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VOLATILE CONTAMINANT SURVEY OF THE ST. CLAIR RIVER

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EXECUTIVE SUMMARY

The analysis of over 60 bottom water samples of the St. Clair River indicates significant sources of several volatile contaminants in the industrial area below Sarnia. In total, 34 different compounds were observed with the method employed, however only 23 of these have been identified, including chloro-, fluoro, and bromo-methane derivatives, and several chlorinated ethanes, ethylenes, propanes, and propenes. The two contaminants perchloroethylene and carbon tetrachloride were found at much higher average concentrations than most others and total loadings of the order of 100 $kg.day^{-1}$ are indicated. The contaminants are shown to spread slowly through horizontal mixing in the river.

RÉSUMÉ EXÉCUTIF

L'analyse de plus de 60 échantillons d'eau au fond de la rivière St. Clair a révélé des sources importantes de plusieurs contaminants volatils dans la zone industrialisée au sud de Sarnia. En tout, on a signalé 34 composés différents avec la méthode. Toutefois, seulement 23 d'entre eux ont été identifiés, y compris les dérivés de chloro-fluoro-méthane et de bromo-méthane, et nombre d'éthanes chlorés, d'éthylènes, de propanes et de propènes. Les contaminants, le perchloroéthylène et le tétrachlorure de carbone, ont été décelés dans des concentrations supérieures à la moyenne des autres contaminants et les charges totales étaient de l'ordre de 100 $kg/jour^{-1}$. Les contaminants se déplacent lentement par voie de brassage horizontal dans le cours d'eau.

ENQUÊTE SUR LES CONTAMINANTS VOLATILS DANS LA RIVIÈRE ST. CLAIR

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RÉSUMÉ

L'analyse de plus de 30 hydrocarbures halogènes volatils dans les échantillons d'eau au fond de la rivière St. Clair à 20 transects, chacun d'eux couvrant trois stations à 10 m, 25 m et 100 m de la rive, a révélé des quantités considérables de perchloroéthylène et de tétrachlorure de carbone dans la zone à proximité de la rive, le long d'un secteur très industrialisé au sud de Sarnia, en Ontario. Les charges minimales de 48 kg/jour^{-1} de perchloroéthylène et de 32 kg/jour^{-1} de tétrachlorure de carbone ont été calculées à partir des concentrations observées. De plus, de plus petites charges de 1,1,1- trichloroéthane, de chloroforme et d'une variété d'autres composés volatils, dont certains n'ont toujours pas été identifiés, ont été signalées.

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ABSTRACT

Analysis of over 30 volatile halocarbon contaminants in St. Clair River bottom water samples at 20 transects, each covering the three stations at 10 m, 25 m, and 100 m offshore shows considerable inputs of perchloroethylene and carbon tetrachloride in the nearshore zone along the highly industrialized area below Sarnia, Ontario. Minimum loadings of 48 $kg.day^{-1}$ perchloroethylene and of 32 $kg.day^{-1}$ carbon tetrachloride are calculated from the observed concentrations. In addition, smaller loadings of 1,1,1-trichloroethane, chloroform, and a variety of other volatile compounds, some of which have yet to be identified, are indicated.

INTRODUCTION

The recent discovery of "blobs" of liquid organochlorine contaminants along parts of the upper St. Clair River near Sarnia, Ontario, has spurred an intensive investigation of the source(s) and spread of these materials. Previous data showed high concentrations of several volatile organochlorine contaminants, notably perchloroethylene (TECE) and carbon tetrachloride (CTC) entering Lake St. Clair from the eastern arms of the St. Clair River. Further investigations as to the location and distribution of these materials in the St. Clair River bottom water were now undertaken along 20 nearshore transects on both sides of the St. Clair River. This report presents the results of this investigation on over 30 volatile halocarbons and related contaminants.

EXPERIMENTAL

Bottom water samples were taken at the 60 stations on 20 transects shown in Figure 1 between November 2 and December 4, 1985 with vertical and horizontal Van Dorn samplers. In the sample descriptions, the letters A, B, and C denote sampling stations 10 m, 25 m, and 100 m offshore, respectively, along the transects denoted by numerals. The samples were transferred to 250 mL screwcap glass bottles, filled right to the top and were kept at or below room temperature until processing. The samples were processed at CCIW within two days from collection according to the procedure by Comba and Kaiser (1983).

