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The Fate and Effects of Contaminants in Canagagigue Creek

1. Stream Ecology and Identification of Major Contaminants

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Cover photograph—

An aerial view looking south over the town of Elmira, Ontario. *Centre*, the Uniroyal complex and fire control pond with the Woolwich/Elmira Water Pollution Control Plant just behind the Uniroyal waste treatment lagoons; *upper left*, sampling site CN-2 near the river bend. *(Courtesy of R. Johnson, Information Services Branch, Ontario Ministry of the Environment)*

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1. Stream Ecology and Identification of Major Contaminants

J.H. Carey,* M.E. Fox,* B.G. Brownlee,†
J.L. Metcalfe,* P.D. Mason‡ and W.H. Yerex‡

*Environmental Contaminants Division, National Water Research Institute
†Aquatic Ecology Division, National Water Research Institute
‡Biological Studies Group, Grand River Conservation Authority, 400 Clyde Road, Cambridge, Ontario

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Abstract

A study of the biological community of Canagagigue Creek was conducted by seasonally collecting fish and benthos from six sites between the Woolwich Reservoir and the confluence with the Grand River, Ontario. Trends of species abundance and diversity are discussed, and a diversity index has been calculated for the benthic fauna at each site. Fish and benthos both demonstrated a clear pattern of markedly decreased abundance and species diversity below the site of contaminant inflow relative to the upstream sites. At the farthest downstream site, virtually complete recovery from the environmental stress was demonstrated by high abundance and species diversity.

A survey of synthetic organic contaminants was also conducted. Chlorophenols, benzothiazoles and lindane were all present at elevated levels downstream from Elmira when compared with their concentrations at the upstream sites. A series of unidentified acidic compounds was also discovered to have been formed in the Woolwich/Elmira Water Pollution Control Plant from unidentified precursors. All of the observed contaminants decreased significantly in concentration with distance downstream. The chlorophenols were found to have accumulated in benthos and fish. This study will form the basis of an in-depth examination of the pathways of accumulation and degradation of these synthetic organic contaminants in the stream.

Résumé

Pour étudier les organismes vivant dans le ruisseau Canagagigue, on a fait le prélèvement saisonnier du poisson et du benthos en six stations situées entre le réservoir Woolwich et le confluent de la rivière Grand en Ontario. On traite des tendances de l'abondance et de la diversité des espèces et on a déterminé un indice de diversité de la faune benthique à chaque station. Chez le poisson et le benthos, l'abondance et la diversité des espèces décroissent en aval du point de contamination. À la station la plus en aval, l'auto-épuration du ruisseau est presque complète comme en témoignent l'abondance et la diversité des espèces.

Pour ce qui est des contaminants organiques de synthèse, on a décelé des chlorophénols, des benzothiazoles et du lindane, à concentrations élevées, en aval d'Elmira, comparativement aux concentrations en amont. On a aussi constaté qu'un ensemble de composés acides indéterminés s'était formé dans l'usine d'épuration de Woolwich/Elmira, à partir de précurseurs inconnus. La concentration de tous les contaminants observés a notablement diminué vers l'aval, en raison de la distance. On a constaté que les chlorophénols s'étaient accumulés chez le benthos et le poisson. L'étude servira de base à un examen fouillé des mécanismes de l'accumulation et de la dégradation des contaminants mentionnés dans le ruisseau.

Acknowledgments

The study team appreciates the aid of Dennis Delorme (National Water Research Institute) in the initial phases of this study and the active cooperation of Archie McLarty, Stan Irwin, Bob Miller, Wayne Jackman (Ontario Ministry of the Environment) and Tony Smith (Grand River Conservation Authority). Thanks are also due to the staff of the Woolwich/Elmira Water Pollution Control Plant and to John Coburn and his staff (Water Quality Branch, Ontario Region, Environment Canada).

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Introduction

There is growing public anxiety concerning the possible effects of synthetic organic chemicals on the environment and the threat they may pose to man. Many potentially toxic chemicals are present at low levels on a widespread basis and can accumulate in organisms, including those used as food by man. Despite the research already conducted on various properties of synthetic organics, our understanding of the overall environmental dynamics of these compounds is unsatisfactory. For regulatory agencies to respond to public concerns, more knowledge about the entry, distribution, movement and fate of these contaminants is needed.

Much of the research into the properties of these compounds is conducted in the laboratory where the scientist can exercise some degree of control over experimental variables. Unfortunately, in reducing the number of variables, the scientist also renders his results less directly applicable to the field. There is a need for complementary studies of the behaviour of contaminants in real situations to obtain results that can be compared with those from laboratory studies. In 1979, as an initial step in meeting this need, the National Water Research Institute decided to initiate a detailed chemical and biological examination of the distribution of synthetic organic compounds in a contaminated aquatic ecosystem and the dynamics of clearance of those compounds from the system. After a preliminary survey of many localities in Ontario, the town of Elmira was chosen as the study site. The study involves collaboration between the Environmental Contaminants Division and the Aquatic Ecology Division of the National Water Research Institute (NWRI) and the Biological Studies Group of the Grand River Conservation Authority (GRCA) (see Appendix for list of team participants).

Elmira, the largest community in the Township of Woolwich (population 16 000), is a centre of manufacturing in what is primarily an agricultural township. A listing of

Table 1. Industrial Activities in Elmira

Manufacturer	Product	Employees
B&L Metal Products (Elmira) Ltd.	Hog pens, cow pens, refuse packers, metal stampings	52
Borg Textiles Canada Ltd.	Synthetic fur, deep pile fabrics	178
Elmira Machine Industries Ltd.	Custom metal machining, vacuum pumps	18
Elmira Stove Works	Wood stoves	22
Ferguson & O'Reilly Co. Ltd.	Textile mill waste reprocessing	26
G.B.R. Metal Fabrication Inc.	Trailers	24
Martin Feed Mills Ltd.	Animal feeds, pet foods, fish food	180
M.K. Martin Enterprises Inc.	Custom metal fabricating, farm equipment	22
McKee Industries Ltd.	Farm equipment	407
Nutrite Inc.	Fertilizer	24
Park Avenue Wear Ltd.	Children's clothing	85
Procast Foundries Inc.	Iron castings	36
Reist Welding Ltd.	Farm equipment	23
Relmech Manufacturing Ltd.	Electrical insulators	64
Roxton Furniture Ltd.	Maple furniture	120
Shoemaker Mill Equipment Inc.	Conveyors, bucket elevators, bins	40
Sulco Chemicals Inc.	Sulphuric acid	15
Uniroyal Chemical, Division of Uniroyal Ltd.	Chemicals for rubber industry, agricultural chemicals, polyurethanes	363
The Wind Turbine Co. of Canada Ltd.	Towers, antennas	39

major industrial activities in Elmira is given in Table 1 (Elmira and Woolwich Chamber of Commerce, 1980). In addition to a number of basically dry industries, there are several which may produce waste water containing synthetic organics. These include Borg Textiles, whose effluent can contain various dyes and dye carriers; Nutrite Inc., a company that manufactures and formulates fertilizers and herbicides for both farm and home use; and Uniroyal Chemical, a company manufacturing a wide range of specialty chemicals for the rubber and agricultural industries. The effluent from these plants is treated at a single sewage treatment facility which discharges into Canagagigue Creek within the town limits. For the purposes of this study, the discharge pipe of the Elmira Water Pollution Control Plant (WPCP) was considered to be a point source of synthetic organics to the stream, and no concerted attempt was made to identify specific industrial sources of each compound.

A number of features make Canagagigue Creek a suitable location for this type of study. First, a specialty chemicals plant is situated in the town, which virtually guarantees that the influent to the sewage plant contains some compounds of interest, many of which could be nonbiodegradable and therefore be discharged to the stream. Secondly, the sewage plant is designed to receive up to 75% of its BOD from industrial sources, and since Canagagigue Creek is relatively small, the sewage plant effluent constitutes a significant part of the flow downstream from Elmira. Based on monthly averages, as much as 15% of the stream flow can be WPCP effluent (see below). Thus, concentrations of individual compounds in the stream should be high enough to be readily measured. Thirdly, the small size of the stream makes a wide variety of biological sampling feasible. In addition, the area is close enough to NWRI and GRCA headquarters to make day trips practical, so that measurements can be made on a year-round basis and various aspects investigated in-depth as needed. Finally, and most important, apart from a severe local effect, the total ecosystem does not appear to be grossly distorted, so that the results should be applicable to other streams of the same general character throughout Canada.

The study, as planned, consists of three phases, each of which could take a year or more to complete. *Phase I* involves (a) an examination of various aspects of the biology of the stream including the determination of ecologically significant zones that are important in the selection of sampling locations for later intensive studies and (b) concurrently, a chemical investigation of the identities of various synthetic organic compounds in the stream and an assessment of which of these are appropriate for further intensive study. During *Phase II*, the following work will be completed: (a) intensive sampling of various compartments of the stream to identify important processes affecting compounds identified in Phase I; (b) examination of selected aspects of the biology of the stream to identify effects of the contaminants; and (c) formulation of hypotheses concerning the factors affecting the accumulation and degradation of contaminants in the stream and concerning possible biological effects of the contaminants. In *Phase III*, a laboratory verification of the hypotheses from Phase II will be done along with an examination of other streams in Canada to test the general applicability of the conclusions of the study.

After preliminary sampling in 1979, Phase I began in 1980. The results of the 1980 research are contained in this report.

The Ecology of Canagagigue Creek

INTRODUCTION

Canagagigue Creek is a minor tributary of the Grand River, which in turn empties into Lake Erie. The watershed is approximately 19 km long, 10 km wide and is roughly triangular. It has a drainage area of 143 km^2 (Crysler, Davis and Jorgenson Ltd., 1965). The Canagagigue watershed can be considered "typically Canadian," as it was formed by glaciation. The creek flows in a general southeasterly direction from the Waterloo hills in Peel Township to the flatter Guelph drumlin fields in the southeasterly section of Woolwich Township. About 80% of the land within the watershed is productive agricultural land and 10% is woodlot (Crysler, Davis and Jorgenson Ltd., 1965).

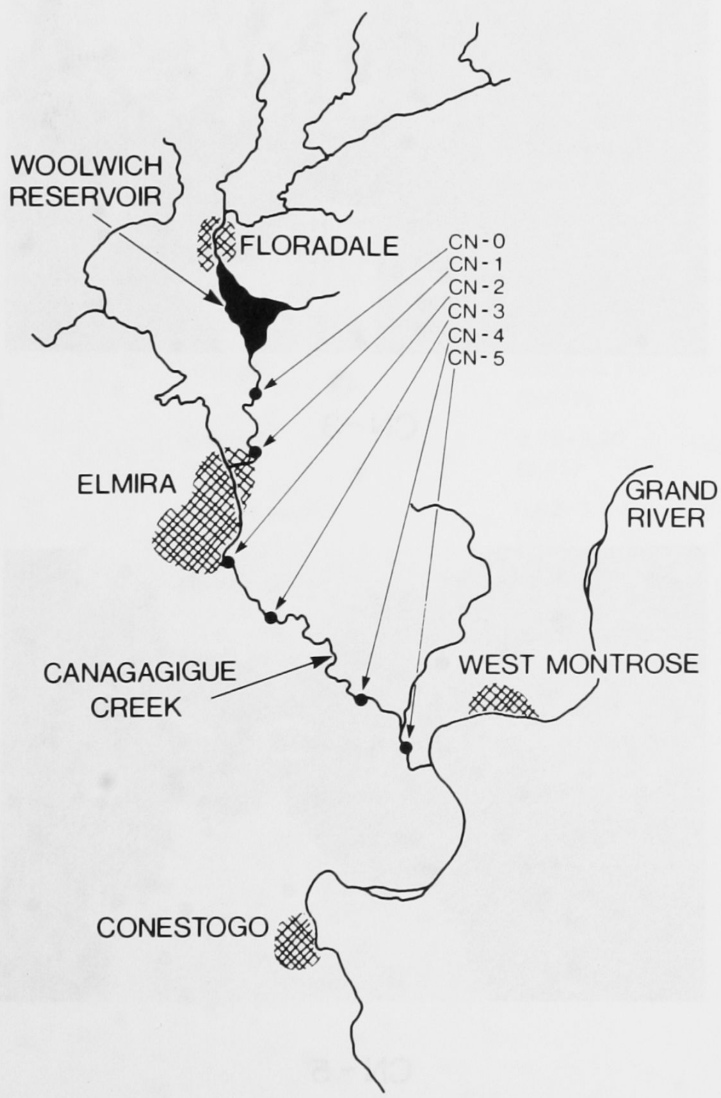


Figure 1. Map of study region showing location of the six sampling sites.

The section of the creek presently under study extends approximately 13 km downstream from the Woolwich Dam, past the town of Elmira, to the confluence of the Grand River (Fig. 1). Three tributaries enter this stretch of the creek, two of which are cleaned and maintained as municipal drains. Municipal drain No. 2 enters the creek on the northern periphery of the town of Elmira and municipal drain No. 1, at the southernmost limit of the town. Both drains carry considerable flows in the spring but have low flows during other times of the year (Crysler, Davis and Jorgenson Ltd., 1965). The remaining stream enters the creek about 1 km upstream from the Grand River confluence.

The Woolwich Dam and Reservoir strongly influence the physical features and water quality of Canagagigue Creek. The purpose of the dam, which was completed in 1974, was to augment low flows in the creek. Analysis of outflows from the Elmira Water Pollution Control Plant indicated that at times of low flow, the volume of actual sewage effluent in the stream consistently exceeded 10% (Crysler and Lathem, 1971). The normal augmentation to stream flow was to be 280 $L \cdot s^{-1}$.

Six sites on Canagagigue Creek were selected for study (Fig. 1). Sites CN-0 and CN-1 are considered to be "controls" and are located 4.13 and 1.38 km, respectively, above the Elmira WPCP. Site CN-2 is approximately 0.16 km below the sewage outfall. Sites CN-3, CN-4 and CN-5, which are 1.67, 5.48 and 7.35 km, respectively, below the WPCP, represent various stages of recovery. The six photographs in Figure 2 represent the study sites and their environs.

WATER QUALITY AND FLOW

Historical water quality data are available from Ontario Ministry of the Environment publications (MOE, 1974, 1977-79). Upstream and downstream sites are at CN-0 and CN-3, respectively. Flow is measured by the

CN-0

CN-1

CN-2

CN-3

CN-4

CN-5

Figure 2. Study sites and environs.

Table 2. Range and Mean of Water Quality Values in Canagagigue Creek

Parameter (mg/L)	1979 CN-0	1979 CN-3	1974 CN-0	1974 CN-3
Temperature °C	0.5-20.0 (9.7)*	1.0-23.0 (10.3)	0.0-25.0 (12.3)	3.0-24.0 (12.2)
pH	7.05-8.46 (8.0)	7.14-8.20 (7.75)	7.4-8.6 (8.05)	7.7-8.4† (7.9)
Oxygen	8.4-13.1 (11.2)	6.1-12.6 (9.6)	1.2-12.2 (6.1)	1.6-12.0 (5.5)
Suspended solids	5.0-54.0 (24.1)	6.0-29.0 (18.3)	5-45 (15)	0.70 (17)
Alkalinity†	175-207 (193)	185-224 (205)	144-240 (202)	184-194 (226)
Calcium	50.0-84.0 (62.4)	57.0-108.0 (78.0)	N.A. N.A.	N.A. N.A.
Sulphate	21.5-61.0 (40.1)	39.5-323.0 (169.1)	N.A. N.A.	N.A. N.A.
Chloride	12.0-25.5 (16.4)	1.9-161.0 (83.4)	9-65 (20)	12-236 (83)
Total P	0.047-0.212 (0.126)	0.121-0.430 (2.251)	0.038-0.360 (0.124)	0.110-0.750 (0.234)
Filtered reactive P	0.001-0.140 (0.034)	0.001-0.250 (0.092)	0.001-0.220 (0.036)	0.034-0.460 (0.100)
Ammonium-N	0.020-0.533 (0.277)	0.430-6.200 (2.629)	0.01-1.60 (0.24)	0.34-34.0 (4.62)
Nitrite-N	0.015-0.130 (0.059)	0.038-0.330 (0.189)	0.019-0.310 (0.081)	0.039-1.600 (0.265)
Nitrate-N	0.38-8.20 (3.05)	0.65-15.70 (3.70)	0.69-7.50 (3.47)	1.90-7.00 (4.27)
Mercury (μg/L)	0.02-5.2 (2.09)	0.02-5.0 (1.79)	N.A. N.A.	N.A. N.A.
Phenols (μg/L)	1.0-2.0 (1.1)	1.0-56.0 (15.4)	N.A. N.A.	N.A. N.A.

