen as carrier gas.

Chlorinated Phenols

Acetylated extracts of the chlorophenols were analyzed on a Hewlett Packard 5880-A instrument with an electron capture detector. Injections of one microlitre were made with an autosampler onto a 25 m x 0.25 mm OV-1 fused silica capillary column. The temperature conditions were typically 90°C for two minutes, then programmed at 4°C min^{-1} to a final temperature of 160°C. Hydrogen was used as the carrier gas at a flow of 1 mL.min^{-1}.

Organochlorine Compounds

All extracts were analyzed by gas chromatography with electron capture detector on a HP 5880-A instrument and chromatographed on a fused silica column (25 m x 0.25 mm OV-1). Aliquots of 1 µL were injected with an autosampler and an acceptance window of +0.03 seconds was used for component identification by retention time comparison. Typical chromatographic conditions were: injection port: 250°C, detector: 350°C, carrier gas: hydrogen at 1 mL.min^{-1}. The temperature regime was typically 90°C for 2 min, then programmed at 4°C.min^{-1} to a final temperature of 280°C.

Polynuclear Aromatic Hydrocarbons

All extracts for polynuclear aromatic hydrocarbons were analyzed on a Varian 3700 gas chromatograph using a flame ionization detector. Manual injections were made onto a conventional 30 m, SE-54 fused silica capillary column (Chromatographic Specialties) at 90°C. After a two minute isothermal period, temperature programming was initiated at $4°C.min^{-1}$ to a final ten minute isothermal period at 310°C. Carrier gas was hydrogen and a 10 to 1 injector split ratio was used.

Nitrogen and Sulfur Compounds

Sample extracts from 1980-1983 were examined for nitrogen containing compounds using a Hewlett Packard 5700 gas chromatograph equipped with a nitrogen-phosphorus selective detector (NPD). Samples collected after 1983 were analyzed on a Varian 3400 series gas chromatograph with a thermionic specific detector. Those samples analyzed for sulfur molecules were detected with a dual flame photometric detector (FPD) on a Varian 3700 gas chromatograph. All samples were chromatographed on fused silica columns of 25 m length at typical chromatographic conditions of 90°C isothermal for two minutes, programmed to a final temperature of 250°C at $4°C.min^{-1}$. Detection limits for nitrogen and sulfur containing compounds was approximately 500 ppt ($ng.L^{-1}$) and 300 ppb ($\mu g.L^{-1}$) respectively for the bulk water samples analyzed.

Mass Spectrometry

Electron impact mass spectra were obtained on a Riber R10-10 quadrupole mass spectrometer under normal conditions of operation. The sample extracts were chromatographed on a Carlo Erba 4160 gas chromatograph with an on-column injector. The gas chromatograph was directly coupled with the mass spectrometer via the OV-1 fused silica capillary column which exits into the ion source block. Best possible compound identifications were made using the system library capacity on hand with gas chromatography data and spectra interpretation of the observed ion fragments.

Quality Assurance

All procedures were checked routinely with method spikes and blanks for recoveries and chromatographic fractionation. Extraction efficiencies of the tabulated organochlorine residues and polynuclear aromatic hydrocarbons are greater than 80% (Millar and Thomas, 1982; Shafer, 1982; Strup, 1982; McCrea and Fisher, 1984; Comba et al., 1985). Extraction and analyses of sediment samples by both the Soxhlet (acetone/hexane) and sonification techniques (methylene-chloride) gave similar electron capture chromatograms. As the methylene chloride sonification procedure resulted in a slightly enhanced overall extraction efficiency with a tendency for larger recoveries on the lower boiling point compounds, it was applied to the

samples reported here. Compounds identified by mass spectrometry were not quantified, as no standards were available for most of the compounds and the analytical methodology to assess the variety of materials observed is outside the scope of this study. Concentration levels are presented for these materials on a comparative scale relative to response factors for aliphatic hydrocarbon components having similar retention index. Only compounds which had a high level of certainty of being correctly identified are reported, the remainder are tentatively unidentified.

RESULTS

Welland River Watershed

Figure 1 presents an overview of the watershed studied and includes the sites where sampling was done. Fish were captured under contract in July 1980 (Table 2) by Dr. P.O. Steele (Brock University, St. Catharines, Ontario) with gill nets at sites A, B and C in the lower reaches of the Welland River, weighed, sexed and examined for neoplasms.

Thirty-one sites were sampled for water in July 1980, in the lower Welland River and measurements taken for volatile halocarbons. These stations were repeated in April 1981 for the same determinations and reported (Kaiser and Comba, 1983). Two zones (B and C) in the

Table 2. Description of fish caught at stations in the Welland River above and below Cyanamid. July, 1980.

Species[b]	Common Name	Station[a]			Total
		A	B	C	
Perca flavescens	yellow perch	7	-	1	8
Ictalurus punctatus	channel catfish	2	1	1	4
Catostomus commersoni	white sucker	2	-	-	2
Cyprinus carpio	carp	1	2	1	4
Ambloplites rupestris	rock bass	1	5	-	6
Notemigonus crysoleucas	golden shiner	1	6	1	8
Ictalurus nebulosus	brown bullhead	-	1	-	1
Pomoxis sp.	crappie	-	2	-	2
Lepomis gibbosus	pumpkinseed	-	5	-	5
Carassius auratus	goldfish	-	1	-	1
Cyprinus carpio x Carassius auratus	carp-goldfish hybrid	-	6	-	6[c]
Moxostoma carinatum	river redhorse	-	1	-	1
Total		14	30	4	48
Percent of total caught on north shore		50%	10%	40%	

[a]See Figure 1 for sample locations.
[b]Identification by P.O. Steele, Brock University, St. Catharines, Ontario.
[c]Three of the six specimens had neoplasms.

river had volatile halocarbon levels significantly above background values and were indicative of municipal and industrial type effluents in the immediate vicinity (Comba and Kaiser, 1985). Bulk water samples of 30 litres, along with sediment samples were taken in July 1980, August 1980 and April 1981 immediately downstream of the former 36 inch outfall at Cyanamid and downstream of the Thompson Creek confluence at the Welland River (C). The intent of collecting these samples was to identify the major organic compounds present and relate those materials to the compounds found in the fish samples collected. The two carp and six golden shiners from site B were composited and subsampled. The three carp hybrid with neoplasms and the three without, from site B, were composited and analysed as separate samples. Preliminary analysis was accomplished by assessing the samples by various gas chromatographic detection systems. Electron capture detector-active materials were present in considerable numbers in the carp and shiner extracts and in significant quantities in the bulk water extracts. The sediment samples had only a few components in comparison (sites 12, 13, 14, 15, 6 and 17 (for locations, see Kaiser and Comba, 1983) with the exception of station C. Responses to nitrogen and sulfur selective detectors were most pronounced at sites B and C, particularly for nitrogen. No response was observed for the shiner or water samples with the flame photometric detector (FPD) at a detection limit of approximately 300 ppb. A large response was obtained from sediment from site C, later confirmed as elemental sulfur, by mass spectrometry.