For the analysis, a Hewlett-Packard 5890 gas chromatograph with a 30 m OV-1 capillary column was used. The temperature regime was a 2 min. hold at -20°C, followed by a programming rate of $4°C.min^{-1}$ to 70°C. The instrument was run in split (15:1)/splitless mode with the initial 0.2 min in splitless mode, using 100 µL head space volume injections. Other instrument conditions were: injector temperature 80°C; electron capture detector temperature 280°C; carrier gas hydrogen at $0.3\ mL.min^{-1}$.

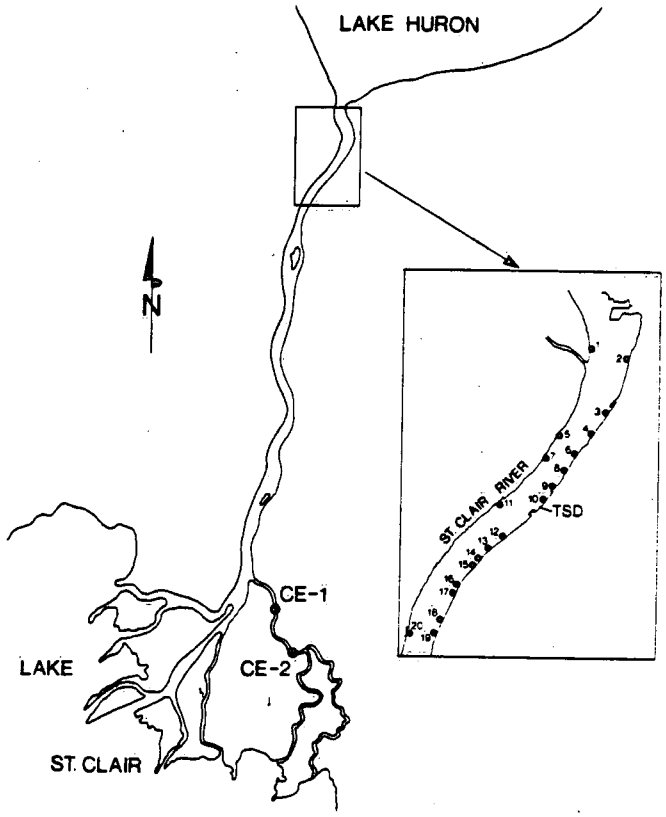

FIGURE 1 Sampling transects in the upper St. Clair River.

It should be noted here that, under the employed experimental conditions, some of the chromatographic separations are inadequate to allow positive identification of the observed chromatographic peaks. For example, the compounds eluting at retention times (RT) 3.39 and 3.42 min., respectively, should be considered as tentatively identified only at this time. The samples will be analyzed further using different chromatographic conditions and/or different detector systems, such as mass spectrometric detector, in order to confirm presently ascribed identities and to elucidate those of the unknown compounds. At present, the following compounds have been confirmed: perchloroethylene, carbon tetrachloride, chloroform, methylene chloride, 1,1,1-trichloroethane, trichloroethylene, 1,2-dichloroethylene, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,2-trichloroethane, tribromomethane, and 1,1,2,2-tetrachloroethane.

RESULTS

Representative results for seven of the 60 stations are summarized in Table 1, which shows the analytical data for each compound. The complete list of data is available on request from the authors. Table 1 lists over 30 compounds, of which so far only a limited number has positively been identified. Therefore, all data in Table 1 are given in form of detector response units, as obtained from the instrument's electronic integration system.

