

From: HYDROCARBONS AND HALOGENATED HYDROCARBONS
IN THE AQUATIC ENVIRONMENT

Edited by B.K. Afghan and D. Mackay
(Plenum Publishing Corporation, 1980)

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CHLORO-ORGANIC COMPOUNDS IN THE LOWER FOX RIVER, WISCONSIN

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ABSTRACT

The Lower Fox River, Wisconsin is one of the most densely developed industrial river basins in the world. During 1976-77 about 250 samples were analyzed by GC and GC/MS including biota, sediments, river water and wastewaters from 15 pulp and/or paper mills and 12 sewage treatment plants. A total of 105 compounds were identified in selected extracts by GC/MS with another 20 compounds characterized but not conclusively identified. Twenty of the 105 compounds are on the EPA Priority Pollutant List. Other compounds identified in pulp and paper mill wastewaters, including chloro-guaiacols, chlorophenols, resin acids and chloro-resin acids have been reported toxic to fish by other investigators. Several compounds apparently not previously reported in wastewaters are chloro-syringaldehyde, chloroindole, trichlorodimethoxyphenol, and various 1-4 chlorinated isomers of bisphenol A. Concentrations of the various compounds, when present in final effluents, ranged from 0.5 to ca. 100 $\mu\text{g/L}$. An exception was dehydroabiatic acid, a toxic resin acid not found on the EPA Priority Pollutant List. It was frequently found in pulp and paper mill effluents in concentrations ranging from 100 to 8500 $\mu\text{g/L}$. PCBs were found in all of the matrices sampled. Sixteen of the 35 fish exceeded the FDA limit of 5 mg/kg while 31 of the 35 exceeded the Canadian limit of 2 mg/kg. Concentrations of PCBs and other chloro-organics were related to point source discharges. There was a direct correlation of the concentrations of these compounds in wastewater with suspended solids values.

INTRODUCTION

Concern over the sources, distribution and fate of organic compounds in natural waters has increased considerably in recent years. With the development of GC/MS/DS instrumentation, thousands of compounds have been identified in industrial and municipal wastewaters, receiving waters and biota (Donaldson, 1977). Also, due to the extensive use of chlorination, numerous chlorinated organic compounds are being formed and these are now a matter of interest to researchers and regulatory officials (Jolley, 1976).

Because of this interest, the U.S. Environmental Protection Agency (Great Lakes Program Office, Region V) contracted with the State of Wisconsin (Department of Natural Resources and Laboratory of Hygiene) to assess the sources and distribution of organic compounds, particularly polychlorinated biphenyls (PCBs) and other chloro-organics, in the 64 km Lower Fox River in northeastern Wisconsin (Figure 1). This river drains into Green Bay-Lake Michigan and is one of the most densely developed industrial river basins in the world. Pulp and paper mills predominate; many of these use extensive amounts of chlorine. Five of the paper mills