*Mean values are given in parentheses.
†Part of year only.
N.A. – Values not available.
Source: MOE data.

Water Survey of Canada (Environment Canada, 1973, 1977-80) at CN-4. Data for the Elmira WPCP are from the MOE WPCP Operating Summary (MOE, 1980).

Daily discharge values are shown in Figure 3 for 1973 (pre-reservoir) and 1980 (post-reservoir). The flows follow the expected pattern of high flow in the spring (March to May) and low flows in the summer (June to September). Fall and early winter flows vary more from year to year.

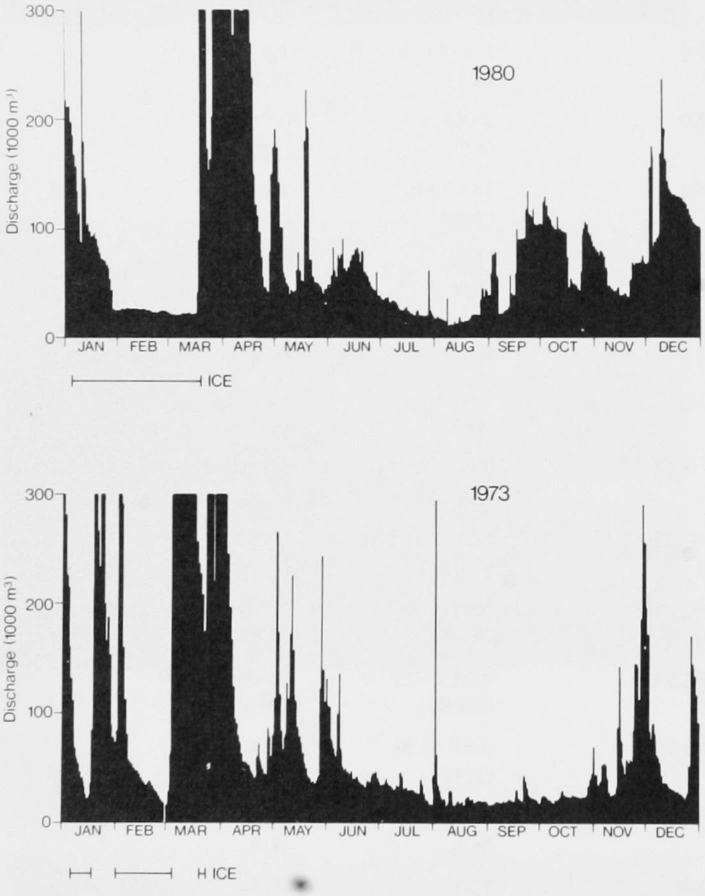


Figure 3. Daily discharge (1000 m³) for Canagagigue Creek at CN-4 in 1973 and 1980 (Environment Canada, 1973, 1980). Values > 300 000 m³ are off scale.

Historical water quality data and our 1980 analyses confirm that Elmira is a point source for several chemical parameters. Water quality information for 1974 and 1979 at CN-0 and CN-3 are given in Table 2. Temperature and pH do not reach any extreme values. Oxygen concentrations have improved somewhat since 1974. Downstream concentrations are elevated for several parameters: ammonium, nitrite, total phosphorus, filtered reactive phosphorus, sulphate, chloride and phenols. Nitrate is only slightly elevated. Mercury concentrations are similar both upstream and downstream. Heavy metal concentrations are generally at or slightly above detection limits and are not included in Table 2.

Further evidence that Elmira is a point source for ammonium, nitrite, total phosphorus, filtered reactive phosphorus, and sulphate is shown in Figures 4 and 5. These are concentration profiles along the stream at all six sites. All of these parameters increase in concentration below the Elmira WPCP. Nitrate, however, does not show this pattern. These profiles show a declining ammonium concentration and increasing nitrate concentration, which is probably the result of nitrification in the stream. Nitrite concentration usually reaches a maximum value at CN-3 or CN-4, as in Figure 4. Since it is an intermediate between ammonium and nitrate in nitrification, this is to be expected.

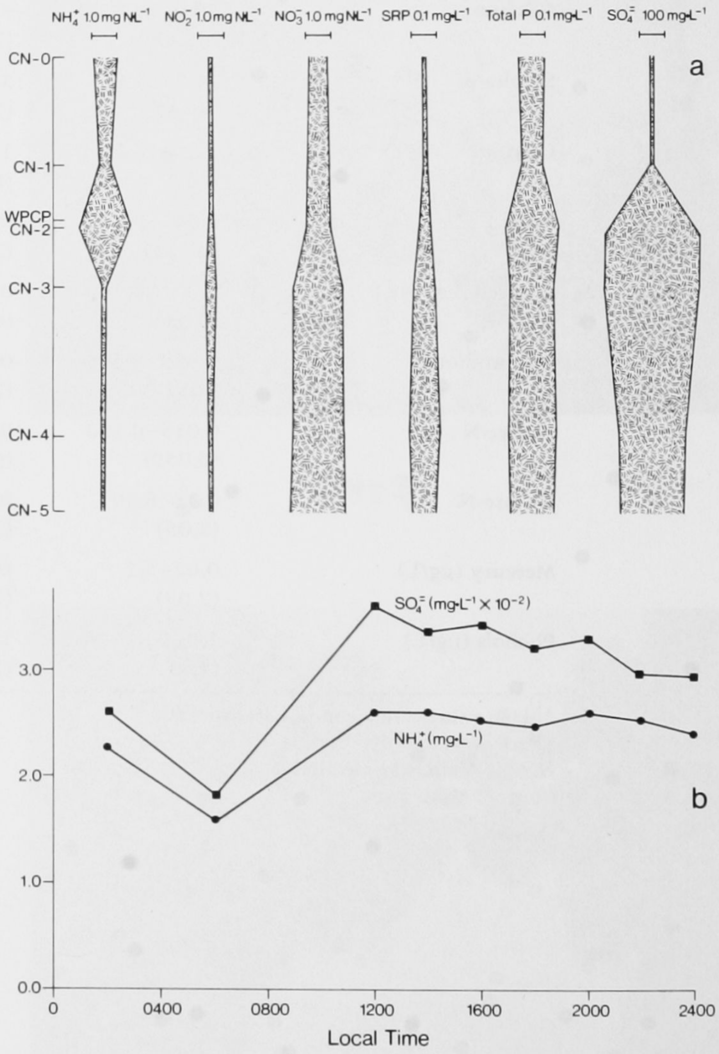


Figure 4. (a) Concentration profiles for ammonium, nitrite, nitrate, soluble reactive phosphorus, total phosphorus, and sulphate along Canagagigue Creek and (b) concentration of ammonium and sulphate at CN-2 over a 24-h period, July 24, 1980.

The diurnal patterns for ammonium and sulphate concentrations at CN-2 are also shown in Figures 4 and 5. Concentrations reach a minimum about 6:00 A.M., rise until midday, fluctuate until midnight, and then decline. This pattern parallels the discharge of the WPCP and is consistent with the WPCP being the principal source of these ions to the stream. Tables 3 and 4 give some idea of the relative flows of the WPCP effluent and Canagagigue Creek. Table 3 compares the total monthly discharge for 1979 and 1980. On this basis, flow from the WPCP can be from 1% to 15% of the creek flow. Table 4 gives the instantaneous relative flows for six sampling dates in 1980, which were obtained from analysis of WPCP effluent and CN-2 water for sulphate, chloride and sodium. These results are imprecise, but they show that WPCP flow can be as much as 20% of creek flow at certain times during the day.

Thus, the Elmira WPCP effluent is a major point source of several parameters, which include nutrients such as ammonium, conservative ions such as sulphate, and organic contaminants such as phenols. Ammonium concentrations can reach several milligrams per litre. Ammonium is a nutrient for the growth of algae and aquatic weeds and an apparent source of nitrite and nitrate as a result of nitrification. Total and filtered reactive phosphorus levels seem to be high enough to stimulate algal and weed growth as well. During the summer when flows are low there is abundant weed growth, especially between CN-3 and CN-4. The effect of this nutrient input on stream productivity and assimilation of organic contaminants merits further investigation.

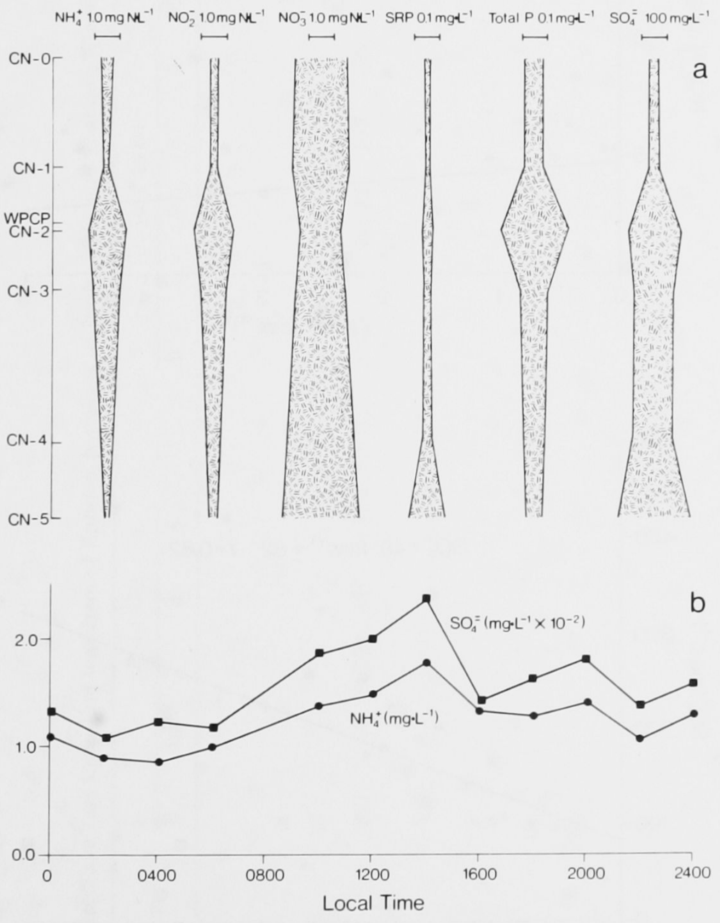


Figure 5. (a) Concentration profiles for ammonium, nitrite, nitrate, soluble reactive phosphorus, total phosphorus, and sulphate along Canagagigue Creek and (b) concentration of ammonium and sulphate at CN-2 over a 24-h period, October 14, 1980.

Table 3. Discharges

Year	Month	Elmira WPCP (1000 m^3)	Canagagigue (1000 m^3)	WPCP as percentage of creek
1979	January	63.	2 108.9	3.0
	February	55.3	841.1	6.6
	March	180.6	15 430.3	1.2
	April	178.2	10 360.3	1.7
	May	91.9	2 819.1	3.3
	June	72.1	1 347.7	5.3
	July	55.2	1 307.1	4.2
	August	51.6	1 231.3	4.2
	September	64.6	1 218.4	5.3
	October	93.3	1 260.9	7.4
	November	138.9	2 126.7	6.5
	December	153.7	7 768.3	2.0
				4.2 (1.2–7.4)*
1980	January	120.0	3 588.1	3.3
	February	99.1	752.8	13.2
	March	146.2	6 594.3	2.2
	April	182.0	7 114.1	2.6
	May	109.3	2 507.9	4.4
	June	75.9	1 948.4	3.9
	July	100.2	893.2	11.2
	August	96.7	663.5	14.6
	September	113.6	2 213.0	5.1
	October	167.3	2 761.3	6.0
	November	134.1	1 768.2	7.6
	December	150.0	4 000.0	3.8
				6.5 (2.2–14.6)*

*Average

Table 4. Instantaneous Relative Flows (%) of Elmira WPCP to Canagagigue Creek at CN-2, May to November 1980

Date	Calculated from conservative ion			Average (%)
	Sulphate	Chloride	Sodium	
May 23	16	16	N.A.	16
July 24	21	20	10	17
September 10	12	10	10	11
October 1	6	6	4	5
October 14	15	7	6	9
November 12	21	15	9	15

N.A. – Not available

Because the watershed of the creek is mainly agricultural there is the possibility of diffuse inputs of herbicides and fertilizer (nitrate and phosphate) from surface runoff and groundwater. In Figure 6, concentrations of ammonium, nitrate, filtered reactive phosphorus, and sulphate are plotted against the reciprocal of flow. A positive slope indicates dilution under conditions of high flow (runoff); a negative slope indicates a diffuse source for that parameter. Positive slopes are obtained for ammonium, filtered reactive phosphorus, and sulphate consistent with the other evidence that the Elmira WPCP is the major source for these parameters. Nitrate has a negative slope, indicating that it could come from fertilizer runoff. The subject of groundwater as a source of organic contaminants is presented in another section.

BENTHIC INVERTEBRATE SURVEY

To evaluate relative water quality at the six sites, the benthic community structure was surveyed. Collections were made in May, July and November of 1980 and in January of 1981.