TABLE 1 **Levels of volatile halocarbon contaminants in some representative St. Clair River bottom water samples. All values given are electron capture detector response units for comparison of the known with the unknown contaminants.**

RT (min)	Compound	Station						
		2-B	8-B	10-B	12-B	14-B	16-B	19-B
2.87	FR-11	440	437	281	378	27728	564	564
3.18	unknown							
3.39	1,1-DCE							
3.42	CS_2				82	70		3721
3.71	$MeCl_2$	312	148	185	691	183	207	30449
4.12	unknown					2124	9	
4.68	1,2-DCE							
4.96	1,1-DCA					569		
6.06	unknown							
6.19	CH_2BrCl	49					26	
6.51	$CHCl_3$	114	151	373	1357	4570	422	1631
7.13	unknown						13	
7.27	2,2-DCPA	8			14	16		13
7.41	1,2-DCA							
7.57	unknown				493	271	573	697
7.73	1,1,1-TCA	118	197	245	2529	1741	2059	3567
8.44	CTC	108	193	277	14434	5830	8277	16917
9.52	1,2-DCP							
9.61	CH_2Br_2			6	40	140	152	120
9.78	TCE		34	18	387	60	43	77
10.11	$CHBrCl_2$	100	95	82	1372	977	1557	3446
10.79	1,3-DCPE							16
12.71	$CBrCl_3$					10	19	5
13.13	1,1,2-TCA			9	60	59	86	108
14.01	$CHBr_2Cl$	72	9	3		20	28	148
14.2	1,3-DCPA		17	5		11		5
14.46	unknown							25
15.32	TECE	235	259	132	51164	19440	22638	69546
16.95	unknown				96	62	119	172
17.73	unknown							
17.94	$CHBr_3$		7			20		26
19.45	$C_2H_2Cl_4$							
21.92	unknown					94		
22.34	unknown							

Of the 34 compounds investigated, most are found in trace quantities (1 to 100 counts) only. However, a number of compounds are observed at low concentrations (10 to 1,000 counts) in almost every sample and several contaminants are found in higher concentrations (1,000 to 1,000,000 counts). The latter include primarily perchloroethylene (TECE), with the retention time (RT) of 15.32 min, carbon tetrachloride (CTC) with RT 8.44 min, 1,1,1-trichloroethane (1,1,1-TCA) with RT 7.73 min, an unidentified compound with RT 7.57 min, and chloroform ($CHCl_3$) with RT 6.51 min.

Several of the compounds commonly observed at low levels are found at much higher concentrations in a few samples. Among these are Freon 11 (FR-11) with RT 2.87 min in sample 13-A, methylene chloride ($MeCl_2$) with RT 3.71 min in samples 2-A, 6-B, 16-A, and 19-B, a compound with RT 6.19 min, tentatively identified as CH_2BrCl at station 2-A, bromodichloromethane ($CHBrCl_2$) with RT 10.11 at stations 17-C and 1-C, and dibromomethane (CH_2Br_2) with RT 9.61 min at station 15-B.

Table 2 gives the concentrations of the four major volatile halocarbon contaminants, namely perchloroethylene, carbon tetrachloride, 1,1,1-trichloroethane, and chloroform at the 60 sampling stations in the upper St. Clair River. For comparison, also the data for one water sample from the Township Ditch (TSD), an industrial outfall at Sarnia, and two from Chenal Ecarte (CE), a St. Clair River channel approximately 40 km below Sarnia, are given in Table 2. The TSD sample shows high values of most of the volatile contaminants found in the river, particularly also high levels of chloroform, which is both an industrial solvent and a byproduct of the chlorination of raw and waste water. In contrast, the CE samples show much lower levels of all compounds.

TABLE 2 **Concentrations of the four major volatile halocarbon contaminants in bottom water samples from the upper St. Clair River, the Township Ditch (TSD), and Chenal Ecarte (CE). All values in $ng.L^{-1}$.**