A number of responses to the nitrogen/phosphorus detector (NPD) in the nitrogen mode of operation were found at site A (shiner 4, water 0, sediment 0); site B (shiner 5, water 6, sediment 7); site C (shiner 5, water 14, sediment 4). Of these responses, three compounds had identical retention times in all three sample matrices. However, no nitrogen compounds were identified as being the same in the shiner, water and sediment extracts at sites A, B and C using mass spectrometry. Determination of nitrogen compounds in the carp samples was not completed. Mass spectrometric examination of the carp, shiner, bulk water and sediment extracts from sites A, B and C are listed in Table 3. Prior to further examination of the collected fish samples (Table 2), the samples were lost due to a mechanical failure of the refrigeration system in December 1980 and had to be discarded. The extracts from the carp and shiner subsamples were analyzed for the same organochlorine contaminants determined in sediment and water samples at sites B and C (Table 4), but the sample extracts were no longer quantitative and only a qualitative result could be achieved. The major electron capture detector (ECD) responses in the fish extracts parallel observations found in the water and sediments from sites B and C. That is, most of the peaks observed do not correspond to the chlorinated biocides analyzed for (Table 4). Less than 10% of the gas chromatographic peaks observed, based on area response, can be accounted for by these compounds with those determined mostly representing polychlorinated biphenyls.

Table 3. Compounds identified by mass spectrometry in samples from the lower Welland River, 1980.

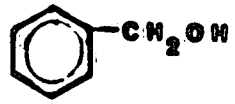
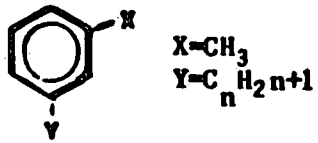
Parameter	Proposed Structure	(a) Locations Found	(b) Frequency	(c) Estimated Concentrations
Benzaldehyde		Carp BHn,C	2	M
		Shiner A,B,C	3	L
		Sediment C	3	L
Benzyl alcohol		Shiner A,B,C	3	L
		Carp B,BHn	2	L
		Sediment C	3	L
Ethyl benzenes (xylenes)	 X=CH_3 Y=C_nH_{2n+1}	Carp BHn	1	
		Shiner B,C	2	L-M
		Sediment C	3	M-H
		Sediment A	3	M
Phenylacetaldehyde (acetophenone)		Shiner C	2	L
Benzoic acid		Sediment C	2	L
Benzyl benzoate	$C_{14}H_{12}O_2$	Sediment C	2	L
Benzyl acetate	$C_9H_{10}O_2$	Sediment C	3	L

Table 3. Compounds identified by mass spectrometry in samples from the lower Welland River, 1980. cont'd.

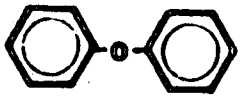
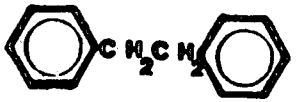
Parameter	Proposed Structure	(a) Locations Found	(b) Frequency	(c) Estimated Concentrations
Diphenyl Ether		Water C	2	L
Benzylidene Acetone		Shiner B,C	2	L
Diphenylethane		Shiner A,B Carp B Water B	2 1 2	L L L
Mesityl oxide	$C_6H_{10}O$	Shiner C	1	L
Ethylene glycol dibenzoate	$C_{16}H_{14}O_4$	Water C	1	L
Ethyl benzyl alcohol		Shiner B	1	L
Benzyl formate		Sediment C	3	L

Table 3. Compounds identified by mass spectrometry in samples from the lower Welland River, 1980. cont'd.

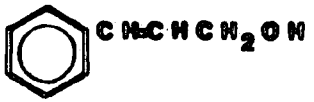
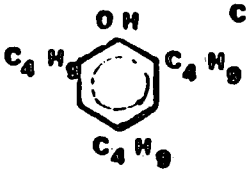
Parameter	Proposed Structure	(a) Locations Found	(b) Frequency	(c) Estimated Concentrations
Benzene propanol (Cinnamyl alcohol)		Water B Carp BHn	1 1	L-M L
Isobutyl phthalate	$C_{16}H_{22}O_4$	Water C Sediment C Shiner C	2 1 1	L L M
Dimethyl phthalate	$C_{10}H_{10}O_4$	Water C Shiner C	2 1	L M
Dioctyl phthalate	$C_{24}H_{38}O_4$	Shiner A,B Water B Sediment B	 3 3	M H H
Tributyl phosphate	$C_{12}H_{27}O_4P$	Water B	2	L
Elemental sulfur	S_8	Sediment C	3	H
2,6-Ditertiary butyl -4-methylphenol (BHT)		Water B Sediment C	3 1	H L
2,4,6-Tributylphenol		Water B Sediment B	2 1	M L

Table 3. Compounds identified by mass spectrometry in samples from the lower Welland River, 1980. cont'd.

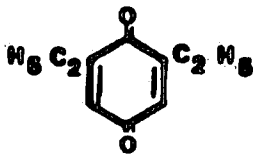
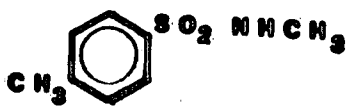
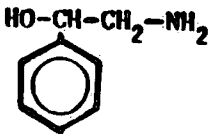
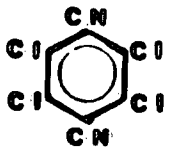
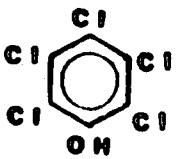
Parameter	Proposed Structure	(a) Locations Found	(b) Frequency	(c) Estimated Concentrations
2,6-Dibutyl-p-benzoquinone		Sediment B	2	L
n-Methyl-p-toluene sulphonamide (d)		Water C	2	M
n-Dimethyl-p-toluene sulphonamide (d)		Water C	2	L-M
Methyl-p-methylphenyl sulphonylacetate (d)		Water C	1	L
Thiazole (series, 30 isomers)	 X,Z,Y=CH_3, C_2H_5, C_3H_7, etc.	Sediment B	3	M
Phenyl hydrazine		Shiner B	1	T

Table 3. Compounds identified by mass spectrometry in samples from the lower Welland River, 1980. cont'd.