Benthos were collected using a 285-mm x 185-mm kicknet of 1-mm mesh to trap the organisms. The stream bottom was kicked and lifted, filling the net with cobble, gravel, sand, detritus and algal mats. All of the available ecotypes at each site were sampled in this manner. Collected material was transferred to 1-gal NALGENE plastic containers and preserved with 10% formaldehyde solution. The samples were later halved, and macroinvertebrates were

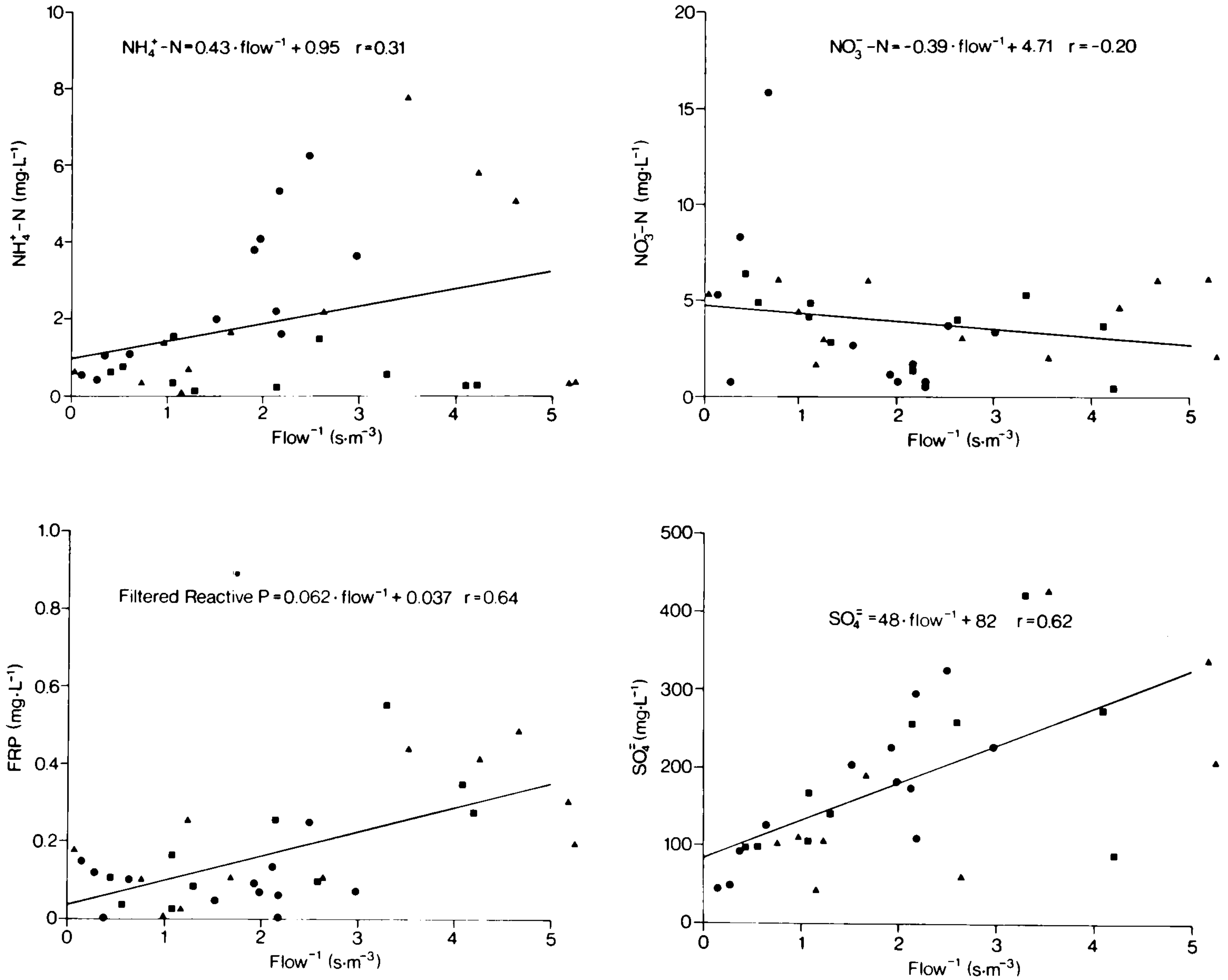


Figure 6. Concentration vs. reciprocal of flow for ammonium, nitrate, filtered reactive phosphorus, and sulphate in Canagagigue Creek for (▲) 1977, (■) 1978 and (●) 1979 (MOE, 1977-79; Environment Canada, 1977-79). The anomalous water quality data for March 14, 1978, were not included.

Table 5. Benthic Invertebrate Taxa List Including Numbers of Species, Numbers of Individuals, and Shannon-Wiener Diversity Index for Each Sample According to Date and Sampling Location (CN site)

Taxa and species	May 1980						July 1980						November 1980						January 1981					
	0	1	2	3	4	5	0	1	2	3	4	5	0	1	2	3	4	5	0	1	2	3	4	5
Tricladida																								
Planariidae								1								1		2		10				
Oligochaeta																								
Unidentified	197	42	1032	432	395	297	310	41	422	143	76	79	127	40	498	377	282	58	16	6	303	180	258	34
Hirudinea																								
Glossiphonia complanata														1		4								
Placobdella sp.					1	1																		
Helobdella stagnalis			1	1	1	2	2		2	3	1	2		7	3	37	3					2	2	
Erpobdella punctata	9		1	1			2		2	3			5		18	15	22	1			6	6	3	11
Crustacea																								
Hyalella azteca					9	6					9	8	17	3	3	6	189	2				2	148	4
Orconectes propinquus						1	4				1	4	1	3				1						1
Mollusca																								
Physa sp.	2					6				1	75	236	14	3			73	27			1	1	118	23
Armiger sp.					2																			
Gyraulus sp.	15												21	1	1		31							5
Promenetus sp.																6								
Goniobasis sp.				2		3								1				1						
Ferrissia sp.	26				1		4	6			2	6	77	115	1		3	18	23	11			12	43
Anodontoides sp.		1																						
Sphaeriidae				2	7	39					8	34				4	46	52				3	54	245
Sphaerium sp.	10	2			1	31	3		4			16	32	13	1		3		3	29	4	1	5	5
Pisidium sp.	6	1					1						17	2					1	4	3			
Ephemeroptera																								
Ephemera sp.						1															2	1	177	4
Caenis sp.			5		3	20	1		1		2	1	7	4	3	5	165	20						
Tricorythodes sp.												179					4							
Ephemerellidae																							1	
Ephemerella sp.		1																						
E. needhami																		3						28
Paraleptophlebia sp.									1															
P. mollis						1																		

Table 5. Continued

Taxa and species	May 1980						July 1980						November 1980						January 1981					
	0	1	2	3	4	5	0	1	2	3	4	5	0	1	2	3	4	5	0	1	2	3	4	5
Baetidae								7																
Baetis sp. A		2	1			51	6	14	1		2	19		2		1		2						11
Baetis sp. B							2																	
Pseudocloeon sp.							2					6												
Isonychia sp.																								1
Stenonema sp.		2												4	1					2				
S. canadense													2	27				19						7
S. frontale														6										
Stenacron sp.							1																	
Odonata																								
Aeshna sp.																							1	
Agrion sp.																	2							
Plecoptera																								
Taeniopteryx parvula														1				1		1				1
Acroneuria ruralis																								2
Hemiptera																								
Corixidae											1													
Trichoptera																								
Psychomyia sp.	206					4	4	42				9	5	67	1			33		29			1	3
Polycentropus sp.						1		1			1	4						7						
Hydropsychidae								4																
Hydropsyche sp.	6					2	9	3																
H. simulans	7												13											
H. betteni	81	12	3				1						10	2			22	2	18	34			41	346
H. recurvata	3																							
H. unidi				4								9		7			34	8					2	2
H. leonardi																								3
Symphitopsyche sp.		3																		1			1	
S. sparna													1						6	5			6	85
S. bifida	107	6	1			1	20	44				51	17	26		4	174	143	3	80			153	675
S. rioli	5	6	1			1	1						4	3				4						
S. slossonae	12	1					2							1				2	1	3				11
S. recurvata							1					3					1							5
S. bronta																		1						

Table 5. Continued

Taxa and species	May 1980						July 1980						November 1980						January 1981					
	0	1	2	3	4	5	0	1	2	3	4	5	0	1	2	3	4	5	0	1	2	3	4	5
S. merosa												3	1											77
Cheumatopsyche sp.	38	15	1	1	7	24	21	32	3		1	8	82	35	2	6	153	30	63	67	1	32	250	504
Agraylea sp.	10				1	5		1			17	25			1	1						2		
Hydroptila sp.							4	8			11	46					1							
Ochrotrichia sp.													1	1		1	2	5			2		1	
Micrasema rusticum														1				6						3
Pycnopsyche sp.						1						1		2										
Limnephilus sp.		1																						
L. submonilifera						1																		
Helicopsyche sp.												3	1					23	1	2				8
Leptoceridae												1												
Ceraclea sp.										1	3							1						
Leptocerus americanis										1														
Oecetis sp.														1		7	1	6			1	21	11	
Nectopsyche Wiggins					2																			2
Chimarra																								4
Megaloptera																								
Sialis sp.			1						1			11					2					1	3	
Chauliodes sp.																		1						
Lepidoptera																								
Cataclysta sp.																		3						8
Coleoptera																								
Haliplus sp.			1										1			4					1		3	
Peltodytes sp.										1					1	5	63				1	2	23	2
Dytiscidae																		2						
Bidessus sp.			1																					
Laccophilus sp.												1											2	1
Psephenus																		2						1
Ectopria sp.					1	1					5	2					12	11			2	4	17	2
Dubiraphia sp.		1			9	6	1				2	10	1	5			47	9		2	2	4	53	6
Stenelmis sp.	6	18	2		7	106	11	8			21	62	8	8	7	2	23	38		51	6	1	22	211
Optioservus sp.																	5		1	12	1		18	363

Table 5. Continued

Taxa and species	May 1980						July 1980						November 1980						January 1981					
	0	1	2	3	4	5	0	1	2	3	4	5	0	1	2	3	4	5	0	1	2	3	4	5
Diptera																								
Antocha sp.	10	14					5						2	28	3		23	81		20			2	23
Tipula sp.																								5
Psychoda sp.																							1	
Culicidae				2																				
Chaoborinae														1										
Simuliidae	78	8	303	763	1 406	387	355	18	1318	358	382	211	23	15	349	1516	123	13	17	84	282	676	408	213
Chironomidae	809	475	3421	1531	4 231	2461	1413	885	1584	409	699	1016	273	440	470	373	101	151	636	1044	1105	1834	2466	664
Stratiomyidae	1					3																		
Tabanus sp.						1							2			1							1	
Atherix sp.	9		9	1				18				9												
Ephydridae							1																	
Ephydra sp.					1																			
Anthomyiidae					2																			
Limnophora sp.	7	5	3	1								1												
Hemerodromia sp.					1	1	1		1		1		53	7	426	28	23		5	12	268	78	63	2
H. Rogatoris			4																					
Unidentified																		1						
Nematoda																								
Unidentified	9		38	29	15	7	1								2	1	1					4		
Acari																								
Unidentified	1	1	2					1	1					3	1									
Number of species	26	22	19	14	22	31	29	18	13	9	21	33	30	37	21	24	31	38	14	22	18	20	35	43
Number of individuals	3336	1234	9660	5542	12 210	6944	4378	2268	6682	1840	2640	4150	1638	1774	3592	4844	3272	1580	1588	3018	3980	5710	8658	7308
Shannon-Wiener Diversity Index	2.68	1.56	1.21	1.53	1.21	1.64	1.65	1.50	1.47	1.56	1.96	2.77	3.35	2.92	2.17	1.74	3.86	3.95	1.26	1.98	1.82	1.54	2.52	3.52

isolated from the debris and placed in 90% isopropyl alcohol. Identification and enumeration of individual taxa were undertaken for each of the 24 samples, and a complete taxa list was compiled.

Annual species diversity indices for the benthic communities at each of the six study sites were calculated using the Shannon-Wiener formula (Southwood, 1966) as follows:

$$\bar{d} = -\sum\left(\frac{N_i}{N}\right)\log_2\left(\frac{N_i}{N}\right)$$

where N = total number of individuals of all species collected and

N_i = number of individuals belonging to the *i*th species.

Diverse communities with abundant taxa are represented by values greater than 3. Stressed communities with few, but dominant species have values of less than 2. A value greater than 3 probably represents a clean water situation, while values of 1 to 3 indicate moderate pollution and values less than 1 point to heavy pollution (Wilhm and Dorris, 1968).

The Shannon-Wiener Index examines the abundance of the more common species, as the formula places greater emphasis on relative occurrence. Taxa that occur in lesser numbers therefore tend to be masked.

Historical benthic collections had been obtained between 1972 and 1976 by the Grand River Conservation Authority at three sites along the stream, two of which correspond to CN-0 and CN-3 of the present survey. A summary is presented for comparative purposes.

Figure 7 presents a summary of benthic community diversity information taken from several sources. According to the present survey (1980 data), there is a general depression in diversity at sites CN-2 and CN-3. Signs of recovery are evident at CN-4, and CN-5 shows considerable improvement. As the taxa list (Table 5) shows, not all organisms were identified to the species level. Significantly, the chironomids and simulids were identified only to family and the oligochaetes, only to order. As a result, the true values of $\bar{d}$ may have been underestimated. This should not, however, affect the general trends. In fact, the data from two comparable studies conducted in January 1980 and September 1981 (Sprague, unpublished data) present a similar overall picture of the community structure in the creek.

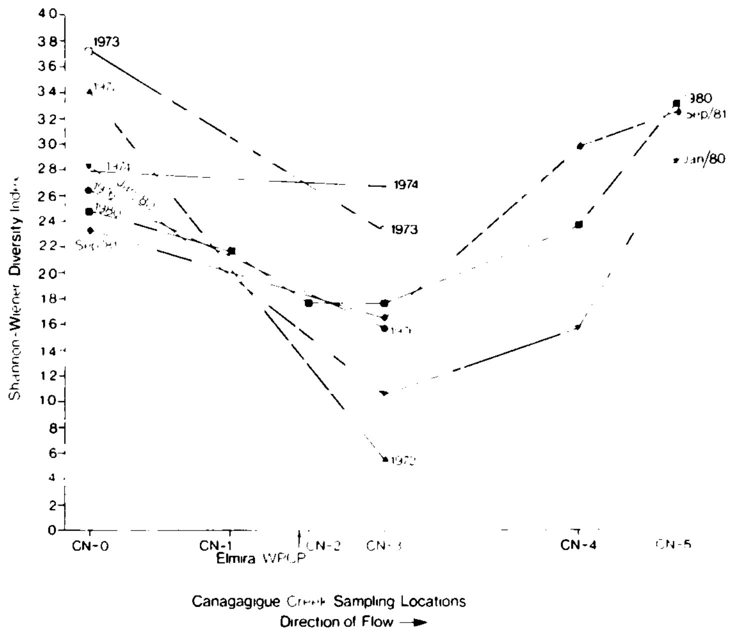


Figure 7. Benthic community diversity.

The historical diversity indices are based on four seasonal collections per year, as with the present survey. A marked decrease in diversity from CN-0 to CN-3 occurs each year. The data for 1975 (not shown) indicated the reverse trend with $\bar{d}$ values of 1.76 and 2.84 for CN-0 and CN-3, respectively. This anomaly may have been due to severe flooding during the spring of that year.

Table 6 shows the total number of individuals and taxa as well as the $\bar{d}$ values for each of the 1980 study sites. The benthic community at CN-0 is strongly influenced by the Woolwich Reservoir. Organisms here must be tolerant of inconsistent flows, cold water temperatures, and periodic anoxic conditions because of the hypolimnetic discharge. Sediment loads may also be heavy at times, leading to high turbidity and destruction of suitable habitat for colonization by certain organisms.

Table 6. Total Number of Individuals and Taxa, and Diversity Indices for the 1980 Benthic Survey

Sampling site	Number of individuals	Number of taxa	$\bar{d}$
CN-0	10 940	48	2.48
CN-1	8 294	53	2.17
CN-2	23 914	38	1.77
CN-3	17 936	37	1.77
CN-4	26 780	53	2.38
CN-5	19 982	72	3.32

Although more taxa were found at CN-1 than CN-0, the $\bar{d}$ value was lower. The infrequent occurrence of the new taxa was apparently masked by the Shannon-Wiener Index. However, the appearance of a "sensitive" organism, the stonefly *Taeniopteryx parvula*, and the presence of representatives of four additional Trichoptera families suggest that CN-1 has more available habitat for a wider range of organisms.

Site CN-2 has a $\bar{d}$ of 1.77, which suggests very stressed environmental conditions at this location. A large number of organisms were collected, although only 38 taxa are represented. Indicative of the degraded state is the large percentage (49%) of the total collection made up of dipteran species and aquatic oligochaetes. The WPCP effluent, which enters the creek here, provides an excellent food source for these gatherer-feeders. Site CN-2 is a very homogeneous zone of degradation and its benthic community reflects this.