Station No.	2A	2B	2C	3A	3B	3C	4A	4B	4C
$ng.L^{-1}$ TECE	2	2	3	3	12	2	6	5	489
$ng.L^{-1}$ CTC	16	2	3	5	11	3	15	2411	48
$ng.L^{-1}$ 111TCA	4174	5	12	7	5	6	21	18	25
$ng.L^{-1}$ CHC13	35	5	8	10	9	5	10	12	8
Station No.	6A	6B	6C	8A	8B	8C	9A	9B	9C
$ng.L^{-1}$ TECE	21	2	6	2	2	10	4	2423	71
$ng.L^{-1}$ CTC	7	2	7	5	4	5	3	4	7
$ng.L^{-1}$ 111TCA	12	12	9	9	8	10	22	19	19
$ng.L^{-1}$ CHC13	10	20	8	6	6	12	11	7	11
Station No.	10A	10B	10C	12A	12B	12C	13A	13B	13C
$ng.L^{-1}$ TECE	246	2	12	552	409	8	646	259	4
$ng.L^{-1}$ CTC	177	6	4	747	289	4	1210	389	5
$ng.L^{-1}$ 111TCA	4 21	10	8	330	101	9	456	148	7
$ng.L^{-1}$ CHC13	13	15	134	46	54	27	65	28	17
Station No.	14A	14B	14C	15A	15B	15C	16A	16B	16C
$ng.L^{-1}$ TECE	440	156	9	593	474	95	438	181	33
$ng.L^{-1}$ CTC	544	117	8	511	462	36	472	166	29
$ng.L^{-1}$ 111TCA	230	70	8	224	198	15	220	82	13
$ng.L^{-1}$ CHC13	34	183	7	72	36	28	52	17	24
Station No.	17A	17B	17C	18A	18B	18C	19A	19B	19C
$ng.L^{-1}$ TECE	740	471	399	464	495	102	253	556	170
$ng.L^{-1}$ CTC	427	274	192	249	269	105	286	338	164
$ng.L^{-1}$ 111TCA	196	127	89	111	118	44	125	143	60
$ng.L^{-1}$ CHC13	37	32	58	273	33	24	30	65	32
Station No.	1A	1B	1C	5A	5B	5C	7A	7B	7C
$ng.L^{-1}$ TECE	8	4	5	5	5	4	663	8	7
$ng.L^{-1}$ CTC	4	3	51	5	36	6	4	3	4
$ng.L^{-1}$ 111TCA	23	10	7	24	26	20	43	41	16
$ng.L^{-1}$ CHC13	30	8	10	26	17	6	14	13	10
Station No.	11A	11B	11C	20A	20B	20C	TSD	CE-1	CE-2
$ng.L^{-1}$ TECE	2	6	5	4	2	2	567	83	104
$ng.L^{-1}$ CTC	2	2	2	3	3	2	95	64	62
$ng.L^{-1}$ 111TCA	11	12	12	8	8	7	103	61	57
$ng.L^{-1}$ CHC13	9	9	9	12	8	26	4482	30	36

DISCUSSION

Chemical analysis of the liquid "tar" patches from the St. Clair River bottom taken in 1984 showed the major constituents to be perchloroethylene (TECE) at approximately 60% and carbon tetrachloride (CTC) at approximately 30% (Canada and Ontario, 1985). As both of these compounds have also been identified as the predominant volatile halocarbons entering Lake St. Clair from the St. Clair River (Kaiser and Comba, 1985), they were also expected to be present at comparatively high concentrations in the river water. Indeed, with only a few exceptions at the upstream stations, both TECE and CTC were the major contaminants in the river bottom water samples discussed here.

Figure 2 shows a bargraph of the TECE concentrations in a logarithmic plot by stations. As evident, low concentrations of 1 to 10 $ng.L^{-1}$ are prevalent in the samples from both nearshore and offshore stations on the western shore of the river (stations 1, 5, 7, 11, and 20). Except for two samples, the same is observed for the upstream locations on the eastern shore (stations 2, 3, 4, 6, and 8). Downstream from station 8, nearshore stations (A and B) show strongly elevated concentrations throughout. In fact, the highest value observed 2411 $ng.L^{-1}$, was found at station 9-B. It is further apparent that there are steady to slightly declining TECE levels in the nearshore samples (A and B) downstream from station 12. At the same time, the TECE concentrations in the offshore samples (C) increase between stations 12 and 19. This observation is consistent with plume models derived from experimental observations (Lau et al., 1986) which show the slow spreading of a contaminant plume from inputs along the river shore.

