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Organic Compounds Found Near Dump Sites in Niagara Falls, New York

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■ Water and sediment samples were taken from sites adjacent to hazardous waste disposal areas in Niagara Falls, NY. The samples were analyzed by gas-chromatographic mass spectrometry. The following compounds were identified: chlorobenzenes, chlorotoluenes, polycyclic aromatic hydrocarbon derivatives, PCBs, trichlorophenol and other phenols, benzotrifluorides, mirex, and phenothiazine. A large number of benzyl derivatives and a few unusual fluorinated compounds were also found; they were probably waste byproducts of the industrial chemical production of benzyl chloride and (trifluoromethyl)chlorobenzene, respectively. The hazardous waste disposal sites were the major sources for most of the compounds which were found.

Introduction

Love Canal is a 6-hta, rectangular site located in the southeast corner of the city of Niagara Falls. Chemicals buried within the boundaries of this unfinished canal 30 yr ago have infiltrated several homes, and some known or presumed carcinogens have been found in their basements (1). Unfortunately, Love Canal is only one of the waste disposal sites in western New York. An interagency task force (state and federal agencies) has identified 152 hazardous waste disposal sites in Erie and Niagara Counties, NY (1). Because leachate from many of these disposal sites could contaminate the Niagara River and because the Niagara River is an important drinking-water source for several United States and Canadian cities and the major source of water for Lake Ontario (2), identifying

the waste industrial organic compounds in the Niagara River–Lake Ontario system is imperative. This paper reports on the identification of anthropogenic organic compounds at three sites in and near the Niagara River.

Experimental Section

The three sampling sites were in the city of Niagara Falls (see Figure 1). The 102nd Street dump site forms a bay 0.8 km long and 0.4 km wide which is actually part of the Niagara River. Four different dump sites make up the shoreline of the 102nd Street bay; it also receives runoff from the Love Canal area through a storm sewer. Bloody Run Creek is 200 m long and is little more than a drainage ditch for the Hyde Park landfill. The third sampling site was Gill Creek, which runs through an industrialized complex; the companies in the complex have several dump sites located on their property (1). All three sampling sites drain directly into the Niagara River.

With the cooperation of the New York State Department of Environmental Conservation, a series of water and sediment samples were collected from these sites during June and November 1979. Gill Creek was sampled midstream at ~100 m upstream from the Niagara River. Bloody Run Creek was sampled at ~30 and 150 m downstream from the boundary of the Hyde Park landfill. The 102nd Street bay was sampled at four places along the bay and ~30 m from the shore.

Water samples were collected in 3.8-L, amber glass bottles with Teflon-lined caps. Sediment samples were collected at each site with a shovel or Eckman dredge and were stored in
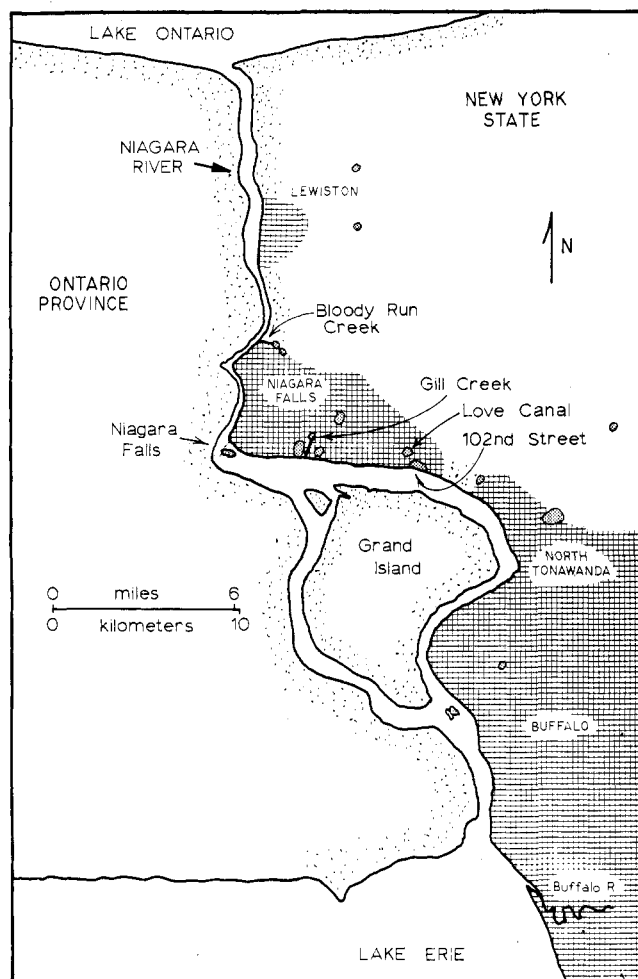
Figure 1. Map of the Niagara River showing the locations of the Bloody Run Creek, Gill Creek, Love Canal, and 102nd Street bay. The cross-hatched areas are built-up cities, and the small striped areas are hazardous waste disposal sites.

