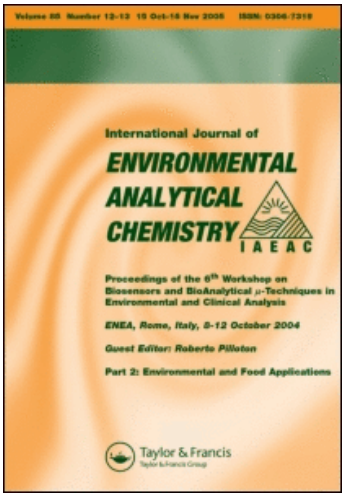

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Analysis of Disinfection By-products in Water and Wastewater†

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Several analytical methods have been utilized to study the products from the chlorination of water from a southern U.S.A. reservoir. Low molecular weight fragments have been assayed by GC/MS following resin accumulation under acidic or basic conditions. High molecular weight products before and after chlorination have been investigated using size HPLC with aqueous solvent and passivated controlled porosity silica columns. The results show a slight lowering of average molecular weight after chlorination, but more importantly, a nearly uniform level of organic chlorine through the polymer. Total organic halogen measurements confirm that the ratio of non-volatile halogen to trihalomethane halogen is at least 2:1 in all cases studied. The ozonation and photolytic ozonation products of 2,4,6,2′,4′,6′-hexachlorobiphenyl have been determined and a reaction scheme proposed.

KEY WORDS: Chlorination, hexachlorobiphenyl, ozonation, surface water, ultraviolet.

INTRODUCTION

This work continues to explore the chemical by-products produced by disinfection processes such as chlorination and ozonation, a subject of great relevance in evaluating water and wastewater treatment practices.

†Presented at the Ninth Annual Symposium on the Analytical Chemistry of Pollutants, Jekyll Island, Georgia, May, 1979.

Much has been written about the potential hazards of the by-products of the chlorination process, particularly the ubiquitous trihalomethanes (THMs).[1]

This paper presents results of laboratory studies which relate to two other important aspects of this problem. The first part of the paper describes recent studies on the non-volatile components in a southern U.S.A. reservoir, before and after chlorination. Size exclusion chromatography[2] and halogen-specific microcoulometry[3] are used to investigate the effects of chlorination on the natural polymers in the lake. Of particular interest is the ratio of non-volatile organic halogen in the polymer (NVTOX) as contrasted to the yield of trihalomethanes.

The second portion of the paper describes the products from incomplete oxidation of 2,4,6,2′,4′,6′-hexachlorobiphenyl (HCB) using ozone and ozone with 254 nm ultraviolet radiation,[4] and proposes a reaction scheme to account for these products.

EXPERIMENTAL

Materials

Water was collected from Cross Lake near Shreveport, Louisiana on several occasions during the late winter and early spring of 1979, during which the lake was in a non-stratified condition. Samples were collected near the intake of the Thomas L. Amiss treatment plant at a depth of approximately one-half meter. Characteristics of the water during this period are shown in Table I.

TABLE I
Characteristics of Cross Lake water
(0.45 μ filtrate)

Color units)	110
pH at 25°C	7.5
Ammonia N mg/L	0.2
Organic N mg/L	0.6
Total P mg/L	0.1
COD mg/L	35
Soluble TOC mg/L	11.0 ± 0.4

2,4,6,2′,4′,6′-hexachlorobiphenyl was obtained from Analabs, Inc. and used as received. Solvents were assayed by chromatography and were the best grades available (pesticide or nanograde).

Chlorination of Cross Lake water

The analytical schemes shown in Figures 1 and 2 were utilized to examine the lake water for volatile and non-volatile organic compounds before and after