The area of active decomposition, as defined by Hynes (1960), extends downstream to CN-3. The $\bar{d}$ of 1.77 is the same as that of CN-2 and indicates similar stressed conditions. The communities are virtually identical at the two sites except that a greater percentage of the dipteran larvae at CN-3 are from the family Simuliidae. As blackfly larvae are filter feeders, this suggests that more riffle areas with increased stream velocity are present at CN-3. Nevertheless, suppressed diversity and dominance by a few taxa characterize the benthic community at this site.

Figure 8 illustrates the population distributions, on a percentage basis, of some of the dominant benthic organisms in Canagagigue Creek. The disappearance of most of the elmid beetles, hydropsychid caddis larvae, and sphaerid clams from sites CN-2 and CN-3 is evident. These taxa are unable to tolerate conditions in this portion of the creek.

On the other hand, the oligochaete population responded favourably to the organic enrichment provided by the Elmira WPCP outfall. As most oligochaetes ingest sediment and derive their nutrition from bacteria (Brinkhurst and Cook, 1974), this situation would be expected. The distribution of the dancefly *Hemerodromia* follows a similar pattern, suggesting that it is quite tolerant

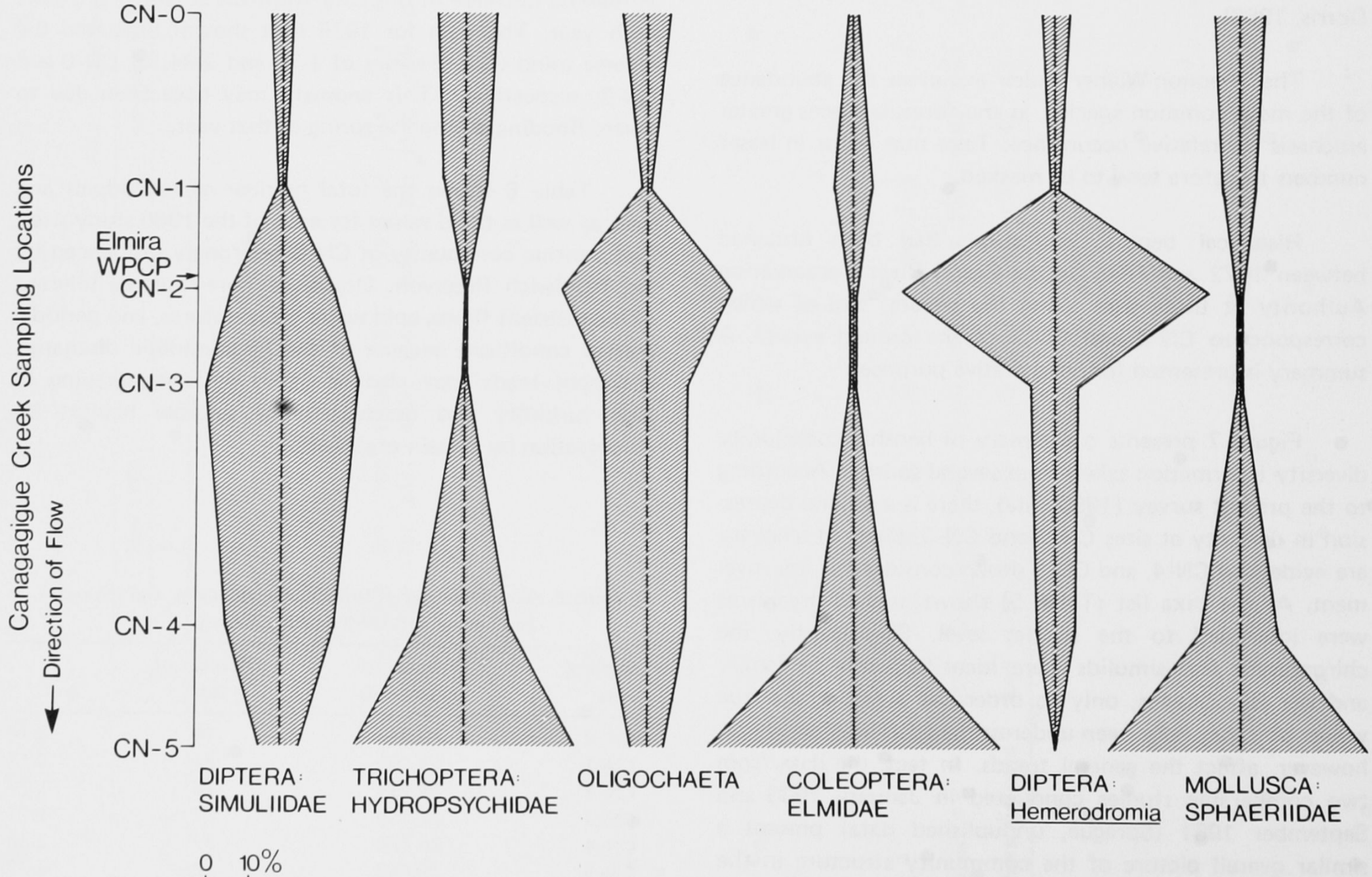


Figure 8. Population distributions of some of the dominant benthic organisms from Canagagigue Creek, 1980.

of organic pollution. The blackfly population has been discussed. No attempt was made to interpret the distribution pattern of chironomids (not illustrated) because the population is undoubtedly made up of many species which differ in their pollution tolerance.

Recovery of the creek has begun to occur at CN-4 where the $\bar{d}$ is 2.38, and the number of benthic taxa has increased dramatically to 53 from 37 at CN-3. The increase in the diversity index is mainly accounted for by large numbers of crustaceans, snails, sphaerid clams, the mayfly *Caenis*, several species of Hydropsychidae, and elmid beetles.

Station CN-5 represents a very diverse community of 72 taxa. The $\bar{d}$ of 3.32 suggests that water quality has improved substantially and recovery from environmental stress is virtually complete. The relatively low numbers of organisms indicate that competition for food and habitat has increased. At this site, the Trichoptera are represented by 25 taxa from nine families, as compared with 14 taxa at CN-4 and only 8 taxa at each of CN-2 and CN-3. A substantial mayfly fauna of eight taxa is also present. Oligochaetes and Diptera now account for only 29% of the total number of individuals as opposed to 49% at both CN-2 and CN-3. The appearance of two stonefly species is indicative of the dramatic improvement in the water quality of Canagagigue Creek at this location.

FISH CENSUS

A fish census of the creek was conducted in May, July, September and November of 1980. The purpose of the census was threefold: to determine the species present and to provide some information on meristics; to compare species and numbers among study sites; and to provide samples of fish to be analyzed for the uptake of organic contaminants.

A fishing effort of 30 min was undertaken at each site during each of the four sampling periods. The creek was sectioned off with seine nets approximately 100 m apart, and the area within these nets was intensively shocked using a portable electroshocker. The fish were subsequently identified, weighed, measured, and frozen in foil for later contaminant analysis.

The fish census data are presented in Table 7. The effects of the source of contamination just above site CN-2 are very clear. The upstream sites, CN-0 and CN-1, have virtually the same fish populations consisting of 16 species and 1120 individuals, and 17 species and 1438 individuals, respectively. There is a drastic decrease to 11 species and only 67 individuals at CN-2. In fact, during the July sampling period, only two animals, both of the same species, were captured here. The recovery zone begins at CN-3 (14 species and 344 individuals) and continues downstream with 16 species and 252 individuals at CN-4, and 18 species and 942 individuals at CN-5.

The lower numbers at CN-4 and CN-5 compared with those at CN-0 and CN-1 are due to fewer small fish such as darters, minnows and dace at the downstream sites. This is likely due to the presence of four species of game fish at these sites (rock bass, smallmouth bass, northern pike, and yellow perch), all of which prey on small fish. Of these, only rock bass is present at CN-0 and CN-1. Rock bass are probably yearlong residents of the creek, but there is a strong likelihood that the other game fish originate in the Grand River. A small dam on Canagagigue Creek at the location of the Uniroyal Plant, just above CN-2, prevents the upstream migration of these fish. Because of confounding factors such as physical barriers and migration from the Grand River, our conclusions concerning the recovery zone must be interpreted with caution. The structure of the benthic community, as discussed in the previous section, is probably a better indicator of water quality because these organisms are far less mobile than fish.

FISH MERISTICS

The fish survey was primarily designed to determine site to site differences in the abundance and diversity of fish species. Therefore, care was taken to ensure a constant fishing effort at each site. Unfortunately, this sampling method does not yield the most suitable data for comparing parameters such as growth rates and condition factors. Samples were unequal in size and often inadequate, and the fish were not aged or sexed. Nevertheless, lengths and weights were recorded for a considerable number of individuals, and site to site comparisons of general fish health were attempted for three of the dominant species.

Common shiners, white suckers, and rock bass were chosen for study because reasonable sample sizes were available from each site. Also, these species were among those selected for contaminant analysis. Condition factors (K), which measure the plumpness or well-being of a fish, were calculated for each individual by using the following formula from Carlander (1969):

$$K = \frac{W(10^5)}{TL^3}$$

where W = weight (g),
TL = total length (mm), and
10^5 = factor to bring the value of K near unity.

Table 7. Canagagigue Creek Fish Census, 1980

Common name	Scientific name	CN-0 May	CN-0 July	CN-0 Sept.	CN-0 Nov.	CN-1 May	CN-1 July	CN-1 Sept.	CN-1 Nov.	CN-2 May	CN-2 July	CN-2 Sept.	CN-2 Nov.	CN-3 May	CN-3 July	CN-3 Sept.	CN-3 Nov.	CN-4 May	CN-4 July	CN-4 Sept.	CN-4 Nov.	CN-5 May	CN-5 July	CN-5 Sept.	CN-5 Nov.
Pike family	Esocidae																								
Northern pike	*Esox lucius*												2	2		1	6			2	2	1			
Minnow family	Cyprinidae																								
Common carp	*Cyprinus carpio*	2	2	8		4	4	3				3		9	1	3	8	13	3	5		1	1	2	1
Longnose dace	*Rhinichthys cataractae*	13	24	15	16	16	22	18	11				1		9			4	4		1	7	6	19	2
Hornyhead chub	*Nocomis biguttatus*	25	11	24	9	27	11	10	15											3		5	3	7	12
River chub	*N. micropogon*	7	11	3		10	19	10															3		6
Creek chub	*Semotilus atromaculatus*	5	3	7	2	3	2			3		4	1	5		29	20		1	2	2		1	11	3
Golden shiner	*Notemigonus crysoleucas*					1								2											
Bluntnose minnow	*Pimephales notatus*	7	2	3	3	21	4	2	3	1								1		6		3	1		3
Common shiner	*Notropis cornutus*	148	124	90	50	+442	174	160		1				19		10	8	26	1	43	6	235	170	14	150
Emerald shiner	*N. atherinoides*																3				3				86
Rosyface shiner	*N. rubellus*															1									
Fathead minnow	*Pimephales promelas*				1																				
Sucker family	Catostomidae																								
Northern hog sucker	*Hypentelium nigricans*	9	5	7	4	13	10	12	20											3	8	1	3	5	7
Common white sucker	*Catostomus commersoni*	24	42	99	99	27	49	20	15	10	2	9	4	58	22	59	16	22	22	14	19	50	8	22	20
Redhorse sucker sp.	*Moxostoma* sp.	4	6	20	5	1	2	5	1					6		1	7	1		1	10	1			4
Catfish family	Ictaluridae																								
Brown bullhead	*Ictalurus nebulosus*	1																3	3			1			
Stonecat	*Noturus flavus*	1	1			3	2	3	1						1							2		4	
Stickleback family	Gasterosteidae																								
Brook stickleback	*Culaea inconstans*																	1							
Sunfish family	Centrarchidae																								
Rock bass	*Ambloplites rupestris*	30	23	13	2	37	37	30	3	17			3	9	2	7	9	4	5	3	1	6	2	15	3
Smallmouth bass	*Micropterus dolomieui*											2	2			9	1			2				3	
Perch family	Percidae																								
Yellow perch	*Perca flavescens*																					6			
Johnny darter	*Etheostoma nigrum*						5	4																1	
Iowa darter	*E. exile*								1					1											
Rainbow darter	*E. caeruleum*	43	38	14	4	2	19	14		1								2				9		14	2
Fantail darter	*E. flabellare*	4	5	2		43	28	34	8				1												
Number of species		15	14	13	11	15	15	14	10	6	1	4	7	9	5	9	9	10	7	11	9	14	10	12	13
Number of individuals		323	297	305	195	+650	388	325	78	33	2	18	14	111	35	120	78	77	39	84	52	328	198	117	299
Total number of species		16				17				11				14				16				19			

Table 8. Comparison of Condition Factors (K) for Three Fish Species

Fish species	Ranked condition factors					
Rock bass						
Site	CN-2	CN-1	CN-0	CN-5	CN-4	CN-3
Mean K	1.44	1.73	1.78	1.90	1.98	2.00
White sucker						
Site	CN-1	CN-5	CN-2	CN-0	CN-4	CN-3
Mean K	0.92	0.96	0.97	0.98	1.02	1.06
Common shiner						
Site	CN-1	CN-5	CN-0	CN-3	CN-4	
Mean K	0.98	1.05	1.07	1.09	1.09	

Note: Underscoring links means not differing significantly from each other ($p > 0.05$).

For each species, mean values of K at each site were compared using Kramer's (1956) extension of Duncan's Multiple Range Test. This modification permits a statistical comparison of group means derived from unequal sample sizes. The results are presented in Table 8 and Figure 9. In addition, a summary of all pertinent meristics data is given in Table 9.

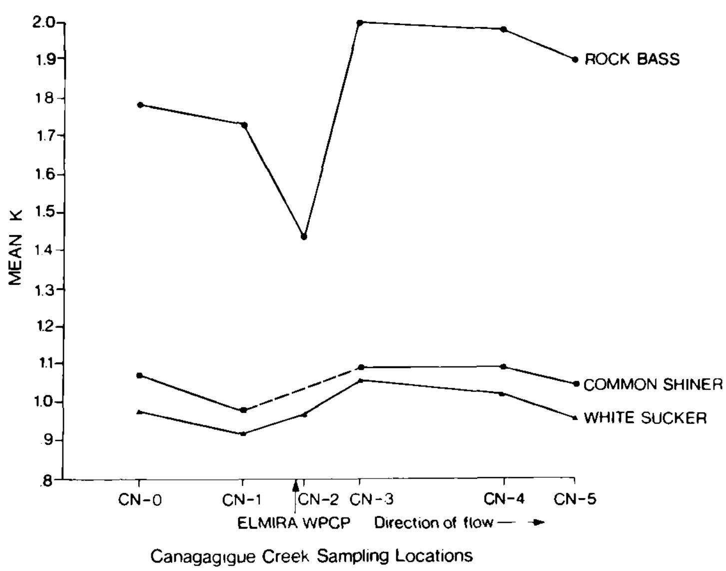


Figure 9. Trends in general fish health for three dominant species.

Common Shiners

The mean K value for shiners at CN-1 was significantly lower than at all other sites. The reason for this difference is unclear, but as more than 600 shiners were caught at this site during the survey, it may be due to overcrowding and/or competition for food. The K values for the remaining four sites did not differ from each other. As only one fish had been caught at CN-2, there is no point in Figure 9 for this site. However, it is interesting to note that this individual had the second lowest K value (0.42) of any of the 371 shiners measured. In general, common shiners tended to avoid the polluted sites CN-2 and CN-3, although the fish caught at CN-3 were not in poor condition when compared with those at other sites.

Since condition factors tended to increase with length (see r values in Table 9) and mean lengths varied from 107.4 mm at CN-5 to 122.1 mm at CN-0 and CN-4, the fish were divided into 20-mm length classes to compare shiners of the same size at each site. The data are given in Table 10. All length classes followed the overall trend of a decrease in K from CN-0 to CN-1 and an increase from CN-1 to CN-3. Values at CN-4 and CN-5 were variable.