1-L glass bottles with Teflon-lined lids. Water samples for volatile analyses and sediment samples were packed in ice to slow biological degradation prior to analysis. Water samples for solvent extraction were immediately preserved by acidification to pH 2 with hydrochloric acid and by adding 250–500 mL of dichloromethane. Sample workup was begun as soon as possible after returning to the laboratory. The sediment samples were kept frozen until analyzed. Analytical techniques for concentration, separation, and identification using solvent extraction, vapor stripping, gas chromatography, and mass spectrometry have been discussed in detail elsewhere (3).

Initial results indicated that most samples were extremely complex, containing high levels of unresolved components along with mixtures of industrial and natural organic compounds. The interferences were removed from the extracts by using a silica gel cleanup procedure. Extracts were evaporated to dryness and transferred to a column (8 cm³) packed with deactivated silica gel (1% water). The samples were then fractionated by successively eluting with 75 mL each of hexane, hexane with 10% dichloromethane, dichloromethane, and methanol. To remove fatty acid interferences, some fractionated extracts were dissolved in dichloromethane and extracted with aqueous NaOH (pH 9–11). Several sediment samples were passed through a colloidal copper column to remove elemental sulfur (3). GC/MS analyses were run on most samples prior to each cleanup procedure to verify that sample integrity was maintained, that contaminants were not

introduced, and that major components were not lost or degraded. Blanks were also run for all extraction and cleanup procedures, and they showed no significant contamination.

Identification of the compounds in these samples was based on coincidence of gas-chromatographic retention times and on equivalence of electron impact and (where possible) chemical ionization mass spectra with those of reference compounds. Those reference compounds not commercially available were synthesized in our laboratory (see below).

It should be emphasized that this study was primarily qualitative in nature. Our principal goal was to identify compounds and their probable sources rather than to measure their exact abundance. For this reason, the concentration data are only semiquantitative. Compounds were quantitated after silica gel fractionation by GC peak heights with a flame ionization detector; an approximate GC response factor was determined with methyl stearate.

Results and Discussion

The organic compounds found in the 102nd Street bay area, Bloody Run Creek, and Gill Creek are listed in Table I. The data include maximum concentrations for major compounds in the sediments. Water samples were not well-quantitated although most compounds which were detected in water were present at levels of 0.1–1 ppb. The structures for a select group of compounds are given in Figure 2. The sources of compounds in Table I can be classified into three general categories: (a) compounds which were known to be in the dump sites, (b) compounds with unknown sources, and (c) compounds which were byproducts of industrial production processes and which were not known to be in the dump sites.

Compounds which had been dumped in large amounts were detected in most water and sediment samples. The Love Canal, 102nd Street, and Hyde Park dump sites all contain large amounts of chlorinated benzenes and toluenes (1), and these compounds (1–12) were present in almost all samples with the highest concentrations in the 102nd Street bay
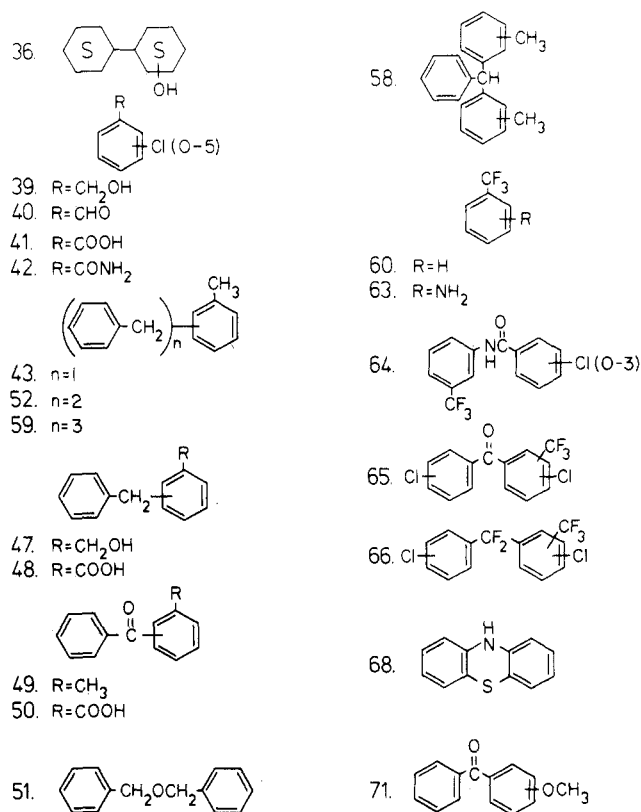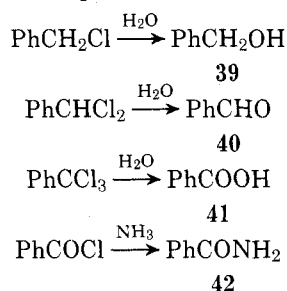

Figure 2. Structures of selected compounds (see Table I).