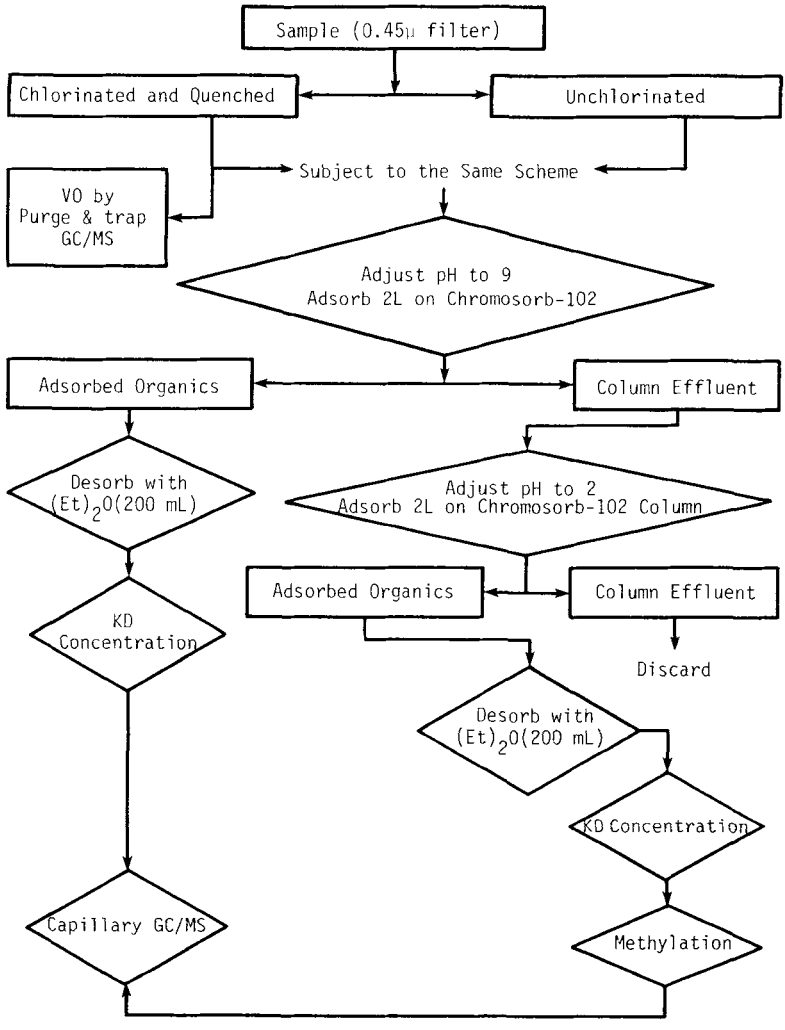

FIGURE 1 Scheme for the separation and analysis of volatile products of water chlorination.

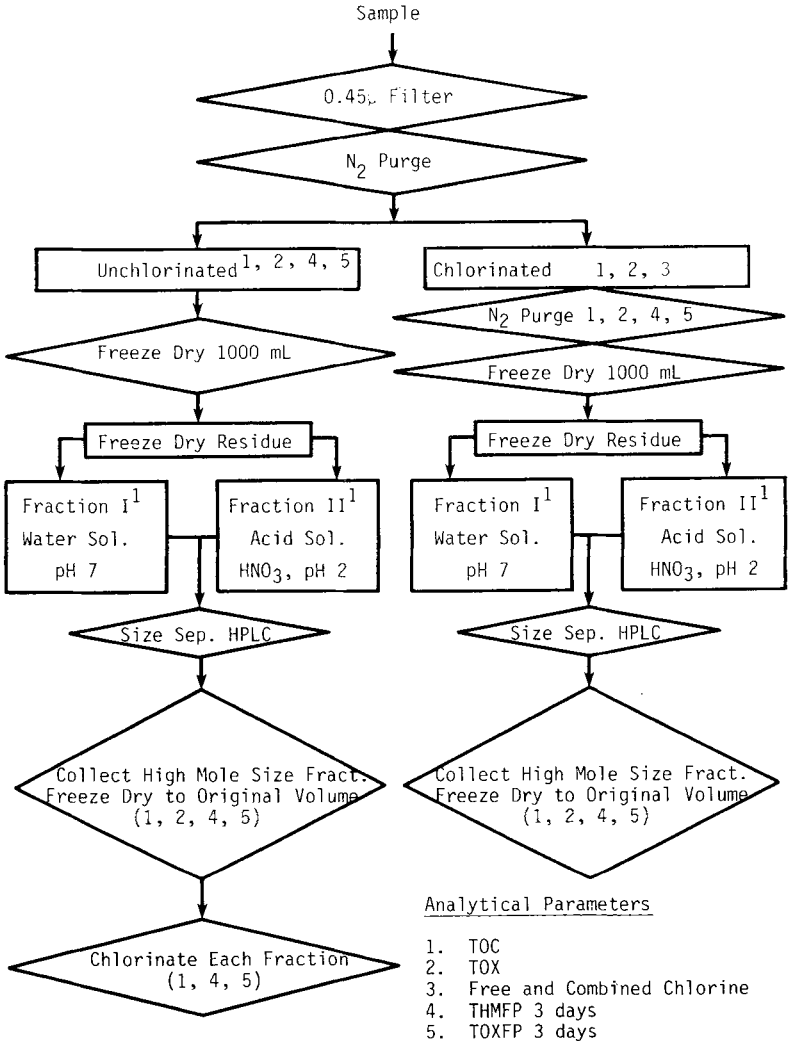

FIGURE 2 Scheme for the separation and analysis of non-volatile products of water chlorination.

chlorination. In each case a system blank was performed. Analysis of the base-neutral fraction and the diazomethane derivatized acid fraction were carried out using a Finnigan 3200/6000 GC/MS system. The purge and trap procedure utilized the Tekmar sampler with Tennax/silica gel trap and a 6 ft × 2 mm I.D. glass column with 0.2% Carbowax 1500 on Carbopac C (Supelco). For most of the other work a 30 m × 0.25 mm I.D. glass capillary with SE-30 coating was utilized (Supelco). Compound identifications were made by *ab initio* interpretative methods and confirmed by comparison with standard reference spectra when possible.