White Suckers

The trends in condition factors for white suckers were remarkably similar to those for common shiners. According to standards of health from the literature (Table 9), the suckers at sites CN-0, CN-1, CN-2 and CN-5 were in poor condition, while those at sites CN-3 and CN-4 were in poor to average condition. Unlike most other species of fish, suckers did not avoid site CN-3. In fact, specimens collected from this site were in the best condition. This may be due to the abundance of oligochaetes and dipteran larvae on which they prefer to feed. Condition factors did not appear to be related to length.

Rock Bass

The rock bass provided a sharp contrast to the other two species. Fish at CN-2 were in distinctly poorer condition than those at all of the other sites. When compared with standards of health from the literature (Table 9), bass at CN-3, CN-4 and CN-5 were in poor to average condition, while those at CN-0 and CN-1 were in poor condition and those at CN-2 were in very poor condition. The majority of the rock bass were either in the size range that feeds primarily on Odonata, Ephemeroptera, Trichoptera, fish fry, and crayfish (76 mm) or the range (120 to 200 mm) that feeds almost entirely on crayfish and damselfly larvae (Scott and Crossman, 1973). Most of these preferred food items were scarce or absent at CN-2. However, the very poor condition of these fish could also be related to the fact that rock bass accumulated the highest levels of organic contaminants in their tissues of any fish species analyzed.

Table 9. Summary of Fish Meristics Data According to Fish Species and Sampling Location

Parameter	Rock bass						Common shiner					White sucker					
	0	1	2	3	4	5	0	1	3	4	5	0	1	2	3	4	5
Number of fish collected	68	107	20	27	13	26	412	632	37	76	569	264	111	25	155	77	100
Number of fish processed	60	67	20	26	13	26	93	71	37	76	93	263	91	24	144	77	82
Mean length (mm)	97.0 (29.9)*	113.5 (36.3)	103.7 (9.9)	133.7 (23.8)	126.2 (18.3)	139.8 (34.2)	122.1 (22.6)	117.2 (32.5)	116.1 (29.8)	122.1 (22.3)	107.4 (25.2)	212.7 (43.4)	186.2 (37.4)	196.0 (71.9)	209.2 (54.9)	204.4 (67.0)	157.2 (63.8)
Mean K	1.78 (0.26)*	1.73 (0.34)	1.44 (0.28)	2.00 (0.34)	1.98 (0.18)	1.90 (0.19)	1.07 (0.15)	0.98 (0.17)	1.09 (0.15)	1.09 (0.13)	1.05 (0.16)	0.98 (0.27)	0.92 (0.15)	0.97 (0.09)	1.06 (0.11)	1.02 (0.19)	0.96 (0.13)
Correlation coefficient (r) for K and length	+0.20	+0.17	+0.64	+0.14	+0.17	+0.03	+0.31	+0.44	+0.63	+0.06	+0.38	-0.22	-0.23	+0.01	-0.05	+0.17	-0.12
Standards of health†																	
Poor			K = 1.80											K = 1.02			
Average			K = 2.02-2.38											—			
Excellent			K = 2.49											K = 1.27			

*Standard deviation is given in parentheses.
†From a Minnesota study reported in Carlander (1969) and Carlander (1977).

Table 10. Mean K Values for Various Length Classes of Common Shiners

Length class (mm)		Sampling sites					
		CN-0	CN-1	CN-2	CN-3	CN-4	CN-5
41 to 60	K		0.94		0.78		0.99
	n	0	1	0	1	0	3
61 to 80	K	0.85	0.87		0.90	0.96	0.88
	n	3	11	0	4	2	12
81 to 100	K	1.05	0.88	0.42	1.01	1.10	1.01
	n	15	13	1	7	13	17
101 to 120	K	1.04	1.01		1.13	1.09	1.09
	n	27	8	0	7	18	33
121 to 140	K	1.08	0.98		1.21	1.11	1.13
	n	27	20	0	7	26	21
141 to 160	K	1.12	1.11		1.13	1.08	1.05
	n	18	12	0	9	16	6
161 to 180	K	1.22	1.12		1.19	1.06	0.89
	n	3	5	0	2	1	1
181 to 200	K		1.04				
	n	0	1	0	0	0	0

Synthetic Chemicals in Canagagigue Creek

INTRODUCTION

For the initial year of the study, our plan was to perform general chemical analysis of the stream water and to identify the synthetic organic chemicals present. Previous studies by NWRI had shown the occurrence of pentachlorophenol and other organochlorine compounds at significant levels in most southern Ontario streams, and methods were available for the extraction and determination of these compounds in a variety of matrices. When it was discovered during the preliminary survey that a considerable range of chlorophenols were present in the creek, it was decided that in addition to the general sampling and analysis, major effort would be devoted to the analysis of various stream compartments for chlorophenols and other organochlorine contaminants.

The analysis of synthetic organics in 1980 was operationally subdivided into four sections: (1) chlorophenols, (2) neutral organochlorine contaminants, (3) neutral compounds (nonchlorinated), and (4) acidic compounds (nonchlorinated).

CHLOROPHENOLS

Water samples for chlorophenol analysis were collected in 1-L amber glass bottles with Teflon-lined screw caps. Five pellets of potassium hydroxide were added to each bottle before sampling. Upon return to the laboratory the samples were acidified to pH 1 to 2 with concentrated HCl, extracted with toluene and analyzed for chlorophenols following the method of Chau and Coburn (1974). Fish and benthic fauna were dissolved in HCl (1 g per 7 mL), extracted with toluene and analyzed for chlorophenols following the method of Chau and Coburn.

Concentrations of chlorophenols in unfiltered water are shown in Table 11. At the two control sites upstream from Elmira, only pentachlorophenol (PCP) and 2,3,4,6-tetrachlorophenol (2,3,4,6-TTCP) were detected, at low concentrations (<20 ng/L). These concentrations are typical for streams in southwestern Ontario and usually derive from leachate of PCP-treated exterior lumber. At CN-2, a significant increase of 2,4-dichlorophenol (2,4-DCP) and 2,4,5-trichlorophenol (2,4,5-TCP) and other chlorophenols occurred. Prominent among the other chlorophenols were 2,6-dichlorophenol (2,6-DCP); 3,4-dichlorophenol (3,4-DCP); and 2,4,6-trichlorophenol (2,4,6-TCP). Other chlorophenols were observed in amounts too small to quantify. A comparison of an analysis of the WPCP effluent with the stream water revealed that much of the 2,3,4,6-TTCP and PCP and some of the 2,4,6-TCP observed at CN-3 enter the creek via the WPCP. The results, summarized in Table 12, indicate that the WPCP was not the principal source of 2,4-DCP; 3,4-DCP; and 2,4,5-TCP. Seasonal variations in the stream concentrations of these latter compounds are quite evident in the data with a spring maximum seen in May, low values in the summer and early fall, followed by an increase in early winter to levels considerably below those observed in the spring. We infer from these results that most of the dichlorophenols and trichlorophenols enter the creek as groundwater seepage from the disused chemical waste disposal area on the east bank of the creek at CN-2. Some of these buried wastes are related to the manufacture of the herbicides 2,4-D and 2,4,5-T which were produced in Elmira until 1969. The observed seasonal fluctuations can be explained by a seasonal dependence in the shallow groundwater seepage into the creek. This input is the highest in spring when the surface soil is saturated with water, whereas it is relatively low in summer when the soil is drier.

All of the quantified chlorophenols decreased in concentration in water with distance from the contaminant source, with the concentration at CN-5 being approximately 0.1 to 0.4 of the concentration at CN-2. Dilution can be ruled out as a major factor in this disappearance, based on both stream gauge measurements and previous observations (Fig. 5) that the soluble conservative ion $SO_4^=$, which enters the stream at the WPCP, showed no appreciable diminution between CN-2 and CN-5. In November 1980, chlorophenols were also analyzed at Station GR-13, which is on the Grand River below the confluence with Canagagigue Creek. With the exception of PCP, no chlorophenols were detected, which is explained by the dilution of the low values observed at CN-5 by a factor of approximately 10 to 12. The PCP observed is present in the Grand River before the confluence, as evidenced by the concentration observed at GR-12 upstream from the confluence.

Table 11. Concentrations of Chlorophenols in Unfiltered Water from Canagagigue Creek, 1980

Date	Site	Chlorophenol concentration (ng/L)						
		2,6-DCP	2,4-DCP	3,4-DCP	2,4,6-TCP	2,4,5-TCP	2,3,4,6-TTCP	PCP
May 23	CN-0	N.D.	N.D.	N.D.	N.D.	N.D.	5	15
	CN-1	N.D.	N.D.	N.D.	N.D.	N.D.	5	32
	CN-2	284	1420	422	668	457	66	122
	CN-3	253	1046	447	505	277	49	78
	CN-4	160	478	309	182	213	41	75
	CN-5	128	145	109	145	75	22	54
	GR-12	N.D.	N.D.	N.D.	N.D.	10	36	68
July 8	CN-0	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	2
	CN-1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	2
	CN-2	94	192	102	311	32	17	14
	CN-3	31	17	26	78	17	3	3
	CN-4	27	9	17	51	5	3	5
	CN-5	20	5	–	41	3	2	2
September 10	CN-0	N.D.	N.D.	N.D.	N.D.	N.D.	5	15
	CN-1	N.D.	N.D.	N.D.	N.D.	N.D.	5	17
	CN-2	60	155	124	199	51	39	63
	CN-3	41	70	54	124	26	27	32
	CN-4	27	22	N.D.	70	12	10	19
	CN-5	27	22	N.D.	66	12	12	22
November 12	CN-0	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	15
	CN-1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	17
	CN-2*	68(68)	252(252)	77(75)	238(230)	82(80)	12(12)	77(68)
	CN-3	N.D.	92	N.D.	70	26	N.D.	27
	CN-4	34	94	48	119	46	7	65
	CN-5	14	29	17†	38	14	2	27
	GR-12	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	31
	GR-13	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	15

*Samples collected midstream; nearshore samples are shown in parentheses.
†Chromatographic interference prevented lower quantitation.
N.D. – Not detected.

Table 12. Contribution of Elmira WPCP to Chlorophenols in Canagagigue Creek, December 12, 1980

Site	Chlorophenol concentration (ng/L)						
	2,6-DCP	2,4-DCP	3,4-DCP	2,4,6-TCP	2,4,5-TCP	2,3,4,6-TTCP	PCP
CN-1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	27
WPCP	119	75	N.D.	367	87	107	2028
CN-3	53	201	87	277	77	10	46

N.D. – Not detected.
Note: Measured ratio of WPCP discharge to Canagagigue Creek was 1 to 40.

Twenty-five species of fish were caught in the survey discussed earlier in this report. Of these, five species were chosen for chlorophenol analysis on account of their reasonable abundance at each site and variety of feeding habits. All are local except for adult white suckers which travel long distances during the breeding season.

The chlorophenol levels in these fish are shown in Table 13. The levels show the same seasonal trend exhibited in the water samples. Although chlorophenols are readily absorbed from water by fish, they are also readily eliminated with a clearance half-life of less than 10 h (Kobayashi and Akitake, 1975), so that the observed levels may be expected to reflect the ambient concentrations in water at that time.

Of all of the five fish species analyzed, the highest chlorophenol levels occurred in rock bass. This fish is a midwater species which eats crayfish, small fish and insects.

The white sucker is a bottom feeder which eats mainly invertebrates. Data are available for July only due to spoilage loss of samples as a result of freezer failure. Levels of 2,4-DCP and 2,4,5-TCP are generally less than the corresponding figures for rock bass at the same site and time of year.

Table 13. Concentrations of Chlorophenols in Fish from Canagagigue Creek, 1980

Fish	Date	Site	Chlorophenol concentration (ng/g wet wt)						
			2,6-DCP	2,4-DCP	3,4-DCP	2,4,6-TCP	2,4,5-TCP	2,3,4,6-TTCP	PCP
Rock bass	May	CN-0	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
		CN-1	N.D.	N.D.	N.D.	N.D.	N.D.	17	17
		CN-2	136	537	292	184	490	75	61
		CN-3	61	253	179	88	376	29	68
		CN-4	68	124	78	31	138	22	20
		CN-5	10	N.D.	N.D.	N.D.	31	9	9
	July	CN-0	12	N.D.	104	14	14	N.D.	5
		CN-1	20	N.D.	41	N.D.	17	N.D.	3
		CN-2	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
		CN-3	N.D.	65	20	39	44	3	15
		CN-4	24	22	56	22	43	N.D.	12
		CN-5	12	N.D.	27	5	7	N.D.	2
	September	CN-0	207	N.D.	N.D.	3	N.D.	3	2
		CN-1	505	3	61	56	15	12	2
		CN-2	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
		CN-3	500	N.D.	122	14	63	15	9
		CN-4	N.D.	36	N.D.	78	68	22	29
		CN-5	41	19	N.D.	2	36	N.D.	12
	November	CN-0	121	N.D.	N.D.	2	2	7	20
		CN-1	53	N.D.	N.D.	N.D.	12	5	3
		CN-2	347	105	N.D.	15	71	22	78
		CN-3	258	116	N.D.	7	48	9	10
		CN-4	14	41	9	5	36	2	24
		CN-5	39	19	N.D.	2	12	3	15
White sucker	May	N.A.							
	July	CN-0	136*	N.D.	N.D.	3	5	5	N.D.
		CN-1	–	N.D.	N.D.	5	7	5	2
		CN-2	326	43	27	36	41	9*	7
		CN-3	N.D.	14	19	36	26	14*	9
		CN-4	422	N.D.	12	14	192	10*	5
		CN-5	83	N.D.	N.D.	3	N.D.	2*	N.D.
	September	N.A.							
	November	N.A.							

* Uncertain identification (see text).
†Quantitation approximate due to chromatographic interference.
‡Rainbow, fantail and Iowa darters.
N.D. – Not detected.
N.S. – No sample.
N.A. – No fish analyzed (see text).

Table 13. Continued

Fish	Date	Site	Chlorophenol concentration (ng/g wet wt) 2,6-DCP	2,4-DCP	3,4-DCP	2,4,6-TCP	2,4,5-TCP	2,3,4,6-TTCP	PCP
Longnose dace	May	CN-0	N.D.	N.D.	N.D.	19	N.D.	N.D.	2
		CN-1	N.D.	N.D.	30	N.D.	N.D.	N.D.	2
		CN-2	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
		CN-3	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
		CN-4	N.D.	77	37	46	51	N.D.	5
		CN-5	N.D.	2	17	26	10	N.D.	3
	July	CN-0	N.D.	N.D.	N.D.	10	N.D.	N.D.	3
		CN-1	N.D.	N.D.	N.D.	3	N.D.	N.D.	7
		CN-2	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
		CN-3	N.D.	71	N.D.	117	66	N.D.	14
		CN-4	N.D.	10	N.D.	27	15	N.D.	5
		CN-5	N.D.	N.D.	N.D.	9	3	N.D.	3
	September	N.A.							
	November	CN-0	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
		CN-1	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
		CN-2	1913	22	N.D.	43	168	66	78
		CN-3	N.D.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
		CN-4	935	77	N.D.	44	85	82	51†
		CN-5	119	N.D.	N.D.	N.D.	N.D.	15	17†
Darters‡	May	CN-0	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
		CN-1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	2
		CN-2	N.D.	213	162	43	95	22	78
		CN-3	N.D.	83	27	31	15	N.D.	17
		CN-4	N.D.	104	56	17	49	N.D.	10
		CN-5	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
	July	N.A.							
	September	N.A.							
	November	CN-0	44	N.D.	N.D.	N.D.	9	9	17†
		CN-1	134	N.D.	N.D.	5	48	10	14
		CN-2	1224	360	109	95	216	N.D.	170
		CN-3	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
		CN-4	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
		CN-5	770	N.D.	N.D.	32	102	61	N.D.
Common shiner	May	CN-0	N.D.	N.D.	N.D.	27	N.D.	31	44
		CN-1	31	N.D.	10	10	N.D.	N.D.	3
		CN-2	428	469	466	330	241	112	150
	•	CN-3	68	163	112	68	71	37	24
		CN-4	77	116	61	41	54	N.D.	9
		CN-5	214	17	N.D.	31	24	20	10

Longnose dace are bottom dwellers which feed on various insect larvae. The data shown in Table 13 are patchy, with no samples available at a number of sites, but in general, levels of 2,4-DCP and 2,4,5-TCP are higher than those observed for the white sucker.