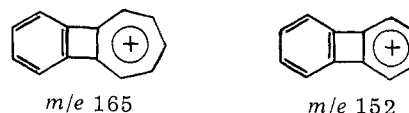## Table I. Organic Compounds Identified in the Niagara River Watershed (ppm) [a]

no.	compd	102nd Street	Bloody Run Creek	Gill Creek	no.	compd	102nd Street	Bloody Run Creek	Gill Creek
	Chlorobenzenes					**C_{14}-Benzyl Derivatives**			
1	chlorobenzene	NA	+	+	43	(methylphenyl)phenylmethane [d]	90	+	−
2	dichlorobenzenes	+	+	+	44	chloro(methylphenyl)phenylmethanes	20	+	−
3	trichlorobenzenes	40[b]	8	+	45	dichloro(methylphenyl)phenylmethanes	−	+	−
4	tetrachlorobenzenes	200	25	+	46	trichloro(methylphenyl)phenylmethanes	30	+	−
5	pentachlorobenzene	100	10	−	47	(phenylmethyl)benzenemethanols [d]	4	−	−
6	hexachlorobenzene	8	10	30	48	(phenylmethyl)benzoic acid [d]	+	−	−
	Chlorotoluenes				49	methylbenzophenone [d]	7	+	−
7	dichlorotoluenes	20	90	−	50	benzoylbenzoic acid [d]	+	−	−
8	trichlorotoluenes	100	50	−	51	benzyl ether [d]	70	+	−
9	tetrachlorotoluenes	40	10	−		**C_{21}-Benzyl Derivatives**			
10	pentachlorotoluenes	40	5	−	52	methylbis(phenylmethyl)benzenes [d]	30	−	−
11	hexachlorotoluenes	40	−	−	53	chloro(methyl)bis(phenylmethyl)benzenes [c]	2	−	−
12	heptachlorotoluenes	20	−	−	54	dichloro(methyl)bis(phenylmethyl)benzenes [c]	9	−	−
	Polycyclic Aromatic Hydrocarbons and Derivatives				55	trichloro(methyl)bis(phenylmethyl)benzenes [c]	5	−	−
13	methylnaphthalenes	+	−	−	56	tetrachloro(methyl)bis(phenylmethyl)benzenes [c]	6	−	−
14	C_2-naphthalenes	+	−	−	57	pentachloro(methyl)bis(phenylmethyl)benzenes [c]	4	−	−
15	C_3-naphthalenes	+	−	−	58	bis(methylphenyl)phenylmethane [d]	20	+	−
16	chloronaphthalene	20	−	−		**C_{28}-Benzyl Derivative**			
17	dichloronaphthalene	8	−	−	59	methyltris(phenylmethyl)benzenes [d]	6	−	−
18	trichloronaphthalene	6	−	−		**Fluorine-Containing Compounds**			
19	biphenyl	8	−	−	60	benzotrifluoride [d]	−	+	−
20	phenanthrene	−	+	−	61	chlorobenzotrifluoride	−	+	−
21	chlorophenanthrene	−	+	−	62	dichlorobenzotrifluoride	−	+	−
22	dichlorophenanthrene	20	+	−	63	3-aminobenzotrifluoride [d]	−.	+	−
23	trichlorophenanthrene	−	+	−	64	N-(3-trifluoromethyl)phenylbenzamide (0–3 Cl) [d]	−	+	−
24	pyrene	+	−	−	65	dichloro(trifluoromethyl)benzophenone [d]	−	25	−
25	fluoranthene	+	−	−	66	dichloro(trifluoromethyl)-α,α-difluorodiphenylmethane [d]	−	15	−
	Polychlorinated Biphenyls					**Miscellaneous**			
26	dichlorobiphenyls	−	−	100	67	mirex	−	+	−
27	trichlorobiphenyls	−	−	300	68	phenothiazine [d]	−	−	80
28	tetrachlorobiphenyls	−	5	600	69	phenyl ether	20	+	−
29	pentachlorobiphenyls	−	−	300	70	DDE (1,1'-(dichloroethylidene)bis(4-chlorobenzene)	−	+	−
30	hexachlorobiphenyls	−	−	300	71	methoxybenzophenone [d]	−	+	−
	Phenols				72	chloromethoxybenzophenone	−	+	−
31	phenol	+	NA	−	73	chlorohydroxybenzophenone	−	15	−
32	dichlorophenol	+	2	−	74	aminoacetophenone	+	−	−
33	trichlorophenol	+	5	−	75	1-dodecanethiol	3	−	−
34	(1,1,3,3,-tetramethylbutyl)phenol	+	+	−	76	trichloroethylene	NA	+	+
	Cyclohexane Derivatives				77	tetrachloroethylene	NA	+	+
35	BHC (hexachlorocyclohexane)	10	+	−	78	hexachlorobutadiene	NA	+	+
36	cyclohexylcyclohexanol [d]	30	−	−	79	furan	NA	−	+
37	cyclohexylcyclohexanone	5	−	−					
38	phenylcyclohexane	+	−	−					
	C_7-Benzyl Derivatives								
39	benzyl alcohols (0–5 Cl) [d]	+	−	−					
40	benzaldehydes (0–5 Cl) [d]	+	−	−					
41	benzoic acids (0–5 Cl) [d]	+	−	−					
42	benzamides (0–4 Cl) [d]	+	−	−					