Parameter	Proposed Structure	(a) Locations Found	(b) Frequency	(c) Estimated Concentrations
Phenyl cyanate (Phenyl isocyanate)		Water C	2	T
Nitroaniline		Water C	1	T
Phenylethanolamine		Water C	1	T
Tetrachloro-isophthalonitrile		Water C	2	T
Pentachlorophenol		Water B	2	T

(a) See Figure 1 for locations; the fish samples were as follows:
Shiner A - Individual site A; Shiner B - composite 6 individuals, site B; Shiner C - individual, site C; Carp A - individual, site A; Carp B - composite 2 individuals, site B; Carp C - individual; Carp BHn - composite 3 hybrid individuals with neoplasms, site B; Carp BH - composite 3 hybrid individuals, without neoplasms, site B.
(b) Number of times observed for 3 separate bulk water and sediment samples or fish species.
(c) Concentration ranges: H - low ppm; M - high ppb; L - low ppb; T - Trace (ppt).
(d) Determined in methylated fraction.

Table 4. Organochlorine contaminants in sediments and water of the lower Welland River in $\mu g.kg^{-1}$ (ppb) (1981).

Compound	Station (a) B Water/Sediment (b)	Station (a) C Water/Sediment (b)
1,2-Dichlorobenzene	ND / ND	.012 / ND
1,3-Dichlorobenzene	ND / ND	.051 / ND
1,4-Dichlorobenzene	ND / ND	.092 / ND
1,2,4-Dichlorobenzene	ND / ND	.012 / ND
1,2,3-Dichlorobenzene	ND / ND	.003 / ND
1,3,5-Dichlorobenzene	ND / ND	.021 / ND
1,2,3,4-Dichlorobenzene	ND / ND	ND / ND
1,2,4,5-Dichlorobenzene	ND / ND	T / ND
1,2,3,5-Dichlorobenzene	ND / ND	ND / ND
Pentachlorobenzene	ND / ND	.060 / 1.5
Hexachlorobenzene	ND / 1.3	.010 / ND
Hexachlorobutadiene	ND / ND	ND / .28
Hexachlorethane	ND / ND	.020 / ND
Aldrin	ND / ND	ND / ND
Heptachlor	ND / ND	ND / .10
Heptachlor epoxide	ND / ND	0.21 / ND
p,p'-DDE	ND / ND	0.05 / T
p,p'-DDT	.08 / T	T / ND
p,p-DDD	ND / ND	ND / ND
alpha-Chlordane	ND / ND	0.01 / ND
gamma-Chlordane	ND / ND	0.01 / ND
Lindane	ND / ND	0.01 / ND
alpha-Endosulfan	ND / ND	ND / T
beta-Endosulfan	ND / ND	0.01 / ND
Dieldrin	ND / ND	ND / ND
Endrin	ND / ND	ND / T
Methoxychlor	ND / ND	ND / ND
Mirex	ND / ND	ND / ND
Polychorinated biphenyls	ND / 40	ND / 330

T = Trace; ND = Not detected.

(a) See Figure 1 for locations.
(b) Dry weight basis

Mass spectrometric data for these extracts supports these observations. As shown in Table 3, the predominant substances identified are not of the organochlorine category but appear to be more related to the production of amino resins, plasticizers (intermediates) or associated products.

The compound types are mostly heterocyclic, containing oxygen, nitrogen and sulfur. The compounds identified by mass spectrometry represent approximately 30% of all compounds observed using the four gas chromatographic detectors (ECD, FPD, NPD and FID) and represent about 80% of the total area response on the flame ionization detector (FID).

In May 1981, fish were collected from the Sir Adam Beck power generation reservoir (see Figure 1, D). The biological data are summarized in Table 5. The six carp and one hybrid carp were analyzed for organochlorine residues and the data are reported in Table 6. Examination of the carp in the Sir Adam Beck reservoir for materials identified in the lower Welland River by mass spectrometry proved to be fruitless as these compounds could not be found, however, these results are inconclusive as the dilution rates are high and most of the compounds found in river water and sediments did not appear to bioaccumulate in the observed form in fish in the river.

Welland Canal/Twelve Mile Creek

Levels of volatile halocarbons found in Lake Ontario and off the mouth of the Niagara River that initiated sampling in the Welland

Table 5. Description of fish caught at the Sir Adam Beck hydro reservoir(a), Queenston, Ontario, May 1981.

	Species	Common Name	#	Fork Length (mm)	Weight (g)	Sex
1.	Cyprinus carpio	carp	1	535	3000	m
			2	530	2950	m
			3	525	2930	m
			4	666	5010	f
			5	634	5160	f
			6	605	3760	f
2.	C. carpio x C. auratus	carp-hybrid	1	366	1058	m
3.	Catostomus commersoni	white sucker	1	422	1132	f
			2	372	739	m
			3	385	878	f
			4	273	241	-
			5	276	250	-
			6	411	986	f
			7	370	757	f
			8	410	782	f
			9	402	883	m
			10	376	711	f
			11	400	839	f
			12	379	702	f
			13	325	501	m
			14	379	775	m
			15	340	534	m
			16	351	635	m
			17	381	621	m
			18	313	451	-
			19	331	538	m
4.	Perca flavescens	yellow perch	1	302	623	f
			2	271	405	f
			3	249	287	f
			4	237	239	f
			5	251	253	f
			6	226	162	f
			7	229	175	m
			8	229	146	m
			9	209	117	m
			10	187	939	f
			11	164	46	m
			12	142	33	m
5.	Moxostoma carinatum	river redhorse	1	374	752	-
			2	356	504	f
6.	Morone chrysops	white bass	1	322	646	f

6 species, 41 individuals, data supplied by P.O. Steele, Brock University, St. Catharines, Ontario.

(a) see Figure 1, site D.

Table 6. Organochlorine contaminants in carp from the Sir Adam Beck hydro reservoir in $\mu g.kg^{-1}$ (ppb) (1981).