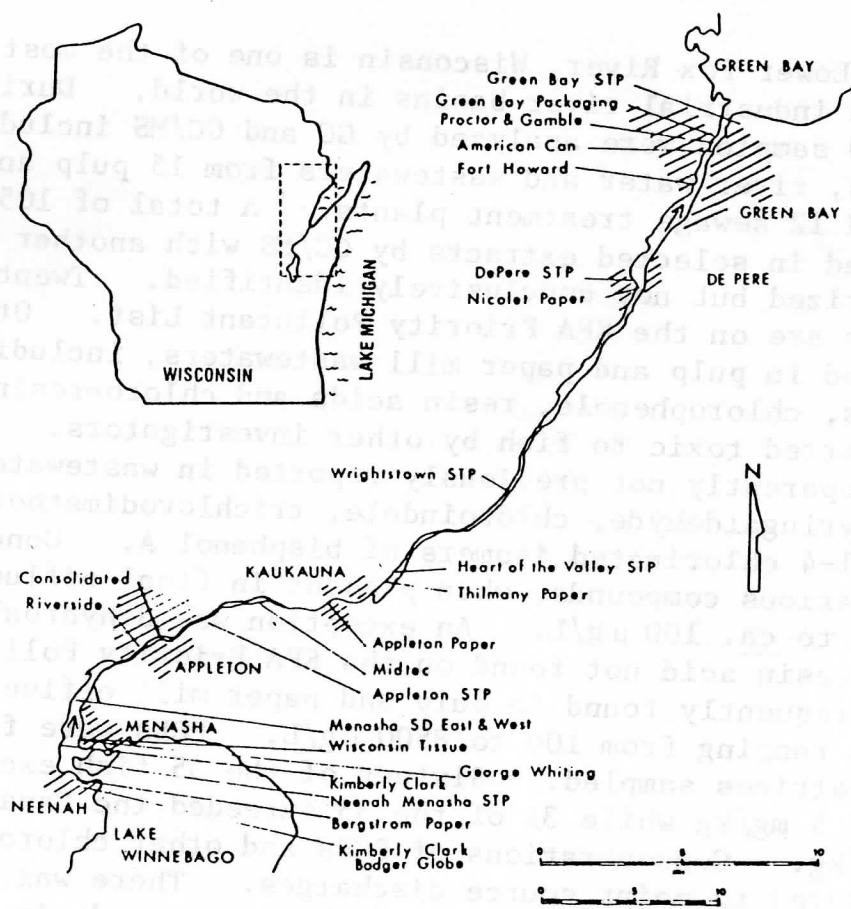


Figure 1. Effluent discharges to the Lower Fox River.

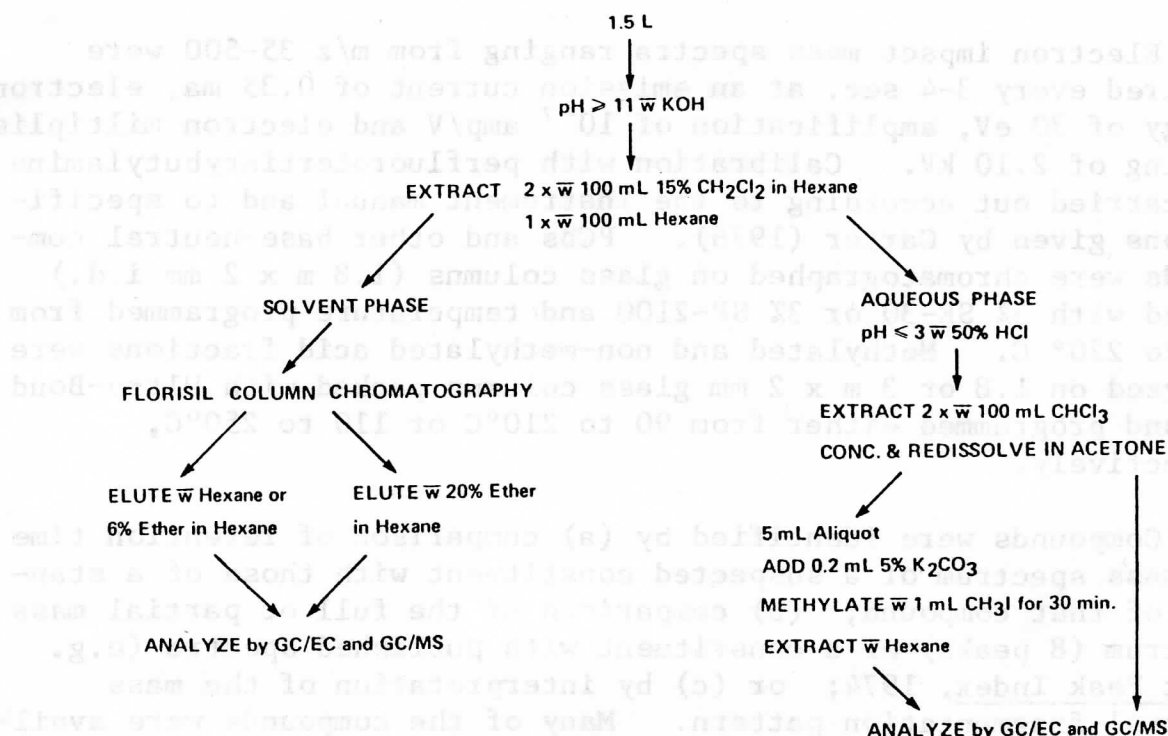


Figure 2. Water and wastewater extraction sequence.

de-ink and recycle paper to produce pulp, leading to the discharge of PCBs in their wastewaters.

EXPERIMENTAL

During 1976-77, ca. 250 samples were analyzed, including river and lake bottom sediments, snowmelt, biota (seston, clams and fish), river water and wastewaters from 15 pulp and/or paper mills and 12 municipal sewage treatment plants. Four of these municipal plants also treat pulp and/or paper mill wastewaters. Wastewaters comprised the majority of the samples received and were analyzed as described in Figure 2. Wastewater samples (1.5 L) were extracted at pH \geq 11 with methylene chloride/hexane, fractionated on Florisil and screened by gas chromatography with electron capture detection (GC/EC) using procedures for chlorinated base-neutral compounds (USEPA, 1973). The remaining aqueous phase of each sample was acidified to pH 3 and extracted with chloroform. The solvent was evaporated and the residue dissolved in acetone. This fraction was analyzed for chlorophenols, chloroguaiacols, and related chlorinated compounds. Selected extracts were derivatized with methyl iodide to facilitate analysis of acidic compounds and to confirm compounds identified by GC prior to methylation. Fractions whose GC/EC chromatograms exhibited significant unknown peaks were analyzed with a Finnigan 3100D Gas Chromatograph/Mass Spectrometer (GC/MS) and 6000 Data System.