[a] NA indicates that sample was not analyzed for this compound. + indicates that compound was detected in water at a level of 0.1–1 ppb or in sediment at a level of 0.5–2 ppm but was not quantitated. − indicates that compound was not detected in water or in sediment; lower limits of sensitivity are ca. 0.1 ppb in water and 0.5 ppm in sediment. [b] Maximum level in ppm of compound detected in sediment. [c] Or another isomer. [d] For structure, see Figure 2.

sediments. Chloro-, dichloro-, and trichlorobenzenes (1–3) were found in water from Bloody Run Creek and Gill Creek. Tetrachloro-, pentachloro-, and hexachlorobenzenes (4–6) are probably byproducts of trichlorobenzene production (4). BHC (35), dichlorophenol (32), and trichlorophenol (33) were dumped in large amounts and were present in water and sediment samples from the 102nd Street bay and Bloody Run Creek. Chloronaphthalenes (16–18) and dodecanethiol (75) had been dumped in either the Love Canal or the 102nd Street sites (1). Mirex (67) was found in sediment of Bloody Run Creek and probably originated from the Hyde Park dump which contains 4100 metric tons of hexachlorocyclopentadiene wastes (1).

The sources of some compounds that occurred in major amounts have not been identified. Although most of these compounds probably leached from dump sites, they did not appear on any list of compounds dumped in western New York (1). Chlorophenanthrenes (21–23) were identified in both 102nd Street bay and Bloody Run Creek sediments. Unusual cyclohexane derivatives (36–38) were also detected at 102nd Street bay. Very high levels (av 300 ppm) of PCBs (26–30) and substantial levels (80 ppm) of phenothiazine (68), a pesticide and intermediate in drug syntheses, were detected in Gill Creek. Normally phenothiazine is biodegradable (5), but microbial activity in the Gill Creek sediment may be limited by the high levels of toxic organic compounds.
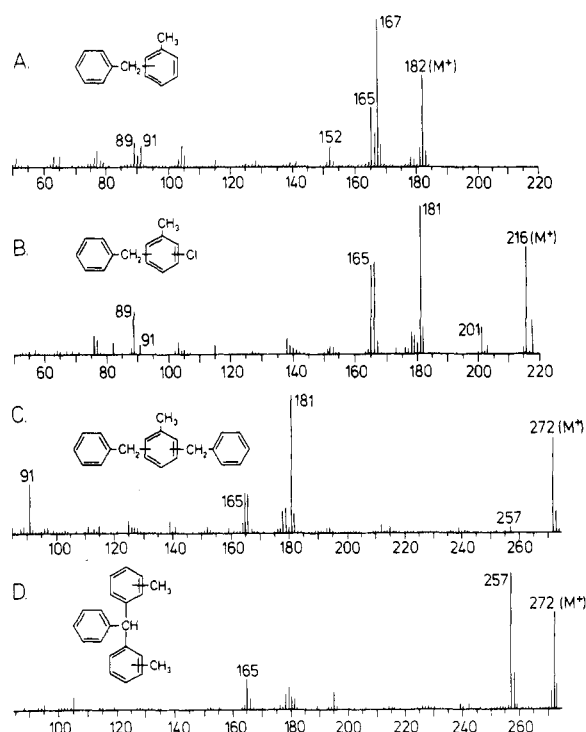
A series of unexpected compounds which were related to benzyl chloride and benzoyl chloride wastes were found at the 102nd Street bay and in Bloody Run Creek. We note that the Love Canal and Hyde Park sites contain 2900 and 8700 metric tons of these wastes, respectively (1). The benzyl derivatives detected in the 102nd Street bay probably came from the Love Canal because the 102nd Street dump is not known to contain benzyl chloride wastes (1) and because the highest concentration of benzyl derivatives in the bay was directly in front of the storm sewer outfall from the Love Canal area (6). Benzyl-related compounds which were commercially produced in the Niagara Falls area before 1970 include benzyl chloride ($PhCH_2Cl$), benzal chloride (α,α-dichlorotoluene, $PhCHCl_2$), benzyl alcohol, benzyl thiocyanate, and benzotrichloride ($PhCCl_3$) (1). Reaction of labile chlorine atoms probably produced compounds 39–42.

$$PhCH_2Cl \xrightarrow{H_2O} PhCH_2OH$$
$$39$$
$$PhCHCl_2 \xrightarrow{H_2O} PhCHO$$
$$40$$
$$PhCCl_3 \xrightarrow{H_2O} PhCOOH$$
$$41$$
$$PhCOCl \xrightarrow{NH_3} PhCONH_2$$
$$42$$

Each of these unsubstituted compounds (39–42) was accompanied by chlorine-substituted analogues containing up to five chlorines (0–5 Cl, see Figure 2). These chlorine atoms were probably derived from chlorine which was required for the synthesis of benzyl chloride and other chlorinated derivatives. Benzyl ether (51) was probably formed by the coupling of two benzyl alcohols.