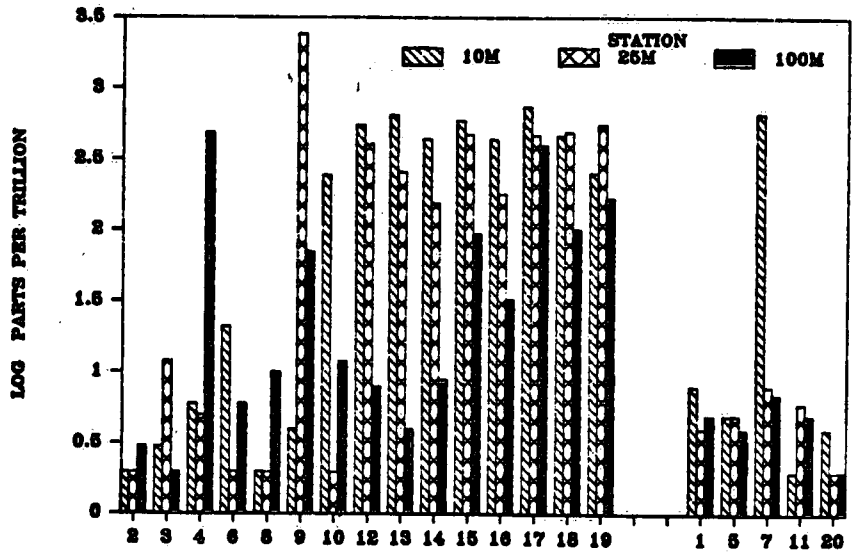

FIGURE 2 Logarithmic scale bargraph of perchloroethylene concentrations in $ng.L^{-1}$ in the upper St. Clair River in November, 1985.

If the TECE levels of approximately 500 $ng.L^{-1}$ observed at stations 17 to 19 can be considered to represent average TECE levels, and given a mean velocity of approximately 1.5 $m.sec^{-1}$, and mean depths of 4, 7, and 10 m at the substations A, B, and C, respectively, the total mass of TECE moving downstream can be calculated to approximately 48 $kg.day^{-1}$. This loading figure is consistent with those calculated from various industrial sewer outfalls. For example, the four sewers at the First Street area (near station 12) have been shown to contribute approximatey 30 $kg.day^{-1}$ TECE (Hamdy et al., 1986).

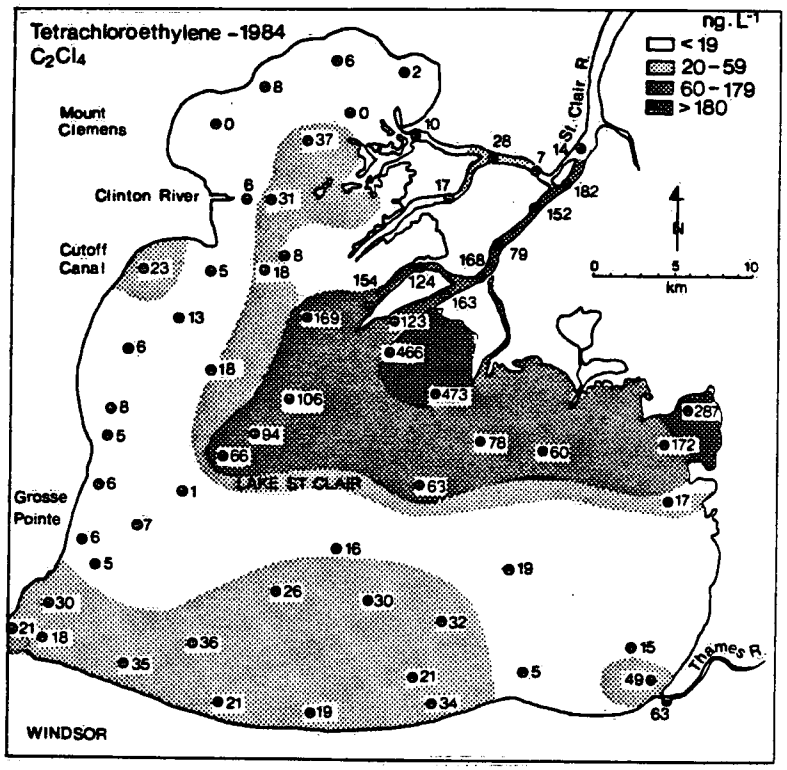

Figure 3 Distribution of perchloroethylene in Lake St. Clair and lower St. Clair River surface water samples in June, 1984.