Electron impact mass spectra ranging from m/z 35-500 were acquired every 3-4 sec. at an emission current of 0.35 ma, electron energy of 70 eV, amplification of 10^{-7} amp/V and electron multiplier setting of 2.10 kV. Calibration with perfluorotertiarybutylamine was carried out according to the instrument manual and to specifications given by Carter (1976). PCBs and other base-neutral compounds were chromatographed on glass columns (1.8 m x 2 mm i.d.) packed with 3% SE-30 or 3% SP-2100 and temperature programmed from 100 to 220° C. Methylated and non-methylated acid fractions were analyzed on 1.8 or 3 m x 2 mm glass columns packed with Ultra-Bond 20M and programmed either from 90 to 210°C or 110 to 250°C, respectively.

Compounds were identified by (a) comparison of retention time and mass spectrum of a suspected constituent with those of a standard of that compound; (b) comparison of the full or partial mass spectrum (8 peaks) of a constituent with published spectra (e.g. Eight Peak Index, 1974; or (c) by interpretation of the mass spectral fragmentation pattern. Many of the compounds were available commercially, while some were provided by other researchers.

One compound that was unavailable from any source was chlorosyringaldehyde. Therefore, an experimental chlorination of syringaldehyde was performed. A commercial standard of syringaldehyde was added to a solution of 5.25% sodium hypochlorite (commercial bleach) in aqueous acetic acid. The reaction proceeded 16 hours, after which time the reaction product was extracted with methylene chloride, evapo-concentrated to dryness with a gentle stream of air, redissolved in acetone, and then injected into the GC/MS. A total ion chromatogram indicated both unreacted syringaldehyde and newly formed chlorosyringaldehyde. A very small amount of dichlorosyringaldehyde was also detected in the reaction product.

RESULTS AND DISCUSSIONS

Chlorosyringaldehyde was one of the 105 compounds identified by GC/MS (Table 1). Compounds in final effluents which were detected several times by GC/MS were quantitated by GC/MS, GC using flame ionization detection (FID) or GC/EC and listed in Table 2. Various effluents and extraction efficiencies were experienced, therefore only concentration ranges are given. The concentrations of these compounds generally corroborate earlier investigations of pulp and paper mill effluents (Rogers, 1973; Keith, 1976). Compounds detected and quantitated by GC/EC in fish, clams, river water, seston and sediments are also included in Table 2. A complete set of these data appears in a technical report (WI DNR, in press).

Table 1 Compounds Identified but not Quantified in
Samples from the Lower Fox River System

c Acetone, Tetrachloro-	Indole, Chloro-
c Acetovanillone	p-Menth-4-ene-3-one
Aniline, Trichloro-	Naphthalene, Isopropyl-
Benzene, Dichloro-diethyl-	Naphthalene, Methyl-
Benzoate, Dimethyl-	Nonadecane
Benzoate, Methyl-methoxy-	Octadecane
Benzoic Acid	c Pentadecane
Benzoic Acid, Isopropyl-	Phenanthrene, Methyl-
Benzophenanthrene, Methyl-	a Phenol
or (Benzanthracene, Methyl-)	Phenol, p-Tertiary Amyl-
Benzophenone	a Phenol, Chloro-
c Benzyl Alcohol	Phenol, p-(α -chloroethyl)-
Biphenyl	Phenol, Decyl-
Biphenyl, Methyl-	c Phenol, Ethyl-
Bisphenol A	Phenol, Nonyl- (3 isomers)
Bisphenol A, Chloro-	Phenol, Trichloro-dimethoxy-
Bisphenol A, Dichloro-	Phenol, Undecyl-
(2 isomers)	Phenyl Decane
Bisphenol A, Tetrachloro-	Phenyl Dodecane
Bisphenol A, Trichloro-	Phenyl Undecane
Borneol, Iso-	Phosphate, Tributyl-
c Caffeine	
Camphor, Oxo-	
Carbazole	
a Chlordane	
a DDD	
a DDE	
a DDT	
c Dodecane	