$$2PhCH_2OH \xrightarrow{-H_2O} PhCH_2OCH_2Ph$$
$$39 \qquad\qquad 51$$

The C_{14}, C_{21}, and C_{28} benzyl derivatives (43–50 and 52–59) were formed by combining benzyl groups. There were no records that these C_{14}, C_{21}, or C_{28}-derivatives had ever been commercially produced or dumped in the Niagara Falls area (1), but large amounts were detected at the 102nd Street bay. None of these benzyl derivatives have been catalogued in the

EPA/NIH Mass Spectral Data Base (7); thus, they were identified by interpretation of their mass spectra and confirmed by synthesis of reference standards.
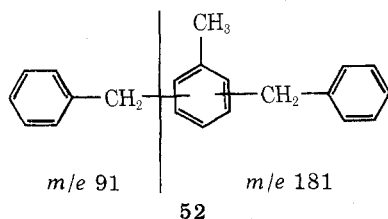
(Methylphenyl)phenylmethane (43) was the key to the identification of the benzyl derivatives (Figure 3A). Its mass spectrum was initially thought to be that of ethylbiphenyl, diphenylethane, or possibly dimethylbiphenyl because it was similar to the catalogued spectra of these compounds (7). However, after reference standards of ethylbiphenyl, diphenylethane, and 4,4'-dimethylbiphenyl were obtained, we found that they had slightly different mass spectra and completely different GC retention times than the unknown. (Methylphenyl)phenylmethane (43) was the only remaining compound with the formula $C_{14}H_{14}$ likely to fit the unknown mass spectrum. The characteristic ions at m/e 165 and 152 are produced by *either* two phenyl rings joined

$$m/e\ 165 \qquad\qquad m/e\ 152$$

directly with an aliphatic carbon attached to one of the rings *or* by two phenyl rings separated by one carbon. After (4-methylphenyl)phenylmethane (43) was synthesized, we found that it and the unknown had identical retention times and mass spectra. After this benzyl dimer was identified, other spectra were readily interpreted. The mass spectrum of chloro(methylphenyl)phenylmethane (44) had the expected shifts due to the addition of chlorine to (methylphenyl)-phenylmethane (43) (Figure 3, A and B).

There were two types of $C_{21}H_{20}$ benzyl derivatives. One type (52) had two benzyl groups linked to each phenyl ring. This compound gave intense fragment ions at m/e 91 and 181 and a low-intensity ion at m/e 257 from methyl loss (Figure 3C).

Figure 3. Electron impact mass spectra of benzyl derivatives: (A) (methylphenyl)phenylmethane (43), (B) chloro(methylphenyl)phenyl-methane (44), (C) methylbis(phenylmethyl)benzene (52), and (D) bis-(methylphenyl)phenylmethane (58).

$m/e\ 91$ | $m/e\ 181$

52

Bis(methylphenyl)phenylmethane (**58**) was the second type of $C_{21}H_{20}$ benzyl derivative, and it had an intense ion at m/e 257 from methyl loss and low-intensity ions at m/e 91 and 181 (Figure 3D):

CH₃   CH₃

CH

$m/e\ 257$

58
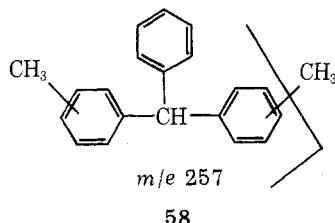
The $(M - 15)^+$ ion of bis(methylphenyl)phenylmethane (**58**) is analogous to the $(M - 15)^+$ ion of (methylphenyl)phenylmethane (**43**); compare Figure 3, A and D.

Most of the C_{14}, C_{21}, and C_{28} benzyl derivatives were probably byproducts of the synthesis of benzyl chloride and related compounds, which were industrially produced by free-radical chlorination of toluene (4):

$$PhCH_3 \xrightarrow{Cl_2} PhCH_2Cl \xrightarrow{Cl_2} PhCHCl_2 \xrightarrow{Cl_2} PhCCl_3$$
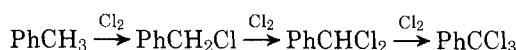
Benzyl chloride readily reacts with toluene at 0–20 °C and atmospheric pressure by Friedel–Crafts alkylation, a reaction which requires a Lewis acid catalyst such as aluminum chloride or ferric chloride and anhydrous conditions (4, 8). In fact, our reference standard of (methylphenyl)phenylmethane (**43**) was synthesized by Friedel–Crafts alkylation.