Compound	Sample*			
	A	B	C	D
1,2-Dichlorobenzene	ND	41	ND	ND
1,3-Dichlorobenzene	ND	ND	ND	ND
1,4-Dichlorobenzene	ND	ND	ND	ND
1,2,4-Trichlorobenzene	ND	ND	ND	8.0
1,2,3-Trichlorobenzene	ND	38	12	ND
1,3,5-Trichlorobenzene	ND	ND	21	ND
1,2,3,4-Tetrachlorobenzene	ND	ND	ND	3.7
1,2,4,5-Tetrachlorobenzene	ND	ND	2.4	ND
1,2,3,5-Tetrachlorobenzene	ND	ND	ND	3.4
Pentachlorobenzene	ND	ND	ND	0.51
Hexachlorobenzene	3.4	7.0	1.6	1.6
Hexachlorobutadiene	ND	ND	ND	ND
Hexachlorethane	ND	ND	ND	7.2
Aldrin	12	14	ND	ND
Heptachlor	8.4	35	ND	0.66
Heptachlor epoxide	10	27	3.9	4.0
p,p'-DDE	98	790	120	140
p,p'-DDT	ND	91	ND	72
p,p'-DDD	13	100	9.6	14
alpha-Chlordane	ND	ND	8.4	T
gamma-Chlordane	12	ND	ND	ND
Lindane	ND	ND	ND	0.11
alpha-Endosulfan	ND	51	5.0	0.10
beta-Endosulfan	ND	16	ND	12
Dieldrin	3.1	21	11	0.50
Endrin	ND	ND	ND	48
Methoxychlor	ND	ND	ND	ND
Mirex	ND	ND	T	ND
Polychorinated biphenyls	550	V	255	490

ND = Not detected; V = value missing; T = Trace.
A Composite sample of carp 1,2 and 3, see Table 5.
B Composite sample of carp 4 and 5, see Table 5.
C Composite sample of carp 6, see Table 5.
D Carp hybrid, see Table 5.
* Concentrations expressed as wet weight, whole fish.

Table 7. Volatile halocarbon contaminants in water samples of the Welland Canal, Welland River and Twelve Mile Creek, 1983

Compound	Station Number*									
	18a	18	17	15	14	27	13	12	11	35
	Concentration as $ng.L^{-1}$ (ppt)									
Trichlorofluoromethane	6.8	33	25	15	15	5.8	15	15	15	12
Methylene chloride		53	41	12	200	72				65
Chloroform	290	7.0	7.6	9.9	11	270	16	7.7	10	13
1,1,1-Trichloroethane	570	6.6	16	12	12	80	9.8	8.9	7.5	12
Carbon tetrachloride	3.8	3.8	4.9	4.8	14	7.0	3.9	5.0	14	3.0
Trichloroethylene	5.0	3.8	0.8	3.0	2.4	1400	33	0.9	2.2	2.4
Dichlorobromomethane	180	2.3	1.8	1.4	3.1	200	7.9	1.5	1.9	2.1
Dibromochloromethane	56	1.0	1.1	0.7	1.6	67	3.2	0.88	0.91	1.0
1,1,2-Trichloroethane		1.6	2.7	3.5	5.1	67	2.0	2.2	2.3	2.0
Tetrachloroethylene	7.5	2.5	5.0	4.1	2.3	20	37	3.9	4.5	3.7
Carbon disulfide			T							

Compound	Station Number*									
	24	23	22	21	20	19	26a	26b	26c	26d
	Concentration as $ng.L^{-1}$ (ppt)									
Trichlorofluoromethane	25	3.8	7.0	4.2	12	15	8.4	5.5	5.0	2.7
Methylene chloride	130	34	-	-	82	43	100	42		160
Chloroform	8.3	3.9	11	0.71	6.8	6.6	13	78	48	7.4
1,1,1-Trichloroethane	7.2	7.6	8.3	2.0	11	12	7.6	18	17	15
Carbon tetrachloride	6.4	14	6.7	3.6	6.1	6.1	4.5	3.8	3.4	3.4
Trichloroethylene	2.7	2.3	3.3		2.8	2.6				
Dichlorobromomethane	1.5	0.5	5.6		0.64	2.9		55	36	
Dibromochloromethane	1.0	0.41	1.6		0.41	1.6		15	10	
1,1,2-Trichloroethane	2.8	1.6	1.9		2.2	2.8				
Tetrachloroethylene	3.0	1.6	3.0	5.7	3.2	2.2	8.4	6.8	56	5.3
Carbon disulfide	T				T	T				

* See Figure 1 for locations.

Table 7. Volatile halocarbon contaminants in water samples of the Welland Canal, Welland River and Twelve Mile Creek, 1983. cont'd.

Compound	Station Number*							
	28	10	34	29	37	30	31a	31b
	Concentration as $ng.L^{-1}$ (ppt)							
Trichlorofluoromethane	5.3	15	5.7	5.5	N	8.2	23	6.8
Methylene chloride	-	41	61	250	O	290	120	97
Chloroform	8.4	5.7	57	41		11	100	130
1,1,1-Trichloroethane	13	8.0	340	660	S	7.8	33	34
Carbon tetrachloride	6.7	3.0	3.0	3.4	A	7.0	4.0	2.7
Trichloroethylene	6.6	4.6	330	685	M	2.5	5.4	3.5
Dichlorobromomethane	2.5	0.75	3.2	-	P	-	63	86
Dibromochloromethane	-	0.58	1.9	-	L	-	22	25
1,1,2-Trichloroethane	-	2.5	-	2.3	E	-	-	-
Tetrachloroethylene	9.0	3.1	17	32		5.3	5.7	10
Carbon disulfide		T		T				

Compound	Station Number*								
	33	32	36a	36b	4	3	2	1a	1
	Concentration as $ng.L^{-1}$ (ppt)								
Trichlorofluoromethane	8.9	7.5	4.2	2.1	15	11	26	23	23
Methylene chloride	2500	890	820	100	35	300	100	350	150
Chloroform	3600	3700	2400	250	1.4	3300	58	570	48
1,1,1-Trichloroethane	1900	1700	126	19	2.5	23	11	32	11
Carbon tetrachloride	3.6	2.7	2.2	3.6	4.2	3.1	18	9.2	3.8
Trichloroethylene	50	130	3.1	3.0		54	7.2	110	5.6
Dichlorobromomethane	100	110	47	5.8		87	29	250	9.7
Dibromochloromethane	13	85	4.4	Trace		5.5	7.2	83	2.7
1,1,2-Trichloroethane	-	91				120	1.4	8.2	1.1
Tetrachloroethylene	38	33	7.1	5.8	41	41	3.9	1200	14
Carbon disulfide	-	-	-	-	-	-	-	-	-
Others		**							

* See Figure 1 for locations.
** 1,2 Dichloropropane 11

TABLE 8. Chlorophenol levels in selected surface waters of the Welland River, Welland Canal and Twelve Mile Creek, January, 1984 (ppt).