FATTY ACIDS AND THEIR METHYL ESTERS

c Heptadecanoic Acid
c Lauric Acid
c Myristic Acid
b Oleic Acid
c Palmitic Acid
c Stearic Acid
c Methyl Palmitate
c Methyl Stearate
c Guaiacol
b Guaiacol, Dichloro- (3 isomers)
Heptadecane
a Hexachlorocyclopentadiene
c Hexadecane

PHTHALATES

a Dibutyl Phthalate
a Diethyl Phthalate
a Dioctyl Phthalate
c Propan-2-one, 1-(4-hydroxy- 3-methoxy phenyl) or guaiacyl acetone

RESIN ACIDS

b 6,8,11,13-Abietatetraen- 18-oic Acid
b 8,15-Isopimardien-18-oic Acid
b Oxo-dehydroabietic Acid
b Pimaric Acid
b Sandaracopimaric Acid

RESIN ACIDS, METHYL ESTERS

b Methyl Dehydroabietate

(Continued next page)

Table 1 (Cont.)

RESIN ACIDS, CHLORINATED

- b Chlorodehydroabietic Acid (2 isomers)
- b Dichlorodehydroabietic Acid

RESIN ACID METHYL ESTERS, CHLORINATED

Methyl Chlorodehydroabietate

Methyl Dichlorodehydroabietate

- c Salicyclic Acid
- c Syringaldehyde
- Syringaldehyde, Chloro-
- Tetradecane
- Toluene, Dichloro-
- Toluene, Trichloro-
- c Vanillin
- c Vanillic Acid
- c Veratrole, Dichloro-
- c Veratrole, Trichloro-
- Xylene, Dichloro-
- Xylene, Trichloro-
- a Compounds on EPA Consent Decree Priority Pollutant List
- b Compounds in paper mill wastewaters reported toxic to fish
- c Other compounds previously reported in paper mill wastewaters

To assess the significance of the compounds detected in this study, certain classifications were assigned. Twenty of the 105 compounds, including PCBs, appear in the EPA Consent Decree Priority Pollutant List (USEPA, 1977). Although the commercial use of Aroclor 1242 and other forms of PCBs in printing inks and carbonless copy paper apparently ended in 1972, PCBs are still being released into the Lower Fox River Basin. Deinking-recycling processes of five paper mills are some of the main sources. PCBs were detected in all of the various matrices sampled. All 35 fish fillet samples, consisting of both rough and sport fish, contained detectable levels of PCBs which were correlated to their fat content. Sixteen of the 35 fish exceeded the U.S. Food & Drug Administration tolerance limit of 5 mg/kg, while 31 of 35 exceeded the Canadian Food & Drug Directorate tolerance limit of 2 mg/kg.

PCBs are lipophilic and accumulate in fat tissue. Clams seeded in the Lower Fox River for 9 - 28 days showed that PCBs can rapidly bioaccumulate (WI DNR, in press). The mean uptake rates varied from 10 to 24 µg/day. The higher PCB uptake rate in the

Table 2 Compounds Identified and Quantified in
Samples from the Lower Fox River System

Compound	Environmental Matrix	Concentration Range	Units
Anisole, Pentachloro-	Wastewaters	0.05 - 0.38	µg/L
	River water	0.002 - 0.02	µg/L
	*Seston	0.02 - 0.05	µg/L
	Fish	0.005 - 0.06	mg/kg
Anisole, Tetrachloro-	Wastewaters	0.04 - 0.08	µg/L
Benzothiazole	Wastewaters	10 - 30	µg/L
Benzothiazole, Hydroxy-	Wastewaters	10 - 30	µg/L
c Benzothiazole, Methylthio-	Wastewaters	10 - 40	µg/L
b Dehydroabietic Acid	Wastewaters	100 - 8500	µg/L
	Sediment	2.7	mg/kg
a Dieldrin	Fish	0.008 - 0.022	mg/kg
b Guaiacol, Tetrachloro-	Wastewaters	10 - 50	µg/L
b Guaiacol, Trichloro- (3 isomers)	Wastewaters	10 - 60	µg/L
a Hexachlorocyclohexane (Lindane)	Wastewater	0.04	µg/L
a Phenols, Dichloro- (2 isomers)	Wastewaters	15 - 40	µg/L
a Phenol, Pentachloro-	Wastewaters	0.1 - 40	µg/L
	Sediments	0.22 - 0.28	mg/kg
Phenol, Tetrachloro-	Wastewaters	2 - 20	µg/L
a Phenols, Trichloro- (2 isomers)	Wastewaters	5 - 100	µg/L
a Polychlorinated Biphenyls (Aroclor 1242, 1248 and 1254)	Raw wastewaters	0.2 - 8200	µg/L
	Final effluents	0.1 - 56	µg/L
	River water	0.05 - 0.85	µg/L
	*Seston	0.002 - 0.029	µg/L
	Sediments	0.05 - 61	mg/kg
	Clams seeded	0.26 - 0.74	mg/kg
	Fish	0.5 - 90	mg/kg
a Polycyclic Aromatic Hydrocarbons (Acenaphthene, Anthracene, Chrysene, Fluoranthene, Pyrene)	Wastewaters	0.5 - 10	µg/L