CH₃   AlCl₃   CH₃

CH₂Cl   +   →   CH₂

43
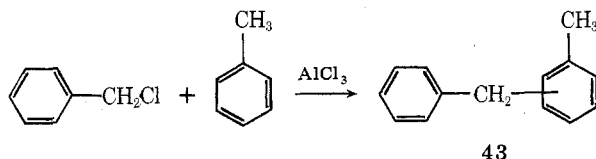
Figure 4 shows synthetic pathways which may explain the accidental synthesis of the benzyl derivatives during industrial benzyl chloride production. The chlorinated C_{14} benzyl derivatives (**44–46**) and chlorinated C_{21} benzyl derivatives (**53–57**) were probably produced by chlorination before or after the Friedel-Crafts reaction, since chlorine is used in the industrial synthesis of benzyl chloride. The ferric chloride catalyst required for the Friedel–Crafts reaction could be produced by corrosion of process equipment with hydrochloric acid. (It is known that benzyl chloride cannot be stored in stainless-steel barrels without a stabilizer that prevents the formation of ferric chloride (4).) After purification of benzyl chloride by distillation, the higher boiling residue contained the C_{14}, C_{21}, and C_{28} benzyl derivatives; wastes in the dump sites were often described as "distillation residues, still bottoms, and tarry residues" (1). The benzyl derivatives could not be formed in the environment by Friedel–Crafts alkylation because this reaction requires anhydrous or highly acidic conditions, but these compounds may have formed when benzyl chloride wastes were stored in steel drums. The benzyl derivatives were not artifacts of the extraction procedure because (methylphenyl)phenylmethane (**43**) was not detected

when uncontaminated sediment was spiked with toluene and benzyl chloride, extracted 3 days later, and analyzed by GC/MS.

Several fluorinated compounds were detected in the Bloody Run Creek which drains the Hyde Park dump; this is not surprising since it is known to contain 7700 metric tons of benzotrifluoride derivatives (1). Benzotrifluorides (**60–62**) were detected in Bloody Run Creek and have also been reported in lower Niagara River fish (9). Compounds **65** and **66** were detected in major amounts in Bloody Run Creek; these were unusual compounds because neither compound has been listed in Chemical Abstracts. The electron impact mass spectrum of compound **65** had a small $(M - F)^+$ ion; however, an unexpected benefit of methane chemical ionization was a much larger $(M - F)^+$ ion (see Figure 5). Figure 6 is the electron impact mass spectrum of compound **66**. Compounds **65** and **66** are clearly related to each other and are probably byproducts of the synthesis of 4-chlorobenzotrifluoride (**61**), which is industrially produced in the following way (4):

CH₃   Cl₂   CCl₃   HF   CF₃

Cl   Cl   Cl

61
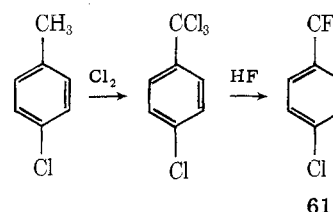
The arrangement of the carbon atoms in compounds **65** and **66** is the same as (methylphenyl)phenylmethane (**43**), which implies that the carbon skeleton of these compounds was produced by a Friedel–Crafts reaction. As outlined in Figure 7, fluorination of the heptachloro, Friedel–Crafts reaction product would produce compound **66** because alkyl chlorines are readily replaced with fluorine while aromatic chlorines are inert to hydrogen fluoride (4). In fact, reference standards for compounds **65** and **66** were synthesized in our laboratory by the reaction sequence given in Figure 7. Compound **66** could not be produced by direct coupling of 4-chlorobenzotrifluoride because the CF_3 group deactivates the aromatic ring so that the Friedel–Crafts reaction does not occur. The ketone group of compound **65** was probably produced by hydrolysis of the heptachloro intermediate (see Figure 7) because compound **66** was resistant to hydrolysis.

The benzyl-related compounds and fluorinated compounds **65** and **66** were waste products associated with benzyl chloride and 4-chlorobenzotrifluoride production, respectively. Although benzyl chloride is no longer produced in the Niagara Falls area, the dump sites probably contain large amounts of these waste products and will remain potential sources of these compounds for years to come. (Methylphenyl)phenylmethane (**43**) is probably biodegradable, but the larger benzyl derivatives (**52–59**) and fluorinated compounds **65** and **66** should be more resistant to biodegradation (10). The larger and more highly halogenated molecules are also lipophilic and should bioaccumulate to a greater extent than the smaller, unhalogenated molecules (11, 12). In fact, benzotrifluorides have been detected in fish from the Niagara River (9); fluorinated compounds **65** and **66** could also have been present in the fish but would not have been reported because of their longer retention times and previously unknown mass spectra. If significant amounts of these waste products are migrating from the dump sites, they should be detectable in Lake Ontario.