Phenol	Station[a]							
	1a	2a[b]	36a	31b	32	33	29	27
2,6-Dichlorophenol	47	-	-	27	-	7	-	-
2,4-Dichlorophenol	105	-	-	12	-	-	-	-
2,4,6-Trichlorophenol	67	-	7	4	-	3	-	-
2,4,5-Trichlorophenol	7	-	-	9	-	-	6	-
2,3,4-Trichlorophenol	7	-	-	-	-	-		-
2,3,4,6-Tetrachloro-phenol	232	1	33	36	1	19	27	6
Pentachlorophenol	103	1	35	25	1	19	21	6

[a]Concentrations expressed as $ng.L^{-1}$ (ppt), see Figure 1 for locations.

[b]Final effluent of Port Dalhousie WPCP.

Table 9. Organochlorine contaminants in water samples from the upper Welland River, Welland Canal and Twelve Mile Creek in $ng.L^{-1}$ (ppt) (1984).

Compound	Station Number[a,b]				
	1a	2a[c]	36	34	27
1,2-Dichlorobenzene	61	80	ND	400	30
1,3-Dichlorobenzene	ND	64	ND	ND	8.7
1,4-Dichlorobenzene	ND	ND	ND	ND	ND
1,2,4-Trichlorobenzene	ND	ND	ND	ND	2.1
1,2,3-Trichlorobenzene	ND	38	ND	ND	ND
1,3,5-Trichlorobenzene	ND	ND	ND	23	ND
1,2,3,4-Tetrachlorobenzene	ND	ND	ND	ND	2.5
1,2,4,5-Tetrachlorobenzene	20	10	ND	ND	1.9
1,2,3,5-Tetrachlorobenzene	ND	ND	ND	ND	ND
Pentachlorobenzene	7.3	ND	ND	2.4	0.8
Hexachlorobenzene	ND	2.0	ND	16	0.6
Hexachlorobutadiene	ND	ND	ND	ND	1.6
Hexachlorethane	ND	ND	ND	8.8	0.6
Aldrin	22	ND	ND	ND	ND
Heptachlor	ND	2.0	4.2	ND	ND
Heptachlor epoxide	8.7	ND	ND	32	ND
p,p'-DDE	17	5.3	ND	ND	T
p,p'-DDT	ND	6.1	ND	ND	T
p,p'-DDD	ND	ND	ND	ND	ND
alpha-Chlordane	ND	ND	ND	65	T
gamma-Chlordane	ND	ND	7.1	ND	0.6
Lindane	ND	ND	ND	ND	ND
alpha-Endosulfan	ND	ND	ND	ND	ND
beta-Endosulfan	ND	ND	ND	33	ND
Dieldrin	ND	ND	ND	ND	ND
Endrin	ND	ND	ND	ND	ND
Methoxychlor	ND	ND	ND	ND	ND
Mirex	ND	ND	ND	ND	ND
Polychorinated biphenyls	20	6.8	9.8	ND	ND

a) See Figure 1 for locations.
b) ND = Not detected
T = Trace.
c) Final effluent of Port Dalhousie WPCP.

Canal and Twelve Mile Creek were reported earlier (Kaiser et al., 1983; Comba and Kaiser, 1984). The sources of these compounds in this area were determined in February 1983 and given in Table 7. This period was chosen, since the Welland Canal was under repair and the section from the Thorold lock to the number 2 lock in St. Catharines was dry. On the basis of these measurements, five sites were chosen for further investigation, namely the mouth of the old Welland Canal spillway (36), the siphon from Beaver Wood Fibre and Hayes Dana to Gibson Lake (34), the Welland River downstream of the Atlas-Mansfield sewer (27), the Port Dalhousie WPCP final effluent (2a) and below the Port Weller WPCP (1a) outfall in the Welland Canal.

In March 1983 and again in January 1984, 16 L bulk water samples were collected at these sites and screened by gas chromatography for heterocyclic compounds and quantitated for organochlorine residues. The results for the chlorinated phenols and organochlorine residues in the 1984 samples are reported in Tables 8 and 9, repectively, with the levels of polynuclear aromatic hydrocarbon for the same stations given in Table 10. As evident from the data, these compounds appear to be present at comparatively low levels at the times sampled, and were not confirmed by mass spectrometry due to their generally low concentrations.

The spillway (site 36) discharges primarily paper manufacturing and processing wastes, at a sizeable mean flow of 177,000 m^3 day^{-1}. The water has a dark brown colour, a strong sulfurous smell and was void of biota other than tubificid

Table 10 Polynuclear aromatic hydrocarbon concentrations in water samples of the Welland River, Welland Canal and Twelve Mile Creek, 1984 in $ng.L^{-1}$ (ppt).

Parameter	Station Number[a]				
	27	34	36	1a	2a[b]
Indene	ND	ND	650	390	ND
1,2,3,4-Tetrahydronapthalene	ND	700	ND	ND	ND
Naphthalene	ND	7400	3100	ND	ND
2-Methylnaphthalene	ND	180	ND	ND	ND
Quinoline	ND	430	ND	350	220
1-Methylnaphthalene	ND	390	ND	870	220
β-Chloronapthalene	ND	ND	ND	ND	ND
Acenaphthylene	ND	ND	ND	ND	ND
Acenaphthene	ND	430	ND	ND	ND
Fluorene	ND	220	ND	ND	ND
Phenanthrene	ND	9200	ND	ND	ND
Anthracene	ND	ND	ND	ND	ND
Fluoranthene	ND	350	ND	ND	ND
Pyrene	ND	260	ND	ND	ND
Chrysene	650	ND	ND	ND	ND
Benzo[j]or[k]fluoranthene	ND	ND	ND	ND	ND
Benzo[b]fluoranthene	ND	ND	ND	ND	ND
Benzo[a]anthracene	310	ND	ND	430	430
Benzo[b]chrysene	ND	ND	ND	ND	ND
Benzo[e]pyrene	ND	ND	ND	ND	ND
Benzo[a]pyrene	ND	ND	ND	ND	ND
Perylene	ND	1100	ND	ND	ND
Indeno[1,2,3,c,d]pyrene	ND	ND	ND	ND	ND
Dibenz[a,h]anthracene	610	ND	ND	390	ND
Benzo[g,h,i]perylene	ND	ND	ND	ND	ND

a)See Figure 1 for locations.

b)Final effluent of Port Dalhousie WPCP.

oligochaetes. The water extracts contained many electron capture detector-active compounds (other than organochlorine biocides), three compounds with moderate responses to the NPD and a signal for elemental sulfur on the FPD. The major products identified from the observed mass spectra as given in Table 11 were benzaldehydes, ketones and alkylated benzene derivatives, typical of pulp wastes. Similar products and odors were also observed at station 34, the flow from the siphon to Gibson Lake. Water samples from that station gave strong responses with both the electron capture and nitrogen specific detectors. The extracts from both sites (34, 36) each contain well over 200 compounds using FID response. Six compounds appear common in the acid extracts and three in the base/neutral fractions given their respective elution times and responses using electron capture detectors. Two of these compounds are elemental sulfur and dioctyl phthalate as identified by mass spectrometry; the others remain undetermined. Chromatograms of the samples from Port Weller (1a) and Port Dalhousie (2a) gave a number of responses (40-50) to the ECD detector of which ten had common relative retention times.