* Entire aqueous sample filtered

a Compounds on EPA Consent Decree Priority Pollutant List

b Compounds in paper mill wastewaters reported toxic to fish

c Other compounds previously reported in paper mill wastewaters

clams occurred at locations having relatively high PCB concentrations in the river sediments. These locations were downstream from discharges containing PCBs.

Other compounds identified in pulp and paper mill wastewaters were those found to be toxic to fish by other investigators (Rogers and Keith, 1974; Leach and Thakore, 1977). These toxicants included chloroguaiacols, resin acids, chloro-resin acids and oleic acid. Our observations of chlorophenols corroborates work by Lindström and Nordin (1976). The source of the chlorophenols in the mill wastewaters investigated in this study has not yet been determined. Chlorophenols may have been used by paper mills for slime control or been present as wood preservatives. Phenolic compounds could also have been chlorinated in the bleaching or wastewater treatment stages. Chlorocatechols may have been present, but the analytical method employed did not appear to give any significant recovery of these compounds.

Previous investigations of toxicants in paper mill wastewater have always involved a pulp mill that derives its pulp from wood, thus releasing wood extractives and lignin-derived compounds such as resin acids, guaiacols and other phenolics, some of which become chlorinated in the bleach plant. In our survey, the highest levels of chloroguaiacols occurred at a sulfite pulp mill which produces mostly bleached pulp. These compounds eluted cleanly from an unmethylated acid extract on the Ultra-Bond 20M column which resolved 3 apparent trichloroguaiacol isomers. Chloroguaiacols were not detected in some Fox River paper mill wastewaters, presumably because these mills either do not bleach their wood-derived pulp, or else they bleach purchased pulp and/or deinked recycled paper. The last two should contain lesser amounts of the wood extractives and lignin-derived compounds.

The GC/MS analysis of a sample extract of a paper mill which bleached either purchased bleached pulp and/or deinked recycled paper is shown in Figure 3. The total ion chromatogram (TIC) of a methylated acid extract of the mill's final effluent shows 39 identified compounds, most of which are methylated derivatives. Thus, chloroanisoles were originally present as chlorophenols, chloroveratroles as chloroguaiacols and the dimethyl ether derivatives as various bisphenol A isomers. Likewise, the fatty and resin acid methyl esters were originally present as the corresponding acids in the acid extract. The scale of the TIC has been limited to 30% of full scale to better show the compounds at lower concentrations. For reference, 75 ng of aldrin (peak 15) were injected as an external standard. Peak 8, representing tetrachloroguaiacol, was quantitated by GC/EC at 14 $\mu\text{g/L}$, while peak 25, representing the resin acid dehydroabietic acid (DHA), was quantitated by GC/FID at 3200 $\mu\text{g/L}$. This concentration approached that of 8500 $\mu\text{g/L}$ which was seen in the aforementioned sulfite pulp mill's

COMPOUNDS

1. Chloroanisole
2. 2, 4, 6 - Trichloroanisole
3. Dichloroanisole
4. Benzothiazole
5. Tetrachloroanisole
6. Nonyl anisole
7. Pentachloroanisole
8. Tetrachloroveratrole
9. Methyl thiobenzothiazole
10. Trichloroveratrole
11. Trichloro-trimethoxybenzene
12. Tributyl phosphate
13. Methoxybenzothiazole
14. Methyl palmitate
15. Aldrin — External standard
16. Methyl heptadecanoate
17. Methyl oleate
18. Methyl stearate
19. Methyl 8, 15 - isopimardien-18-oate
20. Methyl pimarate
21. Methyl sandaracopimarate
- 21 a. Bisphenol a dimethyl ether
22. Unidentified R A M E* (MW 318)
23. Unidentified R A M E (MW 316)
24. Unidentified R A M E (MW 328)
25. Methyl dehydroabietate
26. Methyl 6, 8, 11, 13-abietatetraen-18-oate
27. Unidentified R A M E (MW 328)
28. Dichloro-bisphenol a dimethyl ether
29. Chloro-bisphenol a dimethyl ether
30. Chloro R A M E (MW 362)
31. Chloro-methyl dehydroabietate (A)
32. Chloro-methyl dehydroabietate (B)
33. Tetrachloro-bisphenol a dimethyl ether
34. Dioctyl phthalate
35. Trichloro-bisphenol a dimethyl ether
36. Dichloro-bisphenol a dimethyl ether
37. Dichloro-methyl dehydroabietate (MW 382)
38. Methyl oxo-dehydroabietate (MW 328)