Although their combined flow is only a small fraction of that of all outfalls along the St. Clair River, TECE concentrations as high as 1.1×10^6 ng.L^{-1} have been observed in these effluents, hence their total TECE loading is quite significant. The loading calculated from the present transect data (48 kg.day^{-1}) is also consistent, in fact identical, with that calculated from Lake St. Clair data, which is also 48 kg.day^{-1}, based on a mean of 209+125 ng.L^{-1} TECE at 13 stations in the St. Clair River delta and northern parts of Lake St. Clair. The distribution of TECE in Lake St. Clair, based on surface water samples taken in summer 1984 is shown in Figure 3 (Kaiser and Comba, 1985).

Figure 4 shows a bargraph of carbon tetrachloride (CTC) concentrations in a logarithmic plot by stations. As for TECE, the CTC levels are in the 1 to 10 ng.L^{-1} range for most stations along the western shore (stations 1, 5, 7, 11, and 20) and also the upstream stations on the eastern shore (stations 2, 3, 6, 8, and 9). However, a CTC concentration of over 2000 ng.L^{-1} was found at station 4-B, just upstream of the railway tunnel. Strongly elevated CTC levels were also observed at all sites downstream from station 10-A. As for TECE, the input of CTC appears primarily to be in the nearshore zone (stations A and B), as evident from the pronounced concentration gradients between the nearshore and offshore (station C) zones for the sampling sites 10 to 14. Again, as for the TECE, this gradient diminishes going downstream and the CTC concentrations at the offshore stations 17-C, 18-C, and 19-C are close to those of the respective nearshore values.

Taking the observed CTC concentration at station 19 (mean of 19-A, 19-B, and 19-C is 326+203 ng.L^{-1}), a continuous loading of approximately 32 kg.day^{-1} is calculated. This compares with approximately 75 kg.day^{-1} CTC calculated from its concentrations in the St. Clair River delta and Lake St. Clair, as shown in Figure 5 (Kaiser and Comba, 1985).

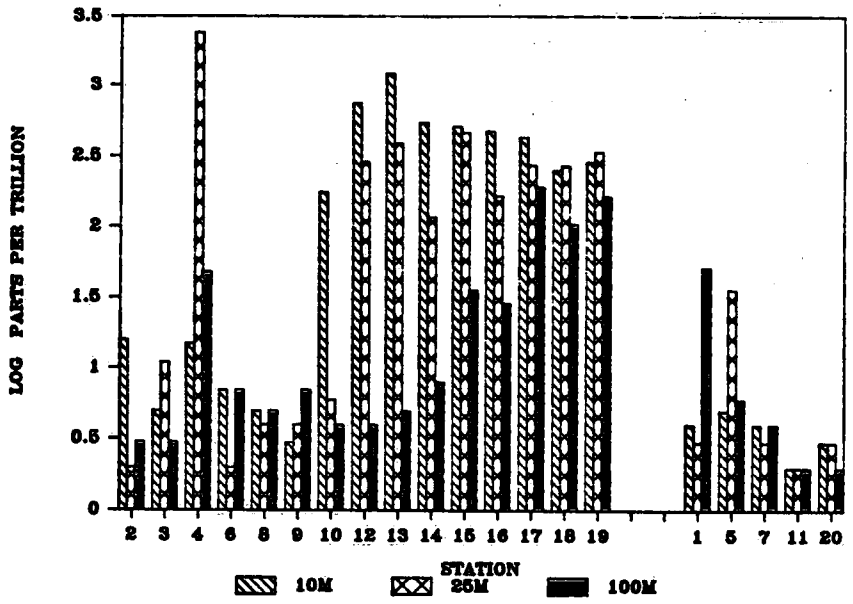

Figure 4 Logarithmic scale bargraph of carbon tetrachloride concentrations in ng.L^{-1} in the upper St. Clair River in November, 1985.