The Port Dalhousie final WPCP effluent also had some 10 to 20 strong FID and 4 NPD responses. Mass spectrometry identification for some of these compounds are toluene, benzothiazole, dioctyl phthalate and a pyridine compound with the remainder still undetermined. No compounds could be identified with confidence by mass spectrometry for the Port Weller sample, although it had substantial ECD and FID responses.

Table 11. Compounds identified by mass spectrometry in water samples from the Upper Welland River, Welland Canal and Twelve Mile Creek, 1983 and 1984.

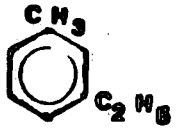
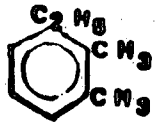
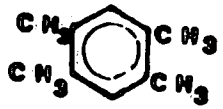
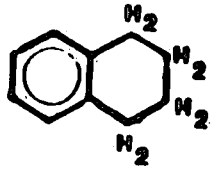
Parameter	Proposed Structure	(a) Locations Found	(b) Frequency	(c) Estimated Concentrations
Toluene		34,2a	2	L-M
Methyl ethyl benzene		36b	2	M
1,4-Dimethylbenzene		36b	2	M
1-Ethyl, 2,3-Dimethyl-benzene		36b	2	M
Tetramethylbenzene (2 isomers)		36b	2	M
Tetrahydronaphthalene		36b	1	M

Table 11. Compounds identified by mass spectrometry in water samples from the Upper Welland River, Welland Canal and Twelve Mile Creek, 1983 and 1984. cont'd.

Parameter	Proposed Structure	(a) Locations Found	(b) Frequency	(c) Estimated Concentrations
Anisole		34	2	
2,4-Dimethoxybenzene		36b	2	
3-Methylphenol		36b	2	
2-Methoxyphenol		36b	2	
1-Methoxy-4-methylbenzene		36b	2	M
2,4-Dihydroxy-6-methyl benzaldehyde		36b	2	M
4-Hydroxy-3-methoxy benzaldehyde (Vanillin)		36b	2	H

Table 11. Compounds identified by mass spectrometry in water samples from the Upper Welland River, Welland Canal and Twelve Mile Creek, 1983 and 1984. cont'd.

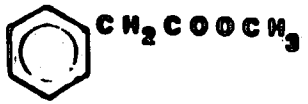
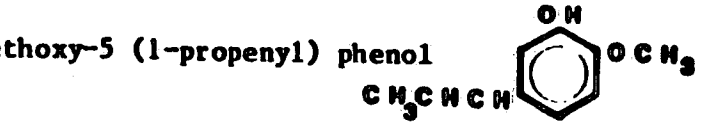
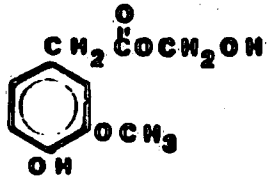
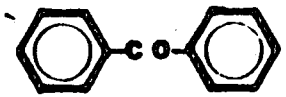
Parameter	Proposed Structure	(a) Locations Found	(b) Frequency	(c) Estimated Concentrations
Benzylacetate		36b,34	2,2	M
2 -Methoxy-5 (1-propenyl) phenol		36b	1	M
2-Propanone-1 hydroxy-3-(4-hydroxy-3-methoxy phenyl)		36b	1	L
4-Hydroxy-3 methyl phenyl) 1-ethanone		36b	1	M
Benzophenone		34	2	L
Phenyl methyl hydroxylamine		36b	2	H

Table 11. Compounds identified by mass spectrometry in water samples from the Upper Welland River, Welland Canal and Twelve Mile Creek, 1983 and 1984. cont'd.

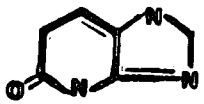
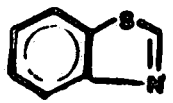
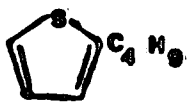
Parameter	Proposed Structure	(a) Locations Found	(b) Frequency	(c) Estimated Concentrations
n-1-(Methylhexylidene)	$C_8H_{17}N$	27	1	L
1-Propylbutylidene methylamine	$C_8H_{15}N$	34	1	L
Imidazo Dihydropyridinone		2a	1	L
Benzothiazole		2a	1	L
Phenyl sulfide (Thiobisbenzene)		27	2	L
Thiophene (substituted)	 C_4H_8	34	1	L
Sulfur	S_8	27,34,36b	2,1,2	M

Table 11. Compounds identified by mass spectrometry in water samples from the Upper Welland River, Welland Canal and Twelve Mile Creek, 1983 and 1984. cont'd.

Parameter	Proposed Structure	(a) Locations Found	(b) Frequency	(c) Estimated Concentrations
Phosphoric Acid (Triethyl/Butyl esters)	$(C_4H_9)_3\ PO_4$	34	2	L
Diethyl phthalate	$C_{12}H_{14}O_4$	34	2	L
Dibutyl phthalate	$C_{16}H_{22}O_4$	34	2	L
Dioctyl phthalate	$C_{24}H_{38}O_4$	36b,27,2a,34	2	L-H

(a) See Figure 1, Table 1 for locations.
(b) Number of observations for 2 separate samples.
(c) Concentration ranges.

H - low ppm
M - high ppb
L - low ppb
T - Trace (ppt)

The fauna and water in the immediate receiving area and on the shoreline downstream of the Atlas-Mansfield sewer discharge are coated with oil. Sediment samples taken up to 1 km downstream also contained a high percentage of oil in their composition. This oil contamination proved difficult in providing proper clean-up of the samples, as the "aliphatic hydrocarbon envelope" obscured identification. Only four compounds could be identified by mass spectrometry which were sulfur, dioctyl phthalate, phenyl sulfide and an alkyl amine.