*R A M E = Resin Acid Methyl Ester

TOTAL ION CHROMATOGRAM : METHYLATED ACID EXTRACT OF A PAPER MILL EFFLUENT

Column Conditions: Ultra-Bond 20M, 3m x 2mm.
temperature programmed 110-250°C @ 4°C/min. for 35 minutes

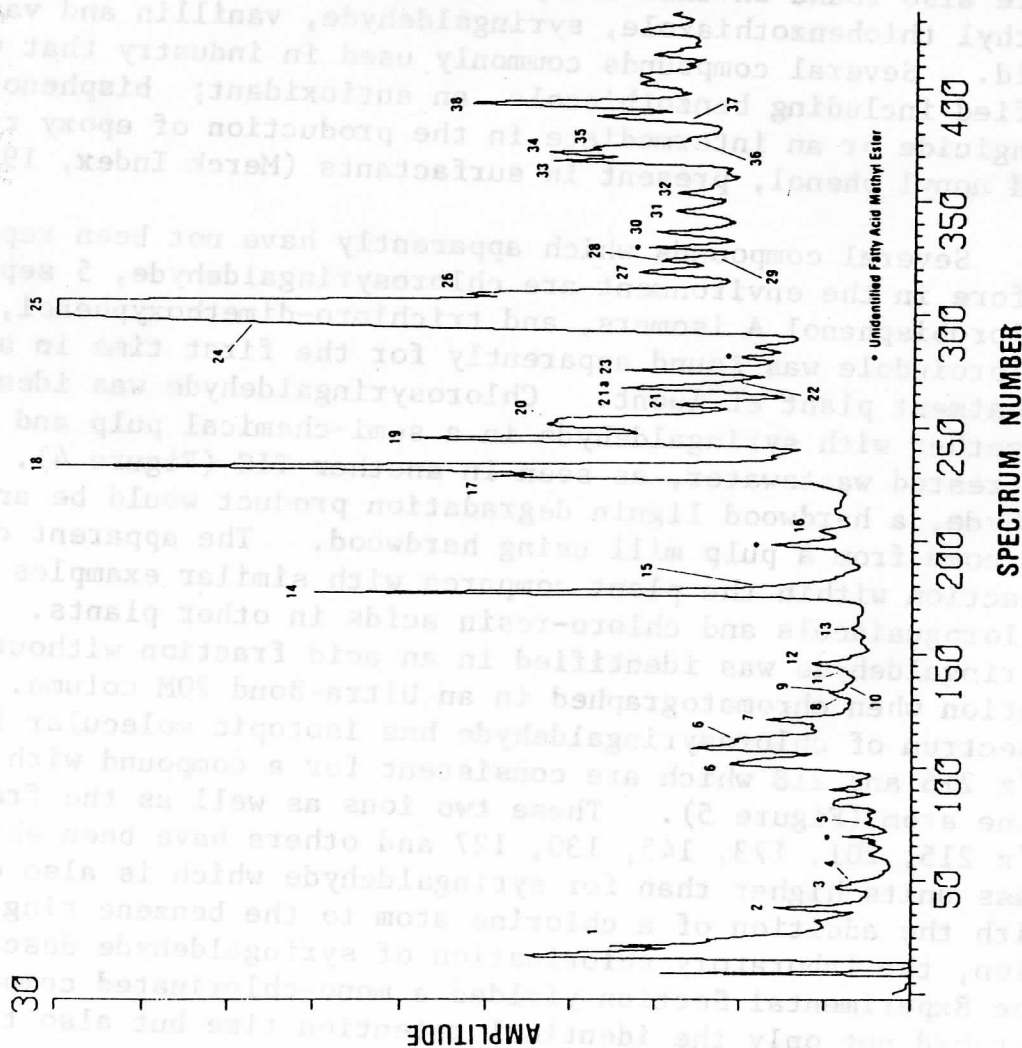


Figure 3. Total ion chromatogram of a methylated acid extract of a paper mill effluent

final effluent. Since the mill whose effluent is represented in Figure 3 lacks a wood pulping process, the relatively large amounts of fatty and resin acids present, especially DHA, could have come from its use of resin sizing (Merck Index, 1976) in the papermaking process. This water-intensive process could have diluted the available chlorine, thereby reducing the effectiveness of formation of chloro-resin acids (peaks 31, 32 and 37, Figure 3).