It is clear from these data (see Table I) that substantial concentrations of many potentially toxic compounds are present in the water and sediment of the 102nd Street bay, Bloody Run Creek, and Gill Creek. These compounds range from those with known hazardous properties (PCBs and
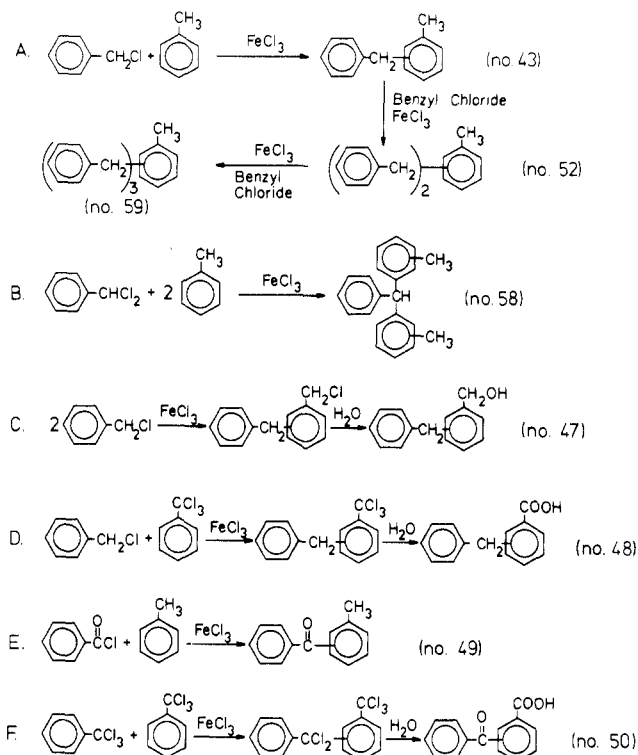
Figure 4. Possible syntheses of benzyl derivatives by Friedel–Crafts reactions.
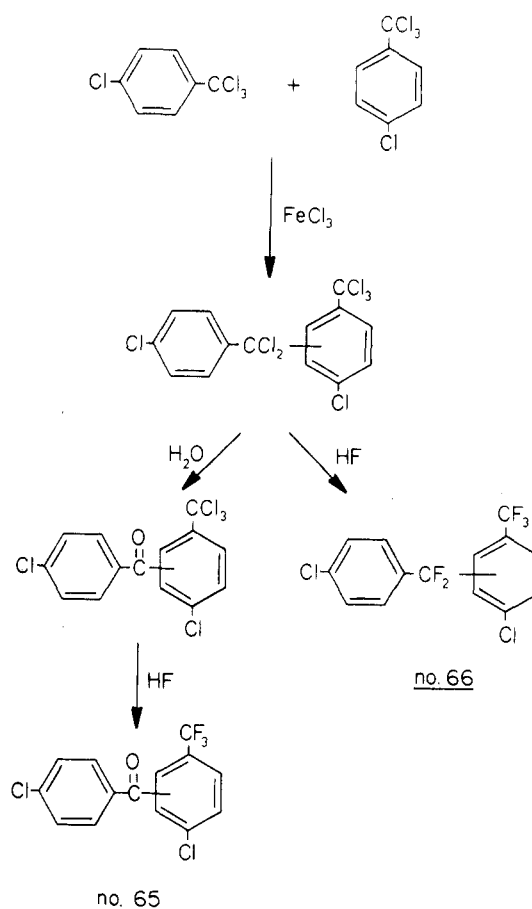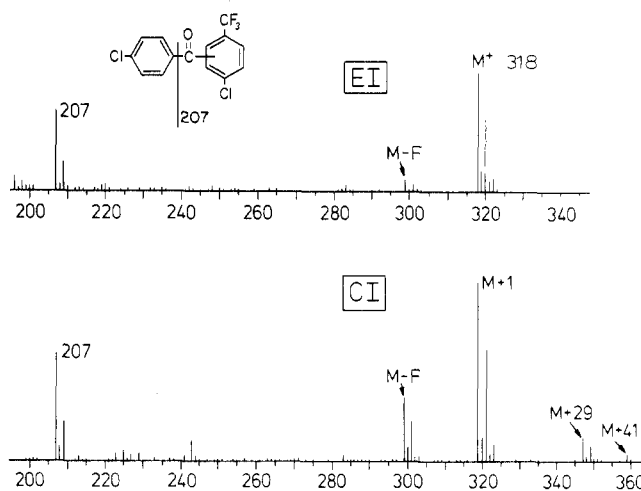

Figure 5. Electron impact and methane chemical ionization mass spectra of dichloro(trifluoromethyl)benzophenone **(65)**.

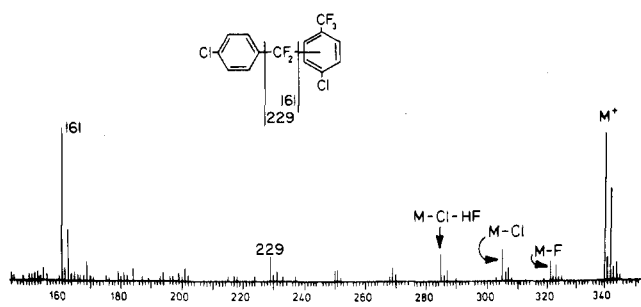**Figure 6.** Electron impact mass spectrum of dichloro(trifluoromethyl)-α,α-difluorodiphenylmethane **(66)**.

no. 65

Figure 7. Possible syntheses of fluorinated compounds **65** and **66**.

polycyclic aromatic hydrocarbons) through those which are highly suspect (chlorobenzenes, chlorotoluenes, and chlorophenols) to those about which nothing is known (the C_{14} and C_{21} benzyl derivatives). The environmental and health hazards associated with our findings depend on the biological effects and the environmental fates of the compounds. Neither of these factors can currently be evaluated for most of the compounds and for this particular aquatic system. Thus, these studies on the identification of the compounds should be followed by studies on their biological and environmental fates.