Darters are bottom feeders which eat large and small insect larvae, fish eggs and snails. Chlorophenol levels shown in Table 13 are lower than those for rock bass in May but higher in November. The reason for this is not apparent. No samples were analyzed for July and September due to spoilage losses.

The common shiner is an omnivore which feeds mainly on surface insects, larvae and adults, and even small fish. Data are available only for May and show relatively high levels of chlorophenols.

In all of the preceding discussions of chlorophenol levels in fish and also in the following benthos data, the concentrations of 2,6-DCP have not been discussed because unlike the other chlorophenols, 2,6-DCP exhibits anomalous values between levels in fish, benthos and water. This may be related to analytical interference and will be investigated further.

Table 14. Concentrations of Chlorophenols in Benthos from Canagagigue Creek, November 1980

Organism	Site	Chlorophenol concentration (ng/g wet wt)						
		2,6-DCP	2,4-DCP	3,4-DCP	2,4,6-TCP	2,4,5-TCP	2,3,4,6-TTCP	PCP
Leech	CN-0	279	63	N.D.	34	117	14	58
	CN-2	510	9 049	3742	7 550	11 436	1479	2798
	CN-3	5350	12 267	6604	13 588	11 883	1380	2671
Clam	CN-0	65	2	N.D.	3	2	3	2
	CN-1	82	N.D.	N.D.	2	2	2	2
	CN-4	109	3	N.D.	19	3	19	7
Snail	CN-4	2	N.D.	N.D.	17	12	14	54
Alderfly larvae	CN-2	161	10	N.D.	N.D.	12	12	36
Damselfly larvae	CN-2	51	44	N.D.	N.D.	N.D.	N.D.	39
	CN-4	N.D.	N.D.	N.D.	10	N.D.	14	2
Caddisfly larvae	CN-4	N.D.	85	87	22	22	20	9
	CN-5	109	54	32	26	20	27	7
Cranefly larvae	CN-4	167	N.D.	N.D.	9	3	2	2
Dragonfly larvae	CN-2	N.D.	N.D,	N.D.	9	N.D.	14	12

N.D. – Not detected.

Chlorophenol analyses were performed on a number of benthic animals from a single benthos collection. A summary of the data appears in Table 14. The extremely high levels of all chlorophenols in leeches, which are approximately 20 times higher than the levels in rock bass, are the most striking feature. Several species of leeches were involved in this composite sample to obtain a sufficient sample size. Leeches vary widely in diet according to the species, ranging from detritus feeders to parasites. Future studies on Canagagigue Creek will include the collection and analysis of various leech species.

Analysis of two molluscs, snails and clams, yielded very low levels of chlorophenols. This is partly because a considerable fraction of the whole animal weight is the calcified shell which is not expected to be a reservoir for chlorophenols.

Analyses of the larvae of several aquatic insects are also included in Table 14. The species of caddisfly larvae collected for analysis (Hydropsychidae) are filter feeders and show significantly higher levels of chlorophenols than the other insect larvae, some of which are predators. If a large proportion of the initial chlorophenol loading becomes associated with micro-particulate material, then it is not surprising to find higher levels associated with an efficient filter feeder.

Levels of chlorophenols in crayfish are shown in Table 15. The levels are fairly low, and significant levels of most chlorophenols were observed at the two control sites. Since problems were encountered with the analysis of crayfish extracts, these results must be treated with caution.

Limited data on frogs are shown in Table 16. Levels are generally low, but the tadpole appears to contain higher levels than the adult.

A potentially important component of the creek ecosystem that has been omitted from this report is the sediment and suspended solids. The only material with long-term stability on the bottom of this rapid flowing creek comprised stones and coarse gravel. Wide-mouthed glass jars that had been placed in the stream bed and left in place for several weeks to accumulate suspended solids proved very susceptible to damage by cows, and this technique will be replaced by sedimentation tubes with metal sleeves for future studies. Sediments, periphyton and suspended solids will be discussed in future reports.

Table 15. Concentrations of Chlorophenols in Crayfish from Canagagigue Creek, 1980

Date	Site	Chlorophenol concentration (ng/g wet wt)						
		2,6-DCP	2,4-DCP	3,4-DCP	2,4,6-TCP	2,4,5-TCP	2,3,4,6-TTCP	PCP
May	CN-0	56	37	N.D.	104	7	228	12
	CN-1	20	N.D.	N.D.	20	12	53	12
	CN-2	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
	CN-3	9	87	43	14	29	9	22
	CN-4	N.D.	34	22	7	15	N.D.	2
	CN-5	14	24	22	3	10	N.D.	5
July	CN-0	787	3	N.D.	19	7	12	2
	CN-1	660	2	N.D.	34	N.D.	15	2
	CN-2	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
	CN-3	286	17	26	10	27	5	2
	CN-4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
	CN-5	162	N.D.	N.D.	9	14	27	17
September	CN-0	122	17	N.D.	22	N.D.	31	2
	CN-1	65	48	22	126	10	600	34
	CN-2	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
	CN-3	78	27	10	29	19	10	15
	CN-4	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
	CN-5	87	N.D.	N.D.	14	10	3	3
November	CN-0	160	17	N.D.	39	N.D.	65	2
	CN-1	51	10	N.D.	27	3	112	10
	CN-2	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
	CN-3	292	5	2	10	3	5	2
	CN-4	357	7	N.D.	29	9	15	2
	CN-5	29	12	N.D.	41	5	32	2

N.D. – Not detected.
N.S. – No sample.
N.A. – Not quantitated owing to chromatographic interference.

Table 16. Concentrations of Chlorophenols in Frogs from Canagagigue Creek, November 1980

Frog	Site	Chlorophenol concentration (ng/g wet wt)						
		2,6-DCP	2,4-DCP	3,4-DCP	2,4,6-TCP	2,4,5-TCP	2,3,4,6-TTCP	PCP
Leopard frog	CN-0	196	2	N.D.	N.D.	3	2	2
	CN-2	N.D.	24	N.D.	N.D.	36	14	N.D.
Bullfrog	•CN-3	328	N.D.	N.D.	2	N.D.	5	37
Bullfrog tadpole	CN-2	243	51	N.D.	65	129	26	N.D.
	CN-3	83	N.D.	N.D.	10	31	N.D.	19

N.D. – Not detected.

NEUTRAL ORGANOCHLORINE CONTAMINANTS

The 1-L water samples collected and extracted for chlorophenols as previously described were also analyzed for neutral organochlorine pesticides and PCBs as follows. The residual toluene extract, after removal of chlorophenols, was cleaned up and separated according to the method of Sampson *et al.* (1977) and analyzed by the Inland Waters Directorate Water Quality Laboratory, Ontario Region. The data for June 1980 are shown in Table 17.

Of the seven neutral organochlorine contaminants for which data are presented, only lindane shows a marked increase at the site of contaminant inflow. Analyses reported elsewhere have demonstrated that lindane enters the creek via the Elmira WPCP. The decrease in lindane concentrations with distance from the contaminant inflow is similar to that of the chlorophenols. The concentrations of PCBs and α-BHC show no particular trend, whereas the chlordanes, total DDTs and methoxychlor show somewhat elevated levels at all stations below the control sites. It should be emphasized that all of these measurements are made on unfiltered water from a very turbid creek. Concentrations of sparingly soluble contaminants at very low levels are easily influenced by natural variations in the amount and nature of solids in the samples. Only lindane, with a somewhat higher solubility, is present at concentrations clearly above background levels.

NEUTRAL COMPOUNDS (NONCHLORINATED)

On five occasions in 1980, 4-L water samples were collected at each of the six sites. The samples were processed to obtain neutral and acidic extracts. Neutral extracts from CN-2 were analyzed by GC/MS to identify the compounds present. Mass spectra were obtained for all of the peaks with areas greater than 5% of the largest peak in the chromatogram. The compounds identified for each date are listed in Table 18.

Table 17. Concentrations of Other Organochlorines in Unfiltered Water from Canagagigue Creek, June 9, 1980

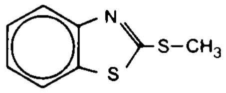
	Organochlorine concentration (ng/L)						
Site	PCBs	α-BHC	Lindane	α-Chlordane	γ-Chlordane	Σ DDTs*	Methoxychlor
CN-0	19.7	13.0	7.2	N.D.	N.D.	N.D.	0.3
CN-1	26.9	11.2	10.2	N.D.	N.D.	N.D.	0.1
CN-2	9.3	10.0	142.5	1.3	N.D.	8.5	1.7
CN-3	12.2	6.5	104.0	2.7	2.4	25.2	4.8
CN-4	11.1	5.1	60.1	1.7	1.8	3.4	0.5
CN-5	37.1	6.9	47.6	1.5	2.1	5.7	6.4

*Total of DDT isomers and metabolites.
N.D. – Not detected.

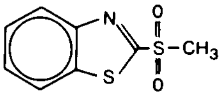
Table 18. Nonchlorinated Neutral Compounds at CN-2, 1980

Date	Compound	Areas as percent of largest peak	Concentration (μg/L)
May 23	Tributyl phosphate	100	–
	2-(Methylthio)benzothiazole	36	13
	Benzothiazole	27	10
	2-(Methylsulfonyl)benzothiazole	23	19
	Diphenylamine	8	2
	2-(Methylsulfinyl)benzothiazole	7	Trace
July 8	2-(Methylsulfonyl)benzothiazole	100	74
	2-(Methylsulfinyl)benzothiazole	61	41
	2-(Methylthio)benzothiazole	13	4
	Di-*iso*-octylphthalate	10	4
July 24	2-(Methylthio)benzothiazole	100	25
	2-(Methylsulfonyl)benzothiazole	70	43
	2-(Methylsulfinyl)benzothiazole	13	7
	Benzothiazole	9	3
	Nonyl phenol	6	25
September 10	2-(Methylthio)benzothiazole	100	22
	2-(Methylsulfinyl)benzothiazole	83	39
	2-(Methylsulfonyl)benzothiazole	67	36
	Benzothiazole	19	4
	Butyl butoxyethylphthalate	6	3
November 12	Benzothiazole	100	47
	2-(Methylthio)benzothiazole	88	44
	2-(Methylsulfonyl)benzothiazole	46	55
	2-(Methylsulfinyl)benzothiazole	15	17
	Dioctylphthalate	11	9
	Diphenylamine	3	1

In Table 18, only two compounds, 2-(methylthio) benzothiazole (MMBT) and 2-(methylsulfonyl)benzothiazole (I), appear at significant concentrations in every sample.

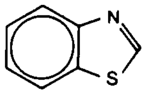


MMBT

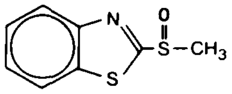


I

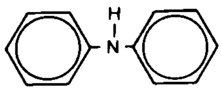
Only three other compounds appear more than once at high levels: benzothiazole (BT), 2-(methylsulfinyl) benzothiazole (II), and diphenylamine (DPA).



BT



II



DPA

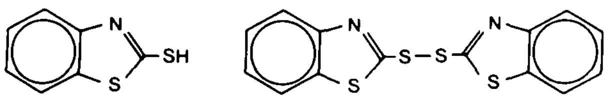
Most of the assigned identities were provided by computer searches of mass spectral libraries. The two oxidation products of MMBT, I and II, were not found in the libraries, but their identities were tentatively assigned after comparison of their spectra with that of MMBT. Good library matches were obtained for the rest of the compounds listed. There were two other compounds,

Table 19. Mass Spectra of Four Major Compounds from Canagagigue Creek

Compound	Description	Mass spectra
Benzothiazole (BT)	C_7H_5NS, mol wt 135	135(100)
		108(37)
		69(24)
		91(13)
		82(13)
		63(13)
		136(9)
		54(8)
		58(7)
		81(7)
2-(Methylthio)benzothiazole (MMBT)	$C_8H_7NS_2$, mol wt 181	181(100)
		148(84)
		108(38)
		180(34)
		136(20)
		69(19)
		135(17)
		63(14)
		182(14)
		122(11)
2-(Methylsulfonyl)benzothiazole (I)	$C_8H_7NO_2S_2$, mol wt 213	150(100)
		213(36)
		134(32)
		90(23)
		63(20)
		151(4)
		149(14)
		106(13)
		135(13)
		108(11)
2-(Methylsufinyl)benzothiazole (II)	$C_8H_7NOS_2$, mol wt 197	151(100)
		182(62)
		150(59)
		154(48)
		63(44)
		181(40)
		90(40)
		134(38)
		197(33)
		108(33)

appearing only once each, for which poor library matches were obtained. Since they were limited in appearance and their areas were small compared with the major peaks, no further effort was made to identify them. Representative mass spectra of these four major compounds are given in Table 19.

When benzothiazoles were found to be the major component in the neutral fraction, we reviewed the literature on these substances in the aquatic environment (Brownlee *et al.*, 1981). Benzothiazoles are used as vulcanization accelerators in the rubber industry, as biocides, as photosensitizers in photography and as corrosion inhibitors in products such as automobile antifreeze. The most widely used benzothiazole appears to be 2-mercaptobenzothiazole (MBT), with some rubber containing as much as 2% MBT. While there is extensive literature on these compounds, very little pertains to their occurrence, effects and fate in the environment. Although MBT and its disulphide DBBT are manufactured in Elmira, neither of these compounds was observed in the creek water.



MBT DBBT

For quantitative analysis of the compounds in the neutral extracts, standards of BT, DPA, nonyl phenol (NP) and various phthalates were commercially available, whereas MMBT, I and II were obtained by synthesis following published methods (Vernin *et al.*, 1978; Hilgetag and Martini, 1972). Analyses were performed using capillary gas chromatography with a flame ionization detector

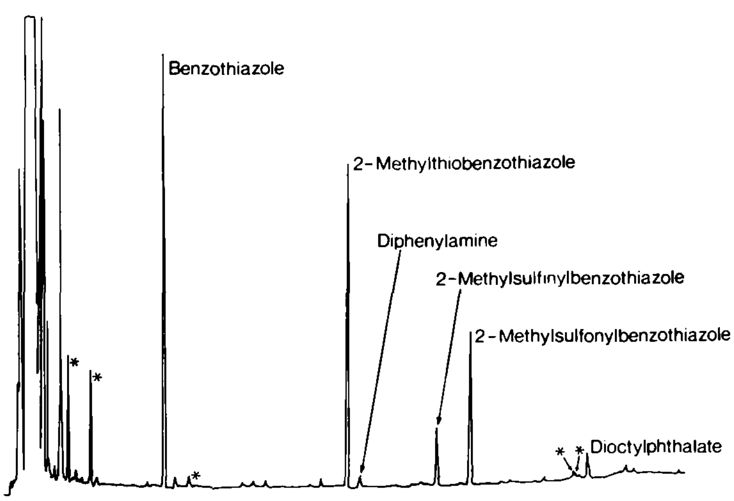


Figure 10. Capillary FID gas chromatogram of neutral extract from Canagagigue Creek, November 12, 1980.