Trihalomethanes were measured by the liquid–liquid extraction procedure on 25 ml samples using a modification of the procedure described by Henderson, Glaze and Peyton.[5] Trihalomethane formation potential (THMFP) was measured by incubating the sample after a dose of 20 mg/L of aqueous chlorine at pH 6.5 for three days. THMFP represents the total amount of $CHCL_3$, $CHCL_2Br$, $CHClBr_2$, and $CHBr_3$ produced by this procedure minus the level of THMs originally present in the sample (Instantaneous THM).[6] InstTHM values in Cross Lake are near the detection limit (0.1 mg/L).

Total organic halogen (TOX) was measured by a modification of the procedure of Glaze, Peyton and Rawley using Chromosorb-102 macroreticular resin as the accumulator material.[3] The sample (usually 125 ml) was percolated through a 6 cm × 2 mm I.D. bed of 100/120 mesh Chromosorb-102 (*c.* 200 mg) at a flow rate of approximately 5 ml/min. The column was washed with 2 ml of 0.001 M HNO_3 in carbon-purified deionized water. Organics were eluted with a two-step solvent elution; (a) 1.0 ml of 1M NH_4OH in MeOH (1 part 2M NH_4OH, 1 part MeOH)[7] and (b) 1.0 ml of *n*-pentane. Solvents were eluted into a sealed mini-vial containing enough nitric acid to neutralize (with a slight excess) the ammonium hydroxide. The sealed vial was shaken to partition the lipophilic organics (THMs) into the pentane layer, then each layer was analyzed by pyrolysis (800°C)/microcoulometry using the Dohrmann system. THMs were measured in the pentane layer by GC with Ni^{63} EC detector as described before.[5]

HPLC exclusion separations were carried out on a Waters ALC-201 instrument with 6000A pump and refractive index detector. The column was 25 cm × 4.6 mm I.D. stainless steel with Partisil 10 (Whatman, 11 μ particle size, 60 Å pore size) deactivated with bonded glycerylpropylsilane according to the procedure of Regnier and Noel,[8] and by treatment with Carbowax 20 M. Columns were packed with the upward slurry technique of Bristow *et al.*[9] Two columns were prepared, the characteristics of which are shown in Table II. A calibration curve which fits both columns is shown in Figure 3. The solvent used for this calibration was carbon-

TABLE II

Characteristics of Partisil 10/glycophase HPLC columns. Packing material: Partisil 10 (Whatman 11 μ particle size, 60 Å pore size) deactivated with glycerolpropyl silane and treated with carbowax 20 M.

	Analytical	Preparative
Length CM	25	25
ID mm	4.6	9.4
Number of theoretical plates N	2500	3500
HETP	0.1	0.07
Linear velocity cm/sec	0.185	0.097
Void volume V_0 mL	2.25	3.1
Permeation volume V_T mL	4.9	7.4
Interstitial volume V_I mL	2.65	4.3

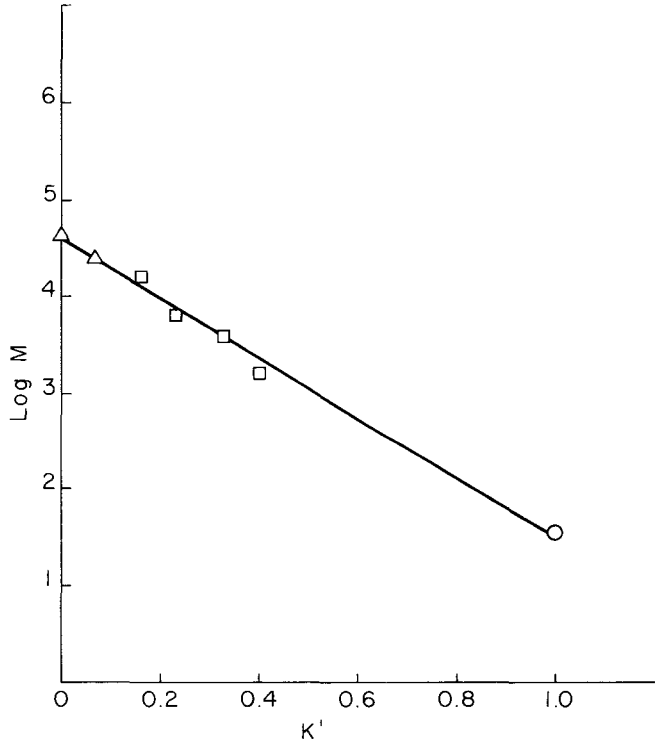

FIGURE 3 Calibration curve for Partisil 10/glycophase size exclusion columns. △ Proteins (ovalbumin, $M = 45{,}000$; chymotrypsinogin A, $M = 25{,}000$). □ Sodium polystyrene sulphonates ($M = 16{,}000$; 6,500; 4,000, 1,600). ○ Methanol.

filtered deionized water, but 2% isopropanol/water was also used for some earlier work.