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NOTES

Sodium Alteration of Chlorine Equilibria. Quantitative Description

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■ Previous data on sodium alterations of hypochlorite equilibria have been reanalyzed under the assumption of existence of the ion pair NaOCl. Computed ion-pair dissociation constants range between 0.9 and 2.3 M.

Introduction

Investigations on the efficiency of microbial inactivation by chlorine have indicated that high salt concentrations can increase rates of inactivation (*1–4*). In particular, the observed enhancement of inactivation by sodium chloride has been observed to be more significant at pH values above the pK_a for dissociation of hypochlorous acid.

Jensen et al. (*3*) have hypothesized that this observed salt effect is due to formation of ion pairs involving OCl^-. In earlier work, Sugam and Helz (*5*) have demonstrated the alteration of the apparent pK_A for hypochlorous acid dissociation in the presence of high concentrations of sodium chloride and developed an empirical correlation for this effect.

To my knowledge, no information has yet been presented describing the formation constant for a putative sodium hypochlorite ion pair. In this communication, the data of Sugam and Helz (*5*) and Jensen et al. (*3*) will be reanalyzed under the assumption of the existence of the species NaOCl per se, and an apparent dissociation constant for this complex will be calculated.

Theory

Since the salt effect inherently operates under conditions of nonnegligible ionic strength, the explicit consideration of activity coefficients is necessary. The HOCl dissociation equilibrium constant may be defined by eq 1.

$$K_A = \gamma_\pm \{H^+\}[OCl^-]/\gamma_0[HOCl] \qquad (1)$$

Square brackets are used to denote molar concentrations while braces are used to denote activity. The variables $\gamma_\pm$ and γ_0 are the activity coefficients for univalent ions and for uncharged HOCl, respectively. On a similar basis, a dissociation constant for the complex NaOCl may be written as eq 2 if it is assumed that the activity coefficient for this complex is identical with that of HOCl.

$$K_D = \gamma_\pm^2[Na^+][OCl^-]/\gamma_0[NaOCl] \qquad (2)$$

Sugam and Helz provide data for a parameter, K_A^{**}, defined on the basis of HOCl and "total hypochlorite" concentrations.

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If the latter term is interpreted as the sum of OCl^- and NaOCl concentrations, it can be shown, by utilization of 1 and 2 that eq 3 must hold

$$K_A^{**}\gamma_\pm/\gamma_0 = K_A + K_A K_D \gamma_\pm^2[Na^+]/\gamma_0 \qquad (3)$$

Jensen et al. (*3*) present data on the fraction of hypochlorite involved in ion-pairing as determined spectrophotometrically. If this fraction is defined as x and if the concentration of HOCl is negligible (i.e., if the pH is much greater than pK_A), then it can also be shown that eq 4 must hold.

$$K_D = \gamma_\pm^2[Na^+](1 - x)/\gamma_0 x \qquad (4)$$

Analysis

Sugam and Helz (*5*) conducted experiments to determine values of K_A^{**} at various temperatures and ionic strengths. Ionic strengths were adjusted by using a synthetic sea-salt mixture, containing the cations sodium, magnesium, and calcium, with sodium being the predominant cation.

According to eq 3, these data may be used to determine values for K_A and K_D providing that activity coefficients are known. The activity coefficient for monovalent ions at low ionic strengths (below 0.2 M) was calculated by using the Davies correlation (*6*). At higher ionic strengths, the mean salt assumption was used in this calculation, and data of Millero (*7*) and Whitfield (*8*) for the activity coefficients of NaCl and KCl, respectively, were used. Additionally, as did Sugam and Helz (*5*), I assumed that the activity coefficient of the hypochlorite anion was identical with that of KCl. The activity coefficient for HOCl (and, it is assumed, NaOCl) was obtained from interpolation of data of Weiss (*9*); this latter correction was always less than 6%. For each temperature range (11.5 ± 1, 18.3 ± 0.5, 25.2, 34.5, and 39.5 °C) values for the two equilibrium constants were calculated. At 25.2 °C, the calculation proceeded by least squares; at all other temperatures constants were determined algebraically. Values for the equilibrium constants thus calculated are shown in Table I.

With regard to the data of Jensen et al. (*3*), in which a

Table I. Equilibrium Constants from Data of Sugam and Helz

temp, °C	K_A, M	pK_A	K_D, M	pK_D
11.5	2.128×10^{-8}	7.667	0.705	0.152
18.3	2.638×10^{-8}	7.567	0.863	0.064
25.2	2.999×10^{-8}	7.520	0.541	0.267
34.5	3.992×10^{-8}	7.389	0.939	0.207
39.5	4.138×10^{-8}	7.371	0.637	0.196