DISCUSSION

Inputs of contaminants that enter Lake Ontario from Canadian sources in the southern Niagara peninsula originate from the Niagara River (Welland River), Twelve Mile Creek and Welland Canal. The effects of such discharges in the Welland River watershed have resulted in stunted or dying vegetation (Dickman et al., 1980; Dickman et al., 1983), increased tumor incidence (Steele and Dickman 1979; Steele, 1980; Dickman and Steele 1986) and a court judgement against Cyanamid under the Fisheries Act (CELR, 1981). Point source discharges of ammonia and oil in the Welland River watershed previously exceeded water quality goals (MOE, 1978), although ammonia discharges have been limited to 252 $kg.day^{-1}$ since April 1, 1985 (COR, 1986).

Because of its contribution to the Niagara River, the levels of priority pollutants from point sources to the Welland River are documented and were calculated to average 145 $kg.day^{-1}$ (NRTC, 1984). Two major sources in the Welland River have had control measures put into place to reduce loadings of heavy metals and cyanide. Data given here, however, suggest that the proportion of "organic priority pollutants" to total extractable organics in the samples are minor in comparison, and the reduction of these other organic constituents by current control measures is uncertain. For example, the levels of PCB, PNA and organochlorine residues in fish, water and sediment of the Welland River are substantial lower than in the Niagara River Allan et al., 1983). Levels of PCB in whole carp from the Sir Adam Beck reservoir (Table 6) are lower than mean levels in carp fillets from Lake Huron (1.0 $\mu g.g^{-1}$), Lake Erie (0.46 $\mu g.g^{-1}$) and the St. Lawrence (1.3 - 1.7 $\mu g.g^{-1}$) (MOE, 1986). Our findings for the lower Welland River are comparable (although not quantitated), i.e., the majority of observed materials do not correspond to traditional organochlorine biocides and for the most part remain undetermined.

The calculated Canadian discharge of organic priority pollutants to the Niagara River, based on concentrations of 20 compounds that represent 99 percent of the loading is 17 $kg.day^{-1}$, of which 5.5 $kg.day^{-1}$ is discharged to the Welland River (NRTC, 1984). Compounds not listed as "priority pollutants" also are discharged at similar rates. For example, the area downstream of the Atlas-Mansfield Sewer had aliphatic hydrocarbon concentrations greater than

10 $mg.L^{-1}$ in water samples. At the lowest mean flow of 7,200 $m^3.day^{-1}$, loadings of 7.2 $kg.day^{-1}$ are calculated. Cyanamid (Welland plant) still discharges 250 $kg.day^{-1}$ ammonia. Total aromatic hydrocarbon concentrations in water samples at the Thompson Creek confluence are conservatively in the low $mg.L^{-1}$ range with an estimated mean flow of 20,000 $m^3.day^{-1}$, on this basis, the loading is calculated to be 20 $kg.day^{-1}$. These loadings do not account for materials transported in the form of suspended sediments, nor do they account for discharges from other industries to this waterway. The compounds identified in these samples represent approximately 80 per cent of the extracted total organic material with another 20 per cent being uncharacterized and excluded from evaluation. Of these 80%, for the Welland River samples, only approximately 10 per cent can be classified under the "priority pollutant" category, as defined by the US Environmental Protection Agency. Therefore, approximately 90% of the total extractable organic materials in the Welland River samples is not routinely monitored.

Loadings from the Welland Canal and Twelve Mile Creek tributaries are currently undefined. Landsat photos (U.S. EPA, 1983) clearly outline plumes of phosphates and nitrates entering Lake Ontario. Volatile hydrocarbon distributions off the mouths of these tributaries indicate significant industrial and municipal inputs (Kaiser et al., 1983; Comba and Kaiser, 1984). Also, recent measurements of dissolved zinc from discharges to the Welland Canal and Twelve Mile Creek provide a conservative annual estimate of

38 $kg.day^{-1}$ (Lum et al., 1986) or, in terms of Canadian point source loadings, an amount equivalent to 25% of the total Canadian discharges of priority pollutants to the Niagara River (154 $kg.day^{-1}$, NRTC, 1984). We obtain a conservative loadings estimate of 177 $kg.day^{-1}$ for benzene-related materials from the spillway (36) alone, using a mean level of 1 $mg.L^{-1}$ (Table 11) and a calculated (1984) mean flow rate of 177 x 10^3 $m^3.day^{-1}$ from the Ontario Paper Co., Fraser Inc., Kimberly-Clark, and Domtar Fine Papers discharges (Table 1). In comparison, the loadings of priority organic pollutants is relatively minor (17 $kg.day^{-1}$). Compound types observed are primarily alkylated benzenes, phenolics, benzaldehydes and heterocyclic compounds. Together, these represent about 30% of the total number of compounds extracted, although as in the case of the lower Welland River, they account for about 80% of the total estimated organic loading as determined by area response to various gas chromatographic detectors.

The potential biological effects of these compounds are unknown. A case in point are the phenolic antioxidants BHT and BHA, common food preservatives. These compounds proved lethal to rabbits at high doses (Laurado, 1984) and BHT is listed as a tumor promotor/ arcinogen (Kraybill, 1983). The trace constituents benzothiazole, phenyl sulfide, anisole, nitroaniline, pentachlorphenol, phenyl-ethanolamine and tetrachloroisophthalonitrile are all listed or suspected highly toxic or hazardous compounds (Sax, 1968). Cresols and dihydroxybenzene are suspected tumor promoters or co-carcinogens in airborne pollutants (Kraybill, 1983). Toluene causes extended

physiological changes in carp (Gluth and Hanke 1985) and is very toxic to fish, as are the lower alkylated benzenes with a 96 hr - LC_{50} of less than 10 mg/L for undefined species (MOE 1978). Although the individual role of each contaminant would be difficult to ascertain, visual effects are documented for specific areas of these water courses (Dickman et al. 1980, 1983; Dickman and Steele 1986).

Current environmental protection concepts focus on the present list of priority pollutants. Consequently, other organic compounds which may have detrimental environmental effects are overlooked and/or excluded from such considerations. However, the water, sediment and fish samples reported here demonstrate the need for broader contaminant definition. In fact, the majority of the compounds found are not routinely monitored. Accurate and timely assessment of the hazards of wastes discharged to any of these interconnecting waterways should be undertaken by the responsible agencies, with a view toward more comprehensive control measures.