Total organic carbon was determined with a Dohrmann Model DC-54 instrument.

Ozonation studies

Ozone was supplied from a model LG-2-L2 corona discharge generator (Linde Division, Union Carbide Corporation) using oxygen gas. Carbon-filtered water containing HCB at levels above its saturation limit (60 μg/l) was used in order to facilitate identification of reaction products. Ozone was passed through the solution at a rate of 1.4 mg/min for a period approximately equal to one half-life of the reaction. The quartz tube reactor (Figure 4) was emptied and the (unquenched) contents were extracted according to the extraction scheme shown in Figure 5.

Photolytic ozonations were carried out by placing the reaction tube in a Rayonet photochemical reactor with two low-pressure mercury lamps.[4]

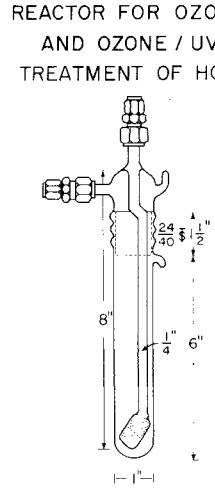

FIGURE 4 Reaction tube used for ozonolysis and photolytic ozonolysis of hexachlorobiphenyl. Lower tube made of quartz; liquid volume 45 mL.

RESULTS

Chlorination of Cross Lake water

Fractionation and analysis of the 0.45 μ filtrate of Cross Lake, Louisiana water before and after chlorination followed the schemes shown in Figures

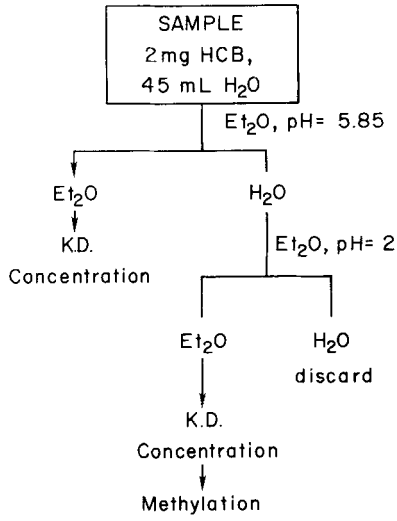

FIGURE 5 Scheme for separation and analysis of ozonation products of hexachlorobiphenyl.

1 and 2. GC/EC and GC/MS analysis of the water showed no detectable amounts of purgeable or volatile extractables before chlorination, with the exception of traces of aliphatic hydrocarbons, possibly from recreational use of the lake. Chlorination of the unbuffered lake water with a dose of 20 mg/L causes the formation of trihalomethanes (THMs) the yield of which reaches a plateau after three days. At a buffered pH of 6.5 the yield of THMs after this period is 189 μg/l, consisting of 81% $CHCl_3$, 16% $CHCl_2Br$ and 3% $CHClBr_2$ (by weight). Expressed as halogen, this yield is 4.47 μmole/L or as chlorine equivalent 159 μg/L. As we shall show in the following portions of this paper, the yield of halogen contained in the trihalomethanes does not represent the majority of bound halogen in chlorinated natural waters. This observation, which has been extensively documented in our laboratory, is consistent with the works of Sontheimer, Kühn and co-workers[10] and of Oliver[11].

GC/MS analysis of the lake water after chlorination using the scheme shown in Figure 1 revealed only one compound in the purgeable fraction other than the THMs. The compound is as yet unidentified. Analysis of the extractable volatiles resulted in the identification of only one compound which was previously unreported, trichloroacetic acid. Morris and Baum[12] postulated the intermediacy of trichloroacetate in haloform reactions of natural waters, however, and Rook[13] and Glaze and

Henderson[14] identified polychlorinated acetone derivatives in chlorinated River Rhine and Denton, Texas wastewater respectively.

As expected, the carbon matrix of Cross Lake is largely a non-volatile fraction, presumably consisting of a mixture of carbohydrates, fulvic acid, and other components. After microfiltration and freeze drying, the residue obtained is mostly soluble in purified water (50% of original TOC) and in dilute nitric acid (24% of TOC). A darkly colored solid remains which is partially base soluble and which probably represents humic acids and clay particles which are presumably colloidal in size in the original sample. The water and acid soluble portions are of interest in this work, but it should be noted that the role of fine particulates may be crucial in the transport of micropollutants and in water treatment processes.