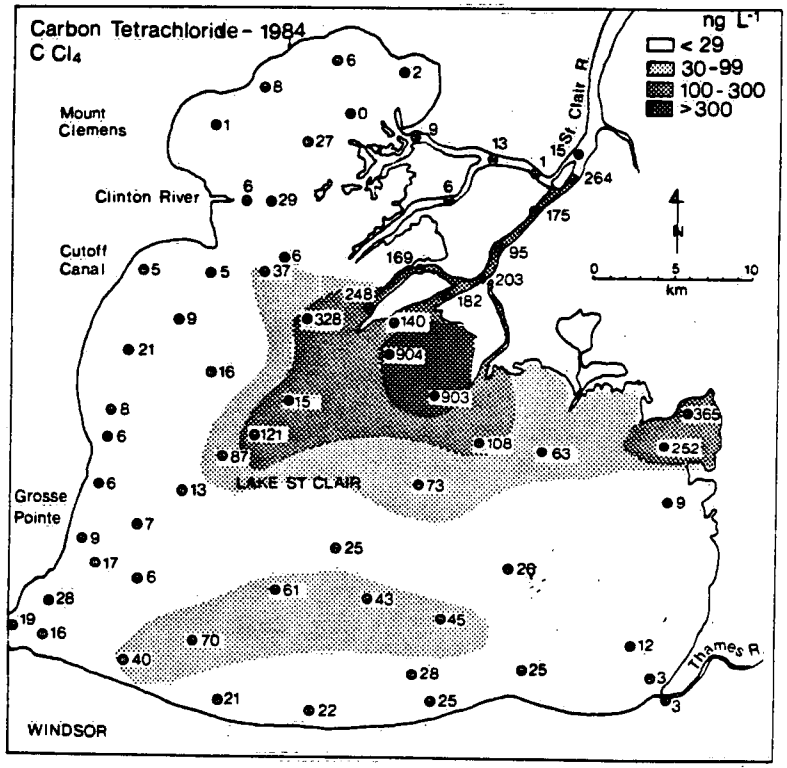

Figure 5 Distribution of carbon tetrachloride in Lake St. Clair and lower St. Clair River surface water samples in June, 1984.

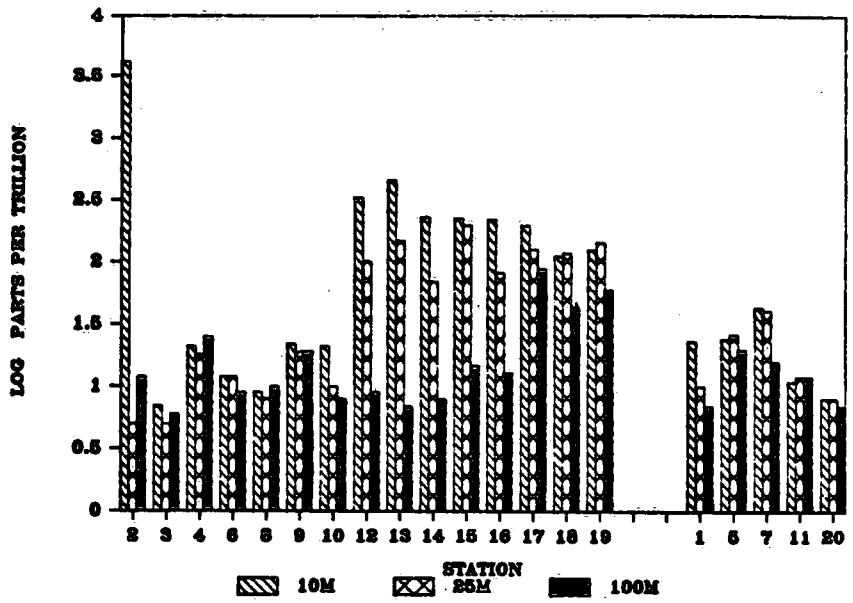

Figure 6 Logarithmic scale bargraph of 1,1,1-trichloroethane concentrations in ng.L^{-1} in the upper St. Clair River in November, 1985.