(FID). A typical chromatogram is shown in Figure 10. None of these compounds was found at analytically significant levels at either upstream site. The quantitative results for the five compounds present at the highest levels are listed in Table 20. With the exception of the November 12 sample, all concentrations decrease significantly with distance downstream at approximately the same rates previously observed for chlorophenols and lindane. The possibility that these decreases follow a single general pathway merits further investigation.

Table 20. Concentrations of Nonchlorinated Neutral Compounds in Canagagigue Creek, 1980-81

Date	Site	Compound concentration (μg/L)				
		BT	MMBT	DPA	II	I
May 23, 1980	CN-2	10	13	2	tr	19
	CN-3	8	10	0.8	tr	14
	CN-4	3	10	N.D.	tr	10
	CN-5	2	7	N.D.	tr	5
July 8, 1980	CN-2	0.3	4	N.D.	41	74
	CN-3	0.1	1	N.D.	24	67
	CN-4	0.1	0.3	N.D.	7	50
	CN-5	0.1	0.4	N.D.	4	43
July 24, 1980	CN-2	3	25	N.D.	7	43
	CN-3	N.D.	18	N.D.	9	33
	CN-4	N.D.	10	N.D.	4	7
	CN-5	N.D.	7	N.D.	4	5
September 10, 1980	CN-2	4	22	N.D.	39	36
	CN-3	4	14	N.D.	17	19
	CN-4	4	6	N.D.	15	10
	CN-5	4	7	N.D.	13	10
November 12, 1980	CN-2	47	44	1	17	55
	CN-3	55	45	N.D.	24	57
	CN-4	20	24	N.D.	24	24
	CN-5	13	13	N.D.	28	17
January 14, 1981	CN-2	20	9	1	0.7	1
	CN-3	13	8	0.9	tr	0.7
	CN-4	8	5	0.3	tr	0.5
	CN-5	5	3	tr	tr	tr

tr – Trace.
N.D. – Not detected.

ACIDIC COMPOUNDS (NONCHLORINATED)

The acidic fraction mentioned in the previous section was also analyzed by GC/MS. Previous studies of stream water downstream from sewage plants had shown that this fraction contained very high concentrations of fatty acids and that contaminants would have to be present at high concentrations in order not to be obscured by these naturally occurring compounds. For this reason, few published studies include data on acidic fractions. Data were included in this study for completeness, rather than from any expectation of significant results. The results, however, proved more interesting than anticipated. In addition to the expected fatty acids, there was what appeared to be a series of up to eight closely related compounds. The most common of these was present in every acidic extract obtained in 1980, and in some cases, its response to the GC or GC/MS was greater than that of the fatty acids. A total ion current chromatogram of the September 10 acid extract (methylated) is shown in the upper part of Figure 11. The mass spectra of the new compounds indicated that they all had a strong ion at m/z 117; a mass chromatogram specifically of this ion is shown in the lower part of the figure. This extract was considered representative and was subjected to further intensive analysis. The results were indicative of a series of compounds not previously reported in the literature. The compound labelled *a* in Figure 11 is 2-hydroxybenzothiazole and may be the result of hydrolysis of substituted

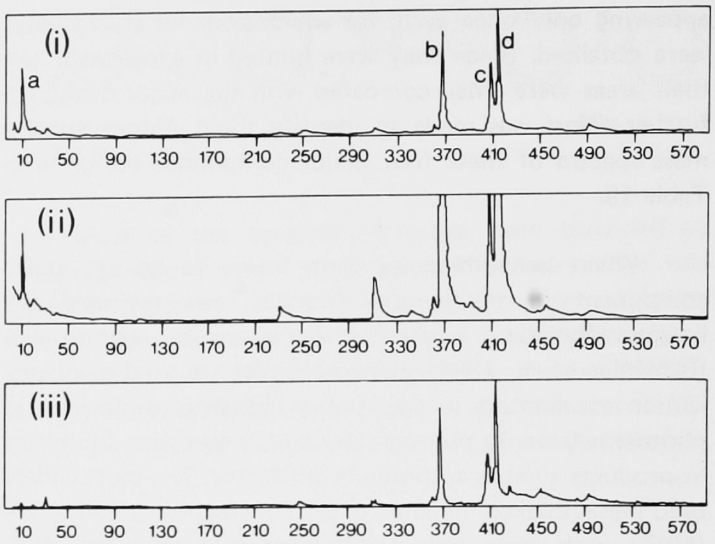


Figure 12. **(i) Total ion chromatogram of the methylated acidic extract of the influent to the Elmira WPCP, December 5, 1979:** ***a*** **— anisole,** ***b*** **— methyl palmitate,** ***c*** **— methyl oleate,** ***d*** **— methyl stearate. (ii) Specific ion chromatogram of the m/z 74 ion of the same extract. (iii) Specific ion chromatogram of the m/z 117 ion of the same extract.**

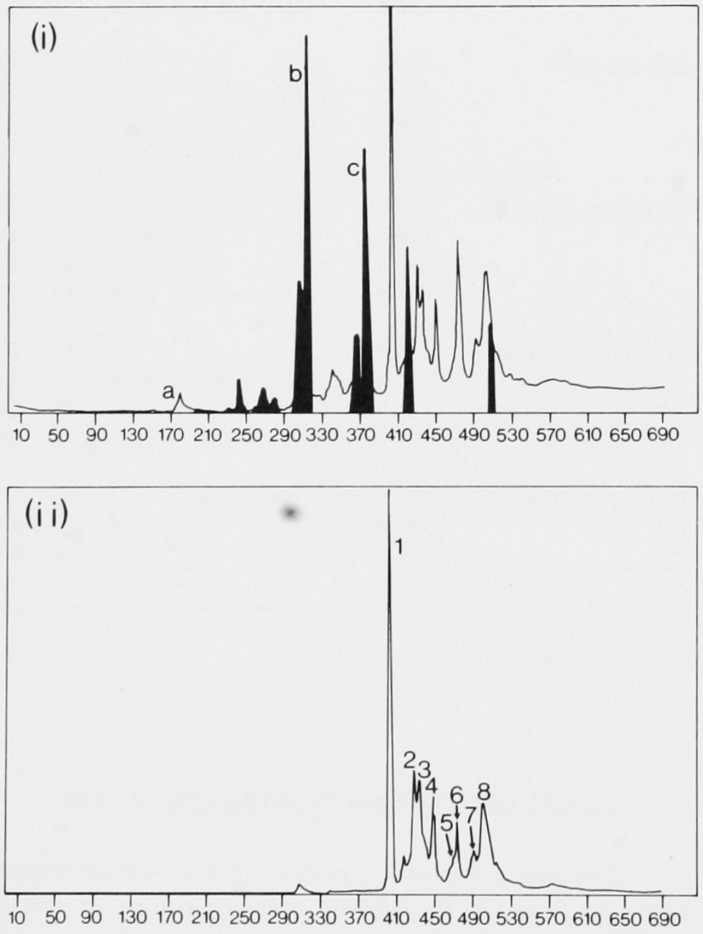


Figure 11. **(i) Total ion current chromatogram of the acidic extract (methylated) from September 10, 1980:** ***a*** **— methoxybenzothiazole,** ***b*** **— methyl palmitate,** ***c*** **— methyl stearate. (ii) Specific ion chromatogram of the m/z 117 ion of the same extract.**

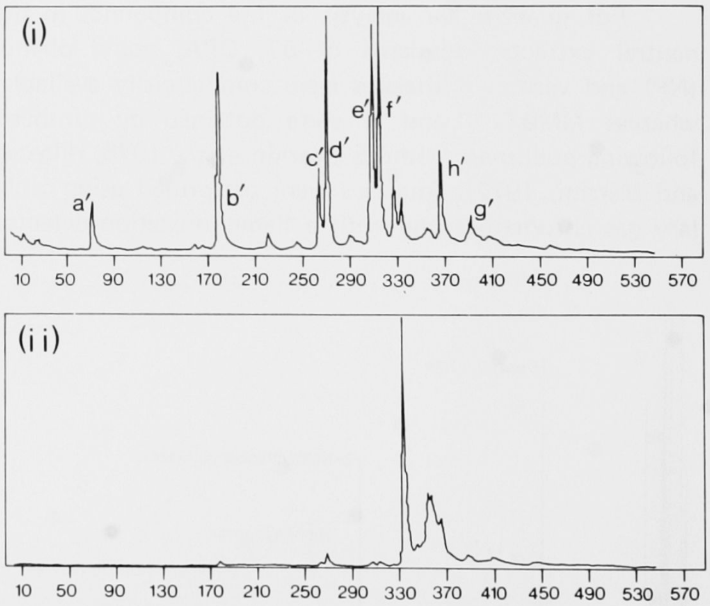


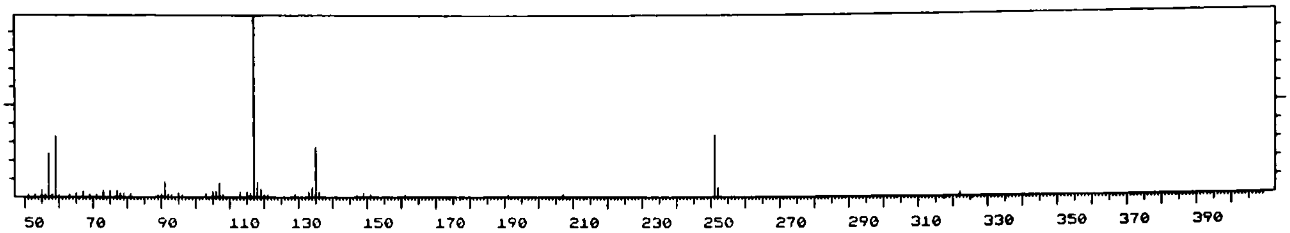
Figure 13. **Total and specific ion chromatogram of the methylated acidic extract of the effluent from the Elmira WPCP, December 5, 1979. (i) Total ion chromatogram:** ***a'*** **— benzothiazole,** ***b'*** **— methylmercaptobenzothiazole,** ***c'*** **— methyl palmitoleate,** ***d'*** **— methyl palmitate,** ***e'*** **— methyl oleate,** ***f'*** **— methyl stearate,** ***g'*** **and** ***h'*** **— impurities from slight sample contamination. (ii) Specific ion chromatogram of the m/z 117 ion of the same extract.**

mercaptobenzothiazoles in the sewage plant. For simplicity, all peaks from fatty acids are coloured black in Figure 11. The most prominent fatty acids are palmitic and stearic acid, as expected.

The mass spectra of all eight new acids (methylated) are presented in Table 21. The compound numbers refer to the peaks of the same number in the lower part of Figure 11. None of these spectra are present in published libraries of mass spectra.

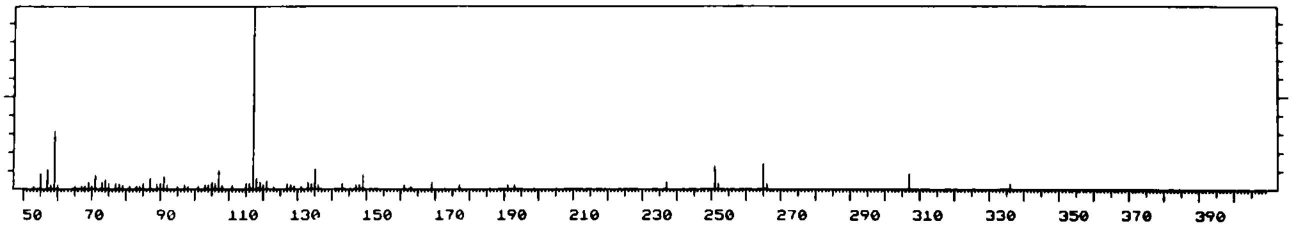
In an attempt to obtain more information about these compounds, acidic extracts of the influent and effluent (24-h composites) of the Elmira WPCP were analyzed. The mass chromatogram of the influent acidic extract (methylated) is shown in Figure 12. The prominent peaks are methyl derivatives of phenol, palmitic, stearic and oleic acids. The specific ion chromatogram for the m/z 117 ion reveals only the small 117 ion associated with fatty acids and indicates that the new compounds observed in Canagagigue Creek are not present in the influent to the WPCP. The mass chromatogram of the effluent acidic extract (methylated) is shown in Figure 13. Along with the fatty acids, benzothiazole and MMBT are present. They may be formed in the WPCP as degradation products of higher substituted benzothiazoles. In addition, the specific ion chromatogram of the m/z 117 ion reveals that the new acids are now present, indicating that they are formed in the Elmira WPCP as degradation products of some unidentified percursor. Further studies of these compounds seem warranted.

Table 21. Mass Spectra of New Acidic Compounds



Compound 1

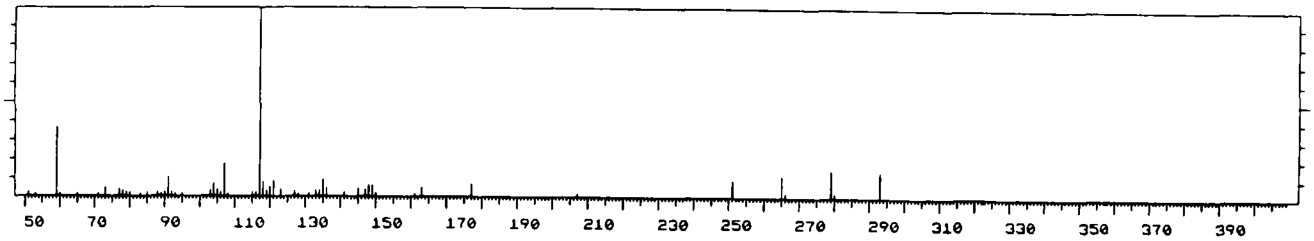
Mass	Intensity	Mass	Intensity	Mass	Intensity
57	24.3	95	1.8	119	3.8
59	34.2	103	1.5	133	2.1
67	2.7	105	2.4	134	4.8
73	3.2	106	2.7	135	27.2
75	3.4	107	6.9	136	2.4
77	3.0	113	2.8	149	1.6
78	1.7	115	2.3	251	31.0
79	1.7	116	1.6	252	4.2
81	1.7	117	100.	322	1.6
91	7.8	118	8.0		



Compound 2

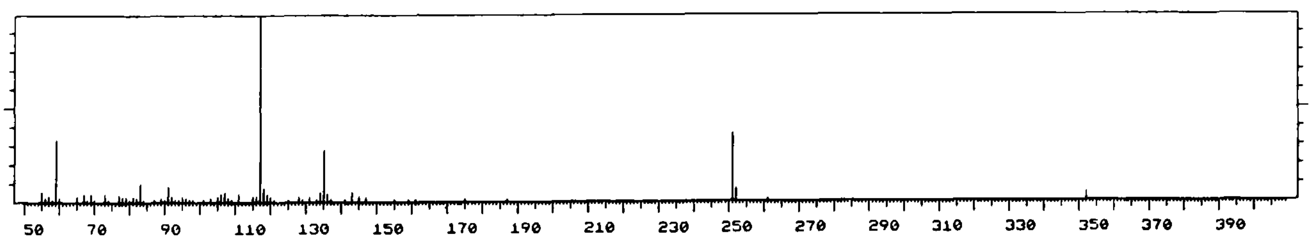
Mass	Intensity	Mass	Intensity	Mass	Intensity
55	8.0	105	3.3	135	10.7
57	10.1	107	9.9	149	7.3
59	31.2	117	100.	169	3.2
69	3.8	118	6.0	237	3.6
71	7.0	119	3.3	251	11.8
74	5.3	121	4.0	265	13.7
87	6.1	127	2.6	307	7.8
91	6.5	133	3.4	336	2.6