After freeze drying, the water soluble fraction of the Cross Lake sample was analyzed in size exclusion HPLC (Table II). Figure 6 shows chromatograms of the water soluble fraction before and after 20 mg/L chlorination for five days. Apparent average molecular weight has shifted slightly downward upon chlorination as might be expected. Tables III and

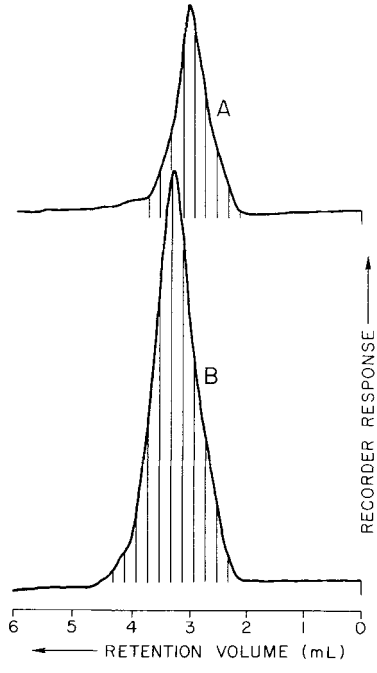

FIGURE 6 Size exclusion chromatogram of water soluble fractions of freeze dried Cross Lake water.

A—Unchlorinated sample, apparent $\bar{M}$ 10.5×10^3; *B*—Sample chlorinated with 20 mgCl_2/L dose, 5 days, apparent $\bar{M}$ 8.2×10^3. Samples concentrated $\times 100$ compared to lake water.

TABLE III

Characteristics of the water soluble fractions of Cross Lake water collected by size exclusion HPLC (unchlorinated)

Fraction No.	Mole wt. range	Mole wt. at Pk maximum	TOC (mg/L)		THMFP[a] (μg/L)		THMFP/TOC	
			$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S
1	31.6×10^3–15.9×10^3	22.4×10^3	0.63	0.04	31	7	49	11
2	22.3×10^3– 7.9×10^3	14.2×10^3	0.93	0.00	73	2	78	2
3	19.1×10^3– 7.1×10^3	10.3×10^3	1.28	0.04	95	10	74	8
4	15.9×10^3– 5.1×10^3	7.9×10^3	1.22	0.20	43	5	35	4
5	6.3×10^3– 0.2×10^3	3.9×10^3	0.91	0.20	62	2	68	2
Average	10.5×10^3						61	5
Sum			4.97		304 (252 as Cl)			

[a]Chlorine 20 mg/L, 3 days, pH 6.5.

IV show some of the characteristics of five fractions of this water soluble portion collected by preparative HPLC. Exclusion chromatograms of the reinjected fractions are shown in Figure 7. It should be noted that the precision of the non-volatile organic halogen values for the chlorinated fraction (NVTOX) is poor primarily because of the small sizes of the samples. Nonetheless, the data allow an important conclusion; namely, that THMFP and non-volatile TOX are evenly distributed throughout the molecular weight range of the polymer, with the possible exception of fraction 4, $\bar{M} \simeq 15.9\text{–}5.1 \times 10^3$.†

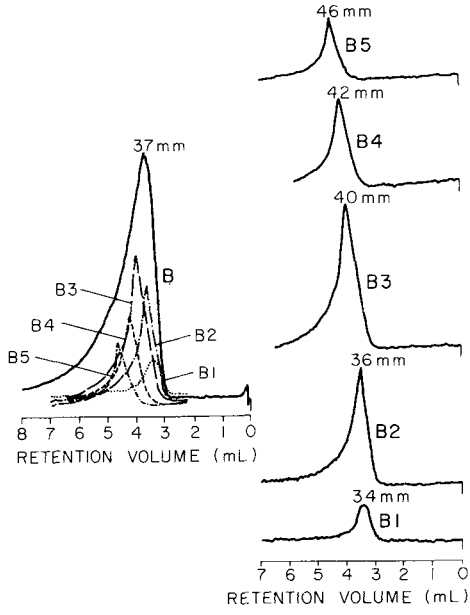

FIGURE 7 Size exclusion chromatograms of water soluble fractions of chlorinated freeze dried Cross Lake water. Fractions collected and reinjected (1-5) and composite curve superimposed on original chromatogram.

Characterization of the acid soluble fraction of the freeze dried sample has not progressed beyond the preliminary stages at this time. However, HPLC data show that the average molecular weight is substantially below that of the water soluble portion. Average values for the chlorinated and non-chlorinated acid soluble fractions are 3.8×10^3 and 4.2×10^3 respec-

†THMFP and NVTOX values from Tables III and IV are not strictly comparable, since the five fractions in Table III have been separated from other components of the original mixture and diluted in the process (relative to the 20 mg/L chlorine dose), while the sample to which Table IV refers was raw lake water after filtration.