ACKNOWLEDGEMENTS

We thank Mr. K. Hill of the Technical Operations Division and Messrs. H. Hunter and J. Ribo for their assistance with the sample collections. Our thanks to Mr. J.W. Dame, Security Investigator with Ontario Hydro, for his friendly assistace in providing access and information to some of the sampling sites. We appreciate the cooperation and technical information supplied by Messrs. Stan Irwin, Allan Baldwin and Tony Pinque from the Ontario Ministry of the Environment. We also thank Mr. M. Brooksbank and Dr. T. Tseng of Environment Canada and the staff of the West Central Region, the Niagara River Project, and the Water Resources Branch, Ontario Ministry of the Environment, for valuable comments on an earlier draft of this report.

REFERENCES

Allan, R.J., Mudroch, A. and Sudar, A. 1983. An introduction to the Niagara River/Lake Ontario pollution problem. J. Great Lakes Res. 9:111-117.

Burns, N.M. 1976. Nutrient budgets for Lake Erie. 1970. J. Fish. Res. Board Can. 33:520-536.

CELR, 1981. Canadian Environmental Law Report, 11:31.

Comba, M.E. and Kaiser, K.L.E. 1983. Determination of volatile contaminants at the ng L^{-1} level in water by gas chromatography with electron capture detection. Intern. J. Environ. Anal. Chem. 16:17-31.

Comba, M.E. and Kaiser, K.L.E. 1984. Tracking river plumes with volatile halocarbon contaminants: The Niagara River-Lake Ontario example. J. Great Lakes Res. 10:375-382.

Comba, M.E., Kaiser, K.L.E., Maguire, R.J., Tkacz, R.J. and Platford, R.F. 1985. A chemical survey of the Detroit River, 1983. Environmental Contaminants Division, National Water Research Institute, Canada Centre for Inland Waters, Burlington, Ontario, NWRI Contribution #85-85: 89 p.

COR, 1986. Canada and Ontario. Report on the 1984 Industrial discharges into the Great Lakes Basin - Ontario. June 10, 1986. Canada-Ontario Agreement respecting Great Lakes Water Quality, ca 150 p.

COR, 1985. Canada and Ontario. Report on the 1984 Discharges from Municipal Wastewater Treatment Facilities in the Great Lakes Basin - Ontario. 1 October 1985. Canada-Ontario Agreement Respecting Great Lakes Water Quality, ca 100 p.

Dickman, M., Smol, J. and Steele, P. 1980. The impact of industrial shock loading on selected biocoenoses in the lower Welland River, Ontario. Water Pollution Res. J., Canada. 15:17-31.

Dickman, M., Prescott, C. and Kaiser, K.L.E. 1983. Variations in the aquatic vegetation of the Welland River, Ontario, Canada, above and below an industrial waste discharge. J. Great Lakes Res. 9(2): 317-325.

Dickman, M. and Steele, P. 1986. Gonadal neoplasms in wild carp - goldfish hybrids from the Welland River near Niagara Falls, Canada. In press, Hydrobiologia.

Environment Canada. 1974. Inland Waters Directorate, Water Quality Branch, Analytical Methods Manual, 1984 Update. Organochlorine Pesticides and PCB in Sediments. Ultrasonic Extraction.

Gluth, G. and Hanke, W. 1985. A comparison of physiological changes in carp, Cyprinus carpio, induced by several pollutants at sublethal concentrations. Ecotoxicology and Environmental Safety, 9:179-188.

IJC. 1979. International Joint Commission. Inventory of major municipal and industrial point source discharges in the Great Lakes Basin. Ca. 200 p.

Kaiser, K.L.E. and Comba, M.E. 1983. Volatile contaminants in the Welland River watershed. J. Great Lakes Res. 9: 274-280.

Kaiser, K.L.E., Comba, M.E. and Huneault, H. 1983. Volatile contaminants in the Niagara River and in Lake Ontario. J. Great Lakes Res. 9:212-223.

Kaiser, K.L.E. 1974. Mirex: an unrecognized contaminant of fishes from Lake Ontario. Science 185:523-525.

Kraybill, H.F. 1983. Assessment of human exposure and health risk to environmental contaminants in the atmosphere and water with special reference to cancer. J. Environmental Science and Health, 175-232.

Llaurado, J.G. 1984. Beware of phenolic antioxidants (BHT and BHA). Inter. J. Environmental Studies, 22: 135-137.

Lum, K.R., Comba, M.E., Yoakim, P.R., and Kokotich, E.A. 1986. A preliminary study of inorganic contaminants and water quality in the Welland River watershed. Environment Canada, National Water Research Institute. Report 86-83; 15 p.

McCrea, R.C. and Fisher, J.D. 1984. Design and testing of an aqueous phase liquid-liquid extractor (APLE) for the determination of organochlorine contaminants. Environment Canada, Inland Waters Directorate, Burlington, Ontario, Canada, 18 p.

Millar, J.D. and Thomas, R.E. 1982. Determination of pesticides and PCBs in industrial and municipal wastewaters. EPA-600/54-82-023: 6 p.

MOE, 1986. Ontario Ministry of the Environment. Contaminants in fish data summary. Aquatic Contaminants Unit, Water Resources Branch, January 1986.

MOE, 1978. Ontario Ministry of the Environment. Water management, goals, policies, objectives and implementation procedures of the Ministry of the Environment. Ca. 67 pp.

NRTC, 1984. Niagara River Toxics Committee. Report of The Niagara River Toxics Committee; US Environmental Protection Agency; Ontario Ministry of the Environment; Environment Canada, Ontario Region; NY State Department of Environmental Conservation. Ca 500 p.

Sax, N.I. 1968. Dangerous properties of industrial materials. Van Nostrand Reinhold Company, 3rd edition, 1251 pp.

Shafer, K.H. 1982. Determination of nitroaromatic compounds and isophorene in industrial and municipal wastewaters. EPA-600/54-82-024: 6 p.

Steele, P.O. 1980. Water quality and fish populations of the Welland River, Ontario. M. Sc. Thesis. Brock University, Biological Sciences Dept., St. Catharines, Ontario.

Steele, P.O. and Dickman, M.D. 1979. Frequencies of neoplasms in wild carp-goldfish hydrids as indicators of carcinogenic contamination in the Welland River, Ontario. Presented at the Great Lakes Annual Conference. September 1979.

Strup, P.E. 1982. Determination of polynuclear aromatic hydrocarbons in industrial and municipal wastewaters. EPA-600/54-82-024: 5 p.

US EPA. 1983. United States Environmental Protection Agency. LANDSAT MSS classification of nearshore water quality in Lake Ontario. TS-AMD-82905; 37 p.