Table 21. Continued



Compound 3

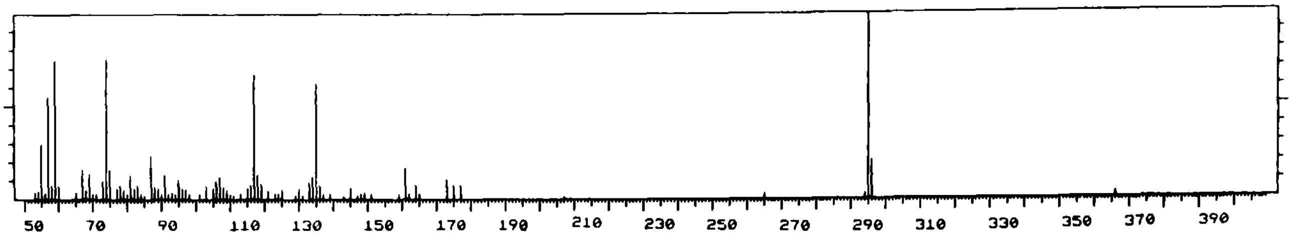
Mass	Intensity	Mass	Intensity	Mass	Intensity
59	36.4	118	7.7	148	5.6
73	3.9	120	4.7	149	5.5
77	3.5	121	8.1	163	4.3
91	9.7	123	3.9	177	6.5
104	6.5	133	3.1	251	9.1
105	3.3	135	8.9	265	11.1
107	17.6	136	4.3	279	14.2
117	100.	145	4.3	293	13.4
		147	3.8		



Compound 4

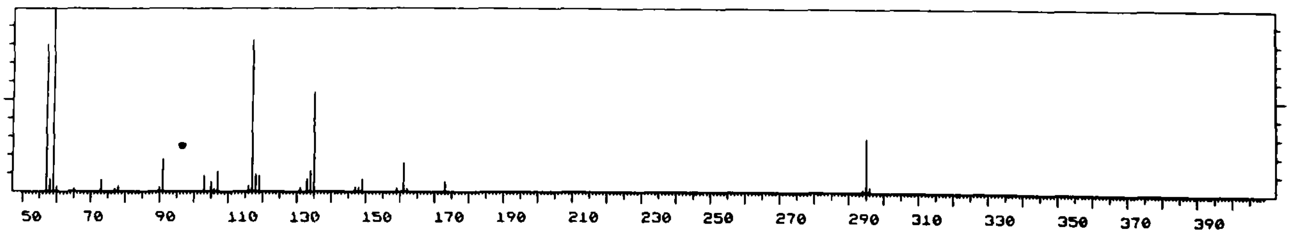
Mass	Intensity	Mass	Intensity	Mass	Intensity
55	4.7	83	9.5	118	7.3
59	32.8	91	8.2	119	4.2
67	4.3	106	4.2	134	4.6
69	4.0	107	4.6	135	27.9
73	4.2	116	3.0	143	5.3
77	3.4	117	100.	251	36.5
				352	4.3

Table 21. Continued



Compound 5

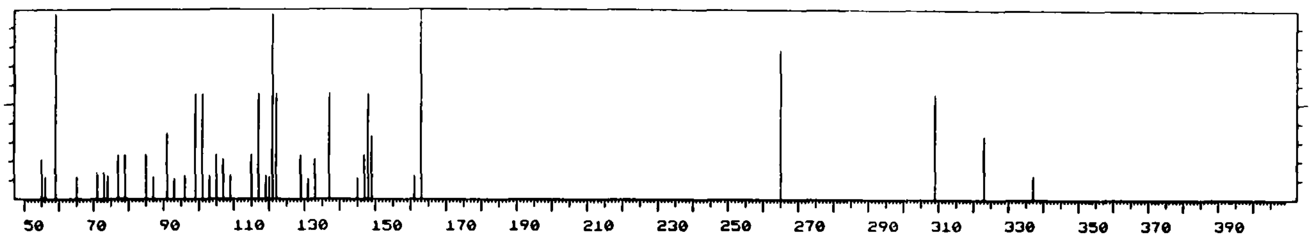
Mass	Intensity	Mass	Intensity	Mass	Intensity
55	29.7	87	24.1	119	8.4
57	56.2	88	6.6	133	8.9
58	7.5	89	6.1	134	11.8
59	75.5	91	13.0	135	63.0
60	7.1	95	10.4	136	7.6
67	15.7	96	6.1	161	21.8
69	13.3	103	7.5	164	7.5
73	10.1	106	9.9	173	10.9
74	76.1	107	12.3	175	7.1
75	16.2	108	6.6	177	7.5
78	7.1	115	6.1	295	100.
81	12.7	116	7.5	296	20.3
83	7.5	117	67.8	366	2.3
		118	12.7		



Compound 6

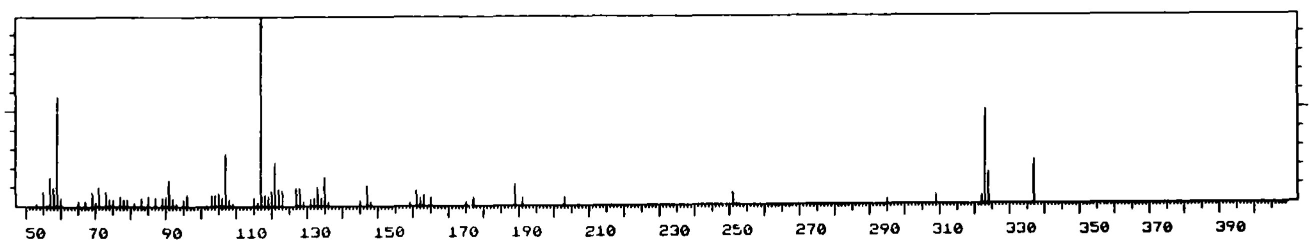
Mass	Intensity	Mass	Intensity	Mass	Intensity
57	81.2	105	5.2	134	11.4
58	6.7	107	10.4	135	54.1
59	100.	117	83.3	149	6.7
73	6.2	118	9.3	161	15.6
91	17.7	119	8.3	173	4.9
103	8.3	133	6.7	295	29.1

Table 21. Continued



Compound 7

Mass	Intensity	Mass	Intensity	Mass	Intensity
55	20.8	105	22.6	147	22.6
59	97.3	107	20.8	148	55.6
77	22.6	115	22.6	149	33.0
79	22.6	117	55.6	163	100.
85	22.6	121	97.3	265	78.2
91	34.7	122	55.6	309	55.6
99	55.6	129	22.6	323	33.0
101	55.6	133	20.8	337	12.1
		137	55.6		



Compound 8

Mass	Intensity	Mass	Intensity	Mass	Intensity
55	7.2	104	5.7	133	10.1
57	15.1	105	6.7	135	15.6
58	9.9	107	27.6	147	10.9
59	58.3	117	100.	161	8.3
69	7.2	118	5.7	163	5.8
71	10.1	120	8.3	189	11.6
73	7.8	121	23.4	251	6.7
91	13.5	122	9.1	323	50.7
96	5.7	123	8.3	324	16.6
103	5.8	127	9.1	337	23.1
		128	9.1		

Discussion

There were two major objectives of this first year of activities. They were

1. to define ecological zones in the creek using biological and water chemistry parameters and

2. to identify major organic contaminants in the creek and to select those worthy of further study.

The discussion of results will cover each objective separately.

ECOLOGICAL STUDIES

The water chemistry data given in Table 2 and Figures 4 and 5 confirm that within the study region, the Elmira WPCP is the only significant point source for ammonium, nitrate, total phosphorus, filtered reactive phosphorus, and sulphate. The sulphate data are particularly interesting. This ion can be considered conservative, and levels of sulphate in the stream, which rise sharply at the WPCP, do not decline significantly downstream. Dilution by surface or groundwater is minimal and therefore unlikely to be a cause of decreased contaminant concentrations downstream from Elmira. Thus, the disappearance of ammonium ion, which can reach several milligrams per litre in the stream near the WPCP, is due to assimilation and nitrification and not to dilution. The water chemistry parameters also indicate that the WPCP effluent can form a very significant portion of total stream flow at certain times of the year.

While these chemical analyses were useful in demonstrating the occurrence of assimilation and nitrification downstream, the benthic survey and, to some extent, the fish survey were of more use in determining the ecological zones in the creek. The benthic results indicate that the Woolwich reservoir has a somewhat detrimental effect on the stream invertebrates, while a severe detrimental effect occurs downstream from the Elmira WPCP and extends as far as CN-3. The occurrence of clean water fauna at CN-4 and CN-5 indicates a general improvement in water quality, and the stream appears to be in better condition at CN-5 than at the sites upstream from Elmira. Thus, recovery from the environmental stress of the WPCP appears to take place over a distance of 7 km and is virtually complete at the confluence of the Canagagigue and the Grand River. These conclusions are supported by the fish surveys, which also indicated a severe local detrimental effect in the vicinity of the WPCP.

All of these results are to be expected downstream from a sewage plant whether or not the plant receives large quantities of synthetic chemicals (Hynes, 1960). In general, the survey of fish meristics also revealed that the Elmira WPCP exhibited no great effect on fish health, although there was a considerable decline in numbers in the immediate vicinity of the plant. Rock bass at CN-2 were in poorer health than those in other parts of the stream, but this could not be unambiguously attributed to organic contaminants, since their preferred food sources were largely absent at this site.

The study area thus appears to represent a fairly typical situation involving the recovery of a stream from the environmental stress of a sewage plant. Since several types of synthetic organic contaminants were found at levels higher than would normally be encountered, the Canagagigue offers a unique opportunity to study the environmental pathways of these chemicals under relatively common environmental conditions.

SYNTHETIC CHEMICALS

In general, fewer types of synthetic organic chemicals were found in the dissolved phase than had been expected. Nevertheless, several compounds were chosen for further intensive study. These were (a) chlorophenols, (b) lindane, (c) benzothiazoles, and (d) unidentified acidic compounds.

Chlorophenols are on the Environmental Contaminants Act priority list and are considered of importance because of their toxicity and distribution in the environment. Since they are much more water soluble than many organochlorine contaminants, their environmental pathways are likely different. Areas on which the study will concentrate are

1. the factors controlling the distribution of chlorophenols in benthic invertebrates,

2. the reasons why chlorophenols are found at such high levels in leeches in Canagagigue Creek,

3. the route of their disappearance from the stream, and

4. the route of bioaccumulation of chlorophenols in fish and the distribution of accumulated chlorophenols in fish organs.

Lindane is the most prominant neutral organochlorine contaminant in the stream. Thus, its distribution in benthic fauna and fish organs will be compared with that of the chlorophenols to determine similarities and differences in the pathways of accumulation and degradation of neutral vs. acidic organochlorines.

Benzothiazoles are an important commercial chemical for the rubber industry. Millions of kilograms of rubber dust are worn from tires each year and deposited along roadsides. This rubber dust can contain as much as 2% benzothiazoles which can be readily leached from the rubber by water. These compounds are also used as antioxidants in applications such as automobile antifreeze, so that considerable quantities can enter the aquatic environment. The pathways of degradation of these compounds are virtually unknown. Future work on these compounds will therefore concentrate on

1. the route of formation of MMBT and its sulfone and sulfoxide (presumably via degradative processes from benzothiazoles manufactured in Elmira),

2. the route of disappearance of these compounds from the stream, and

3. the method of analysis for these compounds in Canagagigue biota.

The unidentified acidic compounds are included for completeness, since all indications are that they are present at high levels. The study will concentrate on

1. the identification of the compounds producing the 117 series in the mass spectrum and

2. the identification of the precursors to these compounds and confirmation of the route of their formation in the WPCP.

References

Brownlee, B., J.H. Carey and M.E. Fox. 1981. A review of benzothiazoles in the aquatic environment. Scientific Series No. 126, Inland Waters Directorate, Burlington, Ontario.

Brinkhurst, R.O. and D.G. Cook. 1974. Aquatic Earthworms (Annelida: Oligochaeta). Chapter 5. *In* Pollution Ecology of Freshwater Invertebrates, C.W. Hart, Jr., and S.L.H. Fuller (eds.), Academic Press, New York, 389 pp.

Carlander, K.D. 1969. *Handbook of Freshwater Fishery Biology*. Vol. 1. The Iowa State University Press, 752 pp.

Carlander, K.D. 1977. *Handbook of Freshwater Fishery Biology*. Vol. 2. The Iowa State University Press, 431 pp.

Chau, A.S.Y. and J.A. Coburn. 1974. Determination of pentachlorophenol in natural and waste waters. J. Assoc. Off. Anal. Chem. 57(2): 389-393.

Crysler, Davis and Jorgenson Ltd., Consulting Engineers. 1965. Grand Valley Conservation Authority Canagagigue Creek Study. GRCA Water Management Library Technical Report.

Crysler and Lathem, Consulting Engineers. 1971. Woolwich Dam — Functional Design Study. GRCA Water Management Library Technical Report.

Elmira and Woolwich Chamber of Commerce. 1980. Industrial Directory.

Environment Canada. 1973, 1977-80. Water Survey Data. Annual reports, Water Survey of Canada, Inland Waters Directorate.

Hilgetag, G. and A. Martini. 1972. *Preparative Organic Chemistry*. John Wiley & Sons, New York.

Hynes, H.B.N. 1960. *The Biology of Polluted Waters*. Liverpool University Press, Liverpool, 202 pp.

Kobayashi, K. and H. Akitake. 1975. Studies on the metabolism of chlorophenols in fish. 1. Absorption and excretion of PCP by goldfish. Bull. Jpn. Soc. Sci. Fish. 41(1): 87-92.

Kramer, C.Y. 1956. Extension of multiple range tests to group means with unequal numbers of replications. Biometrics, 12: 307-310.

MOE. 1974, 1977-79. Water Quality Data: Ontario Lakes and Streams. Annual reports, Ontario Ministry of the Environment.

MOE. 1980. Water Pollution Control Plant Operating Summary. Ontario Ministry of the Environment.

Sampson, R., I. Valdmanis, R.H. Larose and A.W. Wolkoff. 1977. Procedure for the Quantitative Liquid Chromatographic Separation and Clean Up of 18 Organo-Chlorine Pesticides and PCB's in Extracts of Water, Wastewater, Fish or Sediment. Water Quality Branch Report, 8 pp.

Scott, W.B. and E.J. Crossman. 1973. Freshwater fishes of Canada. Fish. Res. Board Can. Bull. 184: 966.

Southwood, T.R.E. 1966. *Ecological Methods*. Chapman and Hall, London, 391 pp.

Sprague, J.B. Unpublished data.

Vernin, G., C. Siv and J. Metzger. 1978. Synthèse et étude physico-chimique de sulfures, sulfoxydes et sulfones en série thiazolique. J. Heterocyl. Chem. 15: 1361-1366.

Wilhm, J.L. and T.C. Dorris. 1968. Biological parameters for water quality criteria. Bioscience, 18(6): 477-481.

Study Team Participants

NATIONAL WATER RESEARCH INSTITUTE

Environmental Contaminants Division

John Carey
Michael Fox
Janice Metcalfe
Lina Coletta
Richard Tkacz
Henri Huneault

Aquatic Ecology Division

Brian Brownlee
Alex Bobrowski
Gordia MacInnis

GRAND RIVER CONSERVATION AUTHORITY

Staff

Peter Mason
Warren Yerex
Don Leslie
Ron Ross

Students

Gill Yeats
Elizabeth McMurray
Susan Sieradzlci
Robert Purdy