TABLE IV

Characteristics of the water soluble fractions of Cross Lake water collected by size exclusion HPLC (chlorinated[a])

Fraction No.	Mole Wt. range	Mole Wt. at Pk maximum	TOC (mg/L)		NVTOX (μg/L)[b]		NVTOX/TOC	
			$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S
1	31.6×10^3–14.2×10^3	19.1×10^3	1.04	0.48	65	11	63	10
2	19.1×10^3– 6.9×10^3	12.6×10^3	0.98	0.16	47	8	48	8
3	15.9×10^3– 6.3×10^3	7.1×10^3	1.00	0.36	86	13	86	13
4	12.6×10^3– 2.2×10^3	3.9×10^3	0.64	0.08	20	9	31	14
5	7.1×10^3– 0.15×10^3	2.5×10^3	0.52	0.04	42	8	81	15
Average	8.2×10^3						62	12
Sum			4.18		260			

[a]Original sample before freeze drying and redissolving, chlorinated at 20 mg/L, 5 days.

[b]μg/l as chlorine.

tively. These lower values may be due to the presence of smaller molecules, possibly containing basic nitrogenous compounds. However, more detailed knowledge of each of the fractions must await analysis of other spectroscopic data which will be contained in continuations of this work.

It is interesting to note that the total non-volatile halogen content of the five water soluble fractions after chlorination is approximately 260 μg Cl/L or 7.3 μmole Cl/L (Table IV). The combined TOC value of the fractions is 4.2 mg C/L or 350 μmole C/L. Thus, the average atomic ratio of chlorine to carbon in the polymer is 1:50, then 4.2 mg C/L would correspond to 8.4×10^3 μg polymer/L. At an average molecular weight of 8.2×10^3, this would correspond to a concentration of 1.0 μmole polymer/L meaning that *the average polymer molecule would contain approximately seven chlorine atoms.* It should be noted that the molecular nature of this organohalogen mixture, its variation from source to source, its environmental fate and biochemical effects are unknown at this time.

Ozonation and photolytic ozonation of 2,4,6,2′,4′,6′-hexachlorobiphenyl

The products identified so far in this study are shown in the reconstructed gas chromatograms (Figures 8 and 9) and in the proposed reaction scheme in Figure 10. To avoid confusion in this figure a short line which is not terminated by a letter is used to represent a chlorine atom, rather than a methyl group, as in the more usual convention. Except for the keto-enol pair shown in Figure 10 all products, starting with 2-chloro-3-(2,4,6-trichlorophenyl) maleic acid and beyond were identified from their mass spectra. The scheme proposed in Figure 10 utilizes five types of reactions which are not uncommon in ozone[15] and photochemistry.[16] Cleavage of a double bond in aqueous solution (*C* in Figure 10) yields an acid and a carbonyl compound. Decarboxylation[16] (*D*) and replacement of halogen by hydroxyl (*R*) are known photochemical processes. Oxidation of an aldehyde to an acid and hydrolysis of an acid chloride are the remaining two reactions which are employed in the scheme.

Most significantly, the scheme proposes that the ring first ruptured is degraded in a series of rapid steps before the second ring is attacked.[17] The repetitive process which destroys these compounds is (a) double bond cleavage resulting in aldehydes which (b) oxidize to carboxylic acids which then (c) decarboxylate. Further cleavage naturally occurs when the system contains additional double bonds, so that organic carbon is converted to carbon dioxide via either intermediate carboxylic acids or the terminal compound in the ozone process, oxalic acid. One of the main advantages