DHA appears to be the most stable of the resin acids (Brownlee and Strachan, 1977; Fox, 1977). The toxicity of resin acids to fish has been known since 1936. The 96 hour LC_{50} concentrations of DHA for young Sockeye Salmon are 2000 $\mu\text{g/L}$ (Rogers, 1973) and 750 $\mu\text{g/L}$ for Coho Salmon (Leach and Thakore, 1977). The latter investigators also reported even lower 96 hour LC_{50} concentrations for mono- and dichlorinated DHA.

Other compounds previously reported in paper mill wastewaters were also found in this study including acetovanillone, guaiacol, methyl thiobenzothiazole, syringaldehyde, vanillin and vanillic acid. Several compounds commonly used in industry that were identified including benzothiazole, an antioxidant; bisphenol A, a fungicide or an intermediate in the production of epoxy resins; and nonyl phenol, present in surfactants (Merck Index, 1976).

Several compounds which apparently have not been reported before in the environment are chlorosyringaldehyde, 5 separate chlorobisphenol A isomers, and trichloro-dimethoxyphenol, while chloroindole was found apparently for the first time in a sewage treatment plant effluent. Chlorosyringaldehyde was identified together with syringaldehyde in a semi-chemical pulp and paper mill untreated wastewater, as seen in another TIC (Figure 4). Syringaldehyde, a hardwood lignin degradation product would be anticipated to come from a pulp mill using hardwood. The apparent chlorination reaction within the plant compares with similar examples of the chloroguaiacols and chloro-resin acids in other plants. Chlorosyringaldehyde was identified in an acid fraction without derivatization when chromatographed in an Ultra-Bond 20M column. The mass spectrum of chlorosyringaldehyde has isotopic molecular ions of m/z 216 and 218 which are consistent for a compound with one chlorine atom (Figure 5). These two ions as well as the fragment ions m/z 215, 201, 173, 145, 130, 127 and others have been shifted 34 mass units higher than for syringaldehyde which is also consistent with the addition of a chlorine atom to the benzene ring. In addition, the laboratory chlorination of syringaldehyde described in the Experimental Section yielded a mono-chlorinated compound which matched not only the identical retention time but also the mass spectrum of the apparent chlorosyringaldehyde in the untreated wastewater (Figure 4).