Figure 6 shows a bargraph of 1,1,1-trichloroethane (111-TCA) in the same bottom water samples. Except for one very high value at the nearshore station 2-A, its concentrations generally range between 10 and 500 ng.L^{-1}. However, as for TECE and CTC, a sharp increase of 111-TA levels is observed for the nearshore stations 12-A and downstream from there. Again, slow horizontal mixing of the plume is evident between stations 12 and 19, resulting in increased concentrations at the offshore stations when going downstream. Assuming a mean of approximately 100 ng.L^{-1}, a loading of 5 kg.day^{-1} 1,1,1-trichloroethane is calculated. This compares with a mean of 54 ng.L^{-1} at 13 Lake St. Clair stations and a loading of 12 kg.day^{-1} calculated from this mean times one half of the total river flow.

Figure 7 shows a logarithmic scale bargraph for chloroform concentrations at the 60 sampling sites. In general, levels of 10 to 20 ng.L^{-1} are observed on both sides of the river. As for the other volatile contaminants, increased levels are found downstream from station 10, with the highest level of 273 ng.L^{-1} found at station 18-A. In contrast to the compounds perchloroethylene, carbon tetrachloride, and 1,1,1-trichlorethane, chloroform is primarily a byproduct of raw and waste water chlorination and its industrial use as solvent or process material is smaller. The observed concentrations are to be expected from the large volume of cooling water discharged along the St. Clair River. In addition, intermittent chloroform discharges between stations 10 and 19 are apparent from the strong fluctuations of the chloroform levels in that reach of the river. Similarly, fluctuating levels of chloroform were observed in water samples from Lake St. Clair in summer 1984, indicating intermittent discharges of higher concentrations on lower level background concentrations in the St. Clair River.

Overall, the observed levels of perchloroethylene, carbon tetrachloride, 1,1,1-trichloroethane, and chloroform in the upper St. Clair River, particularly between stations 12 and 19 on the eastern shore, account for roughly one and one half times the loadings found to be emitted from the First Street sewer complex at Sarnia. Therefore, it appears that for all of these contaminants, but especially for perchloroethylene and carbon tetrachloride, additional loading of up to the same order of magnitude as from the First Street sewer complex may exist.

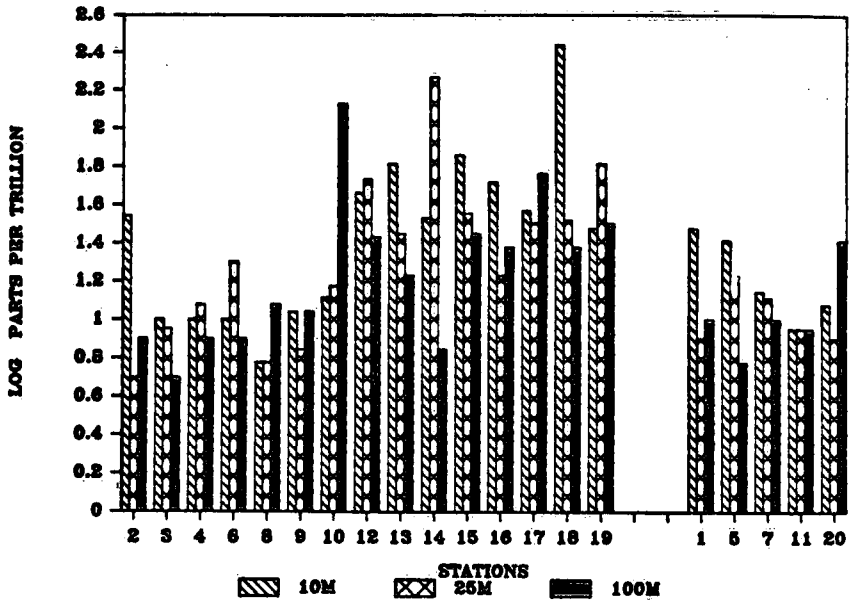

Figure 7 Logarithmic scale bargraph of chloroform concentrations in $ng.L^{-1}$ in the upper St. Clair River in November, 1985.

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