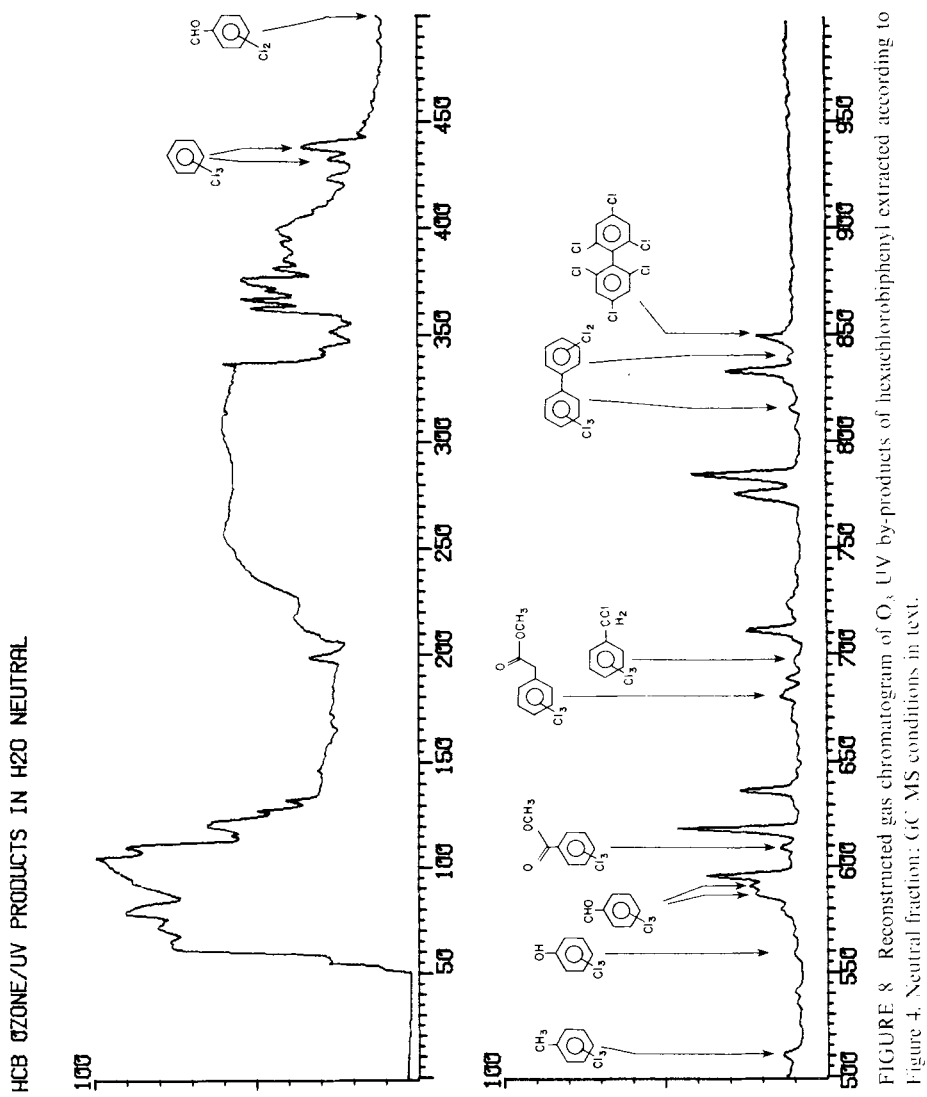

FIGURE 8 Reconstructed gas chromatogram of O_3 UV by-products of hexachlorobiphenyl extracted according to Figure 4. Neutral fraction: GC MS conditions in text.

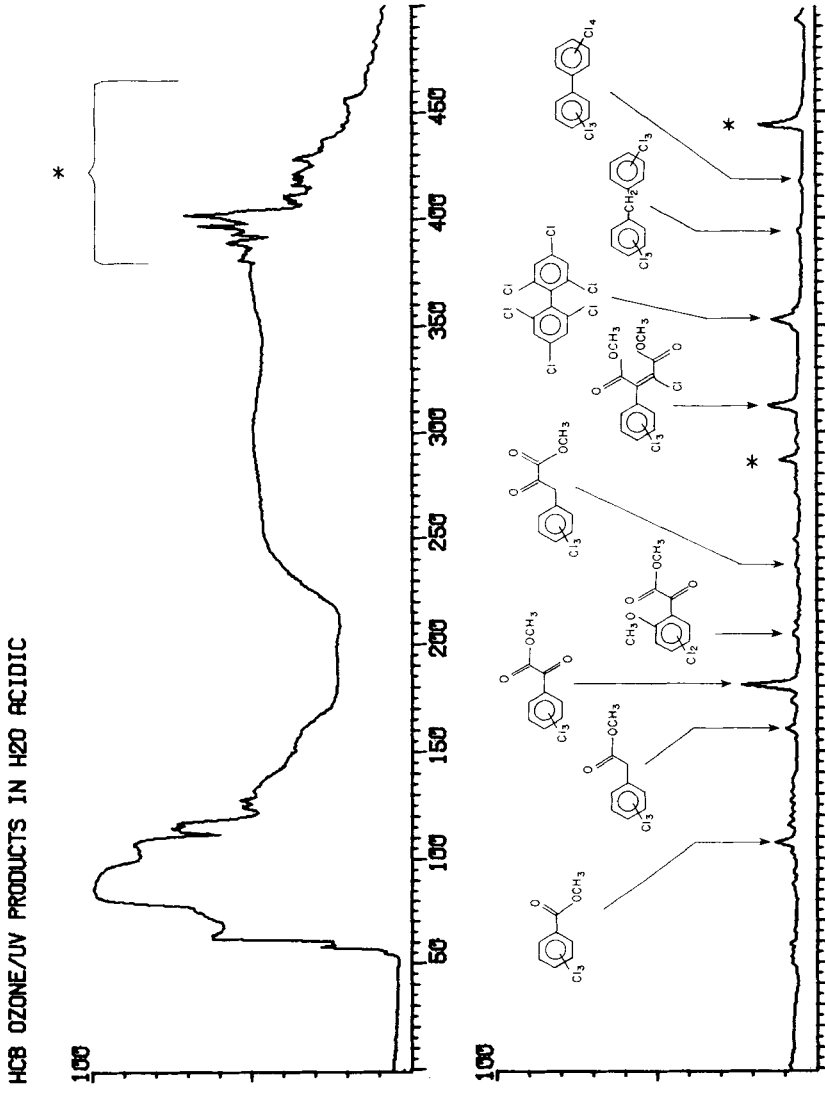

FIGURE 9 Reconstructed gas chromatogram of O_3 UV by-products of hexachlorobiphenyl extracted according to Figure 4. Acid fraction after methylation; GC/MS conditions in text.

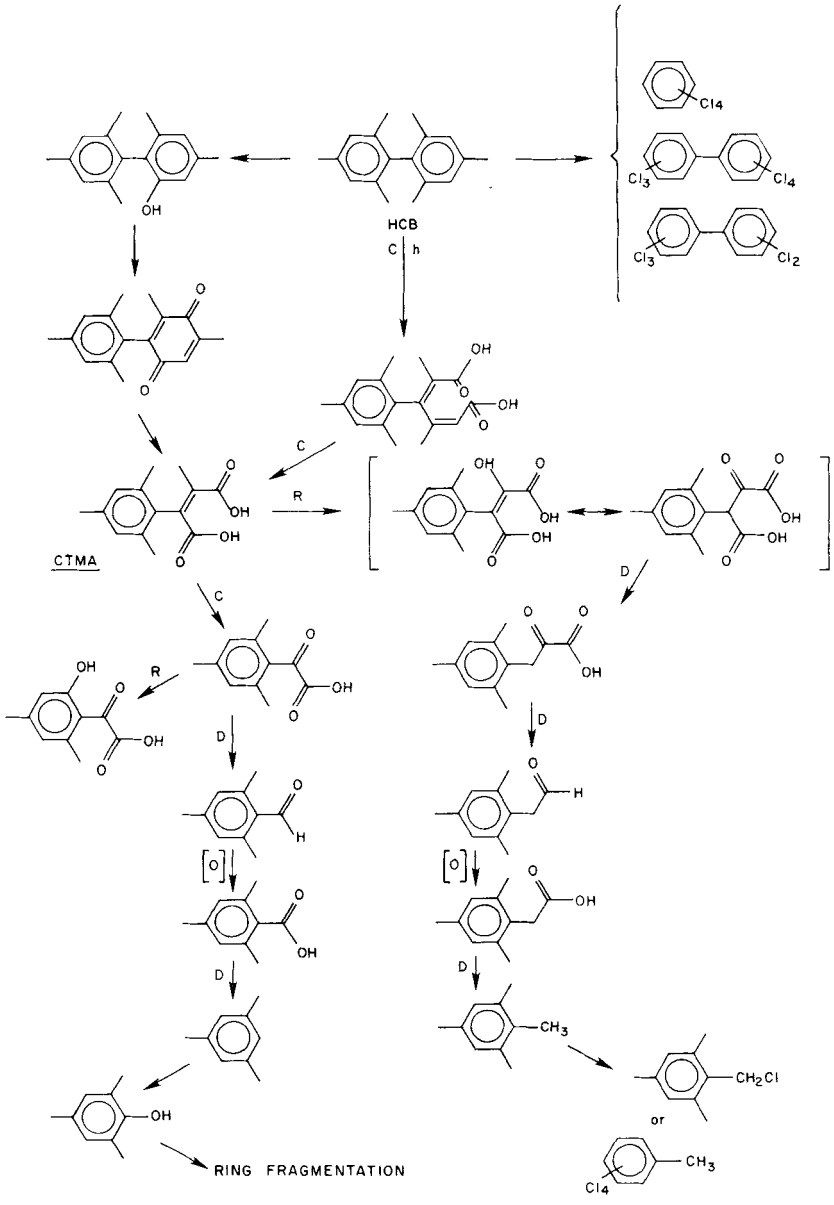

FIGURE 10 Proposed reaction scheme for photolytic ozonolysis of hexachlorobiphenyl in aqueous solution. From CTMA [2-chloro-3(2,4,6-trichlorophenyl) maleic acid] to end of scheme have been identified from mass spectra (unconfirmed by analysis of authentic sample). Reaction type code: *C*–Criegee cleavage; *D*—decarboxylation ($RCO_2H \rightarrow RH$); *R*—replacement ($RCL \rightarrow ROH$); [*o*] oxidation of aldehyde to carboxylic acid; *h*—hydrolysis of acid chloride to acid.

of the ozone/UV process over ozone only seems to be that UV facilitates decarboxylation by a strictly photochemical process[16] and/or by generation of an active specie from ozone which speeds the decarboxylation process. The decarboxylation reaction of carboxylic acids has been used to measure the rate of radiochemical generation of hydroxyl radicals, which have been shown to be one pathway of ozone attack, particularly at elevated pH.[18] This decarboxylation explains the finding of alkanes in ozone reaction mixtures by other investigators.[19]

Further studies on the ozonation and photolytic ozonation of organic substrates are currently active in our laboratory. Detailed kinetic studies of several systems and intermediate oxidation products will be reported subsequently.

Acknowledgement

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