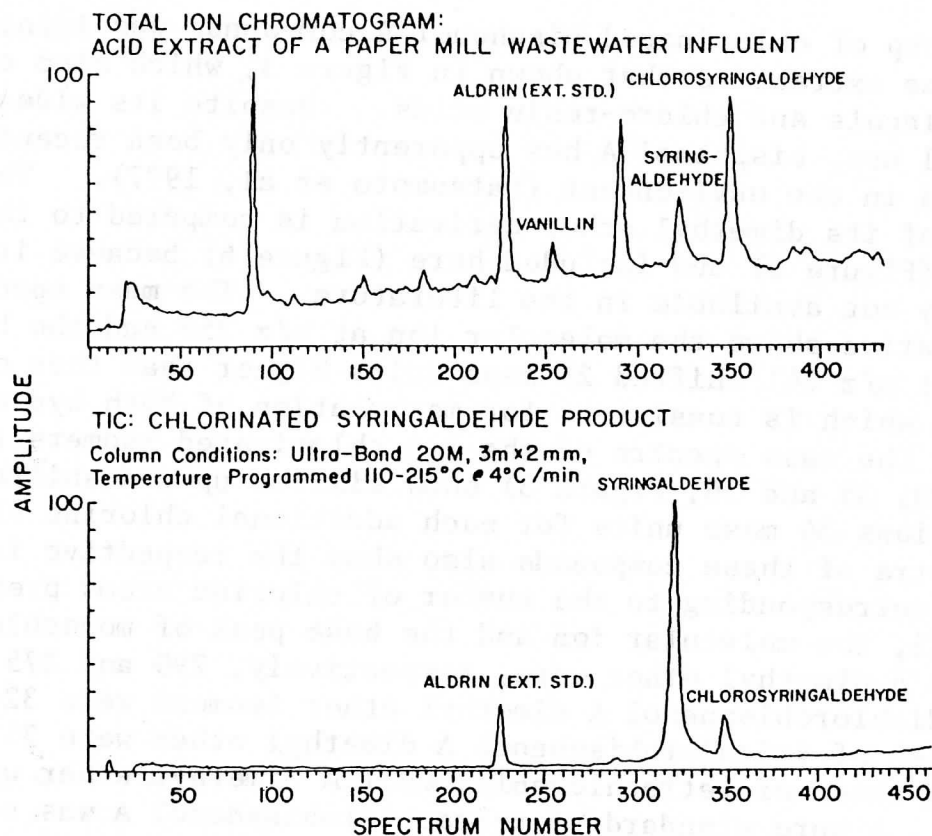


Figure 4. Total ion chromatograms: syringaldehyde and chlorosyringaldehyde

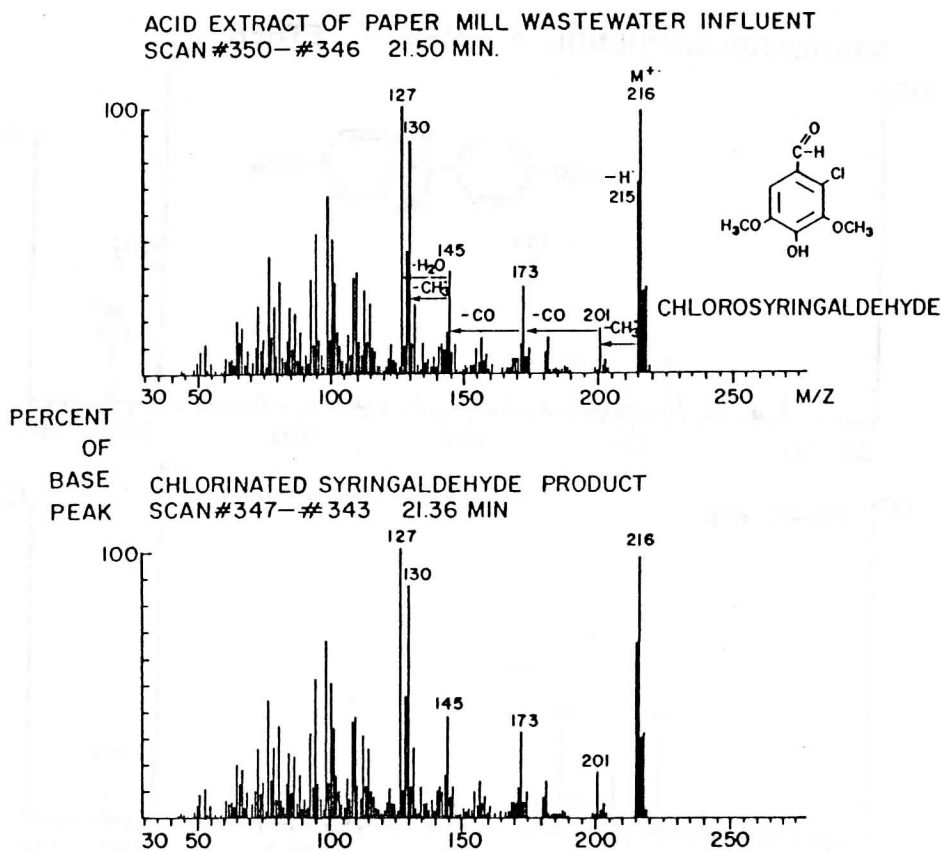


Figure 5. Mass spectra of chlorosyringaldehyde

A group of chlorinated bisphenol A compounds was identified in the same extract as that shown in Figure 3, which also contained chloroguaiacols and chloro-resin acids. Despite its widespread industrial use, bisphenol A has apparently only been recently identified in the environment (Matsumoto et al, 1977). The mass spectrum of its dimethyl ether derivation is compared to that of peak 21a (Figure 3) and included here (Figure 6) because it was apparently not available in the literature. The mass spectrum of its derivative shows the molecular ion at m/z 256 and the base peak $(-CH_3)^+$ at m/z 241 shifted 28 mass units higher than that of bisphenol A, which is consistent for methylation of both hydroxyl groups. The mass spectra of the 1-4 chlorinated isomers (peaks 28, 29, 33, 35 and 36, Figure 3) show similar upward shifts of the two main ions 34 mass units for each additional chlorine atom. The mass spectra of these compounds also show the respective isotopic clusters corresponding to the number of chlorine atoms present. Using ^{35}Cl , the molecular ion and the base peak of monochloro-bisphenol A dimethyl ether were, respectively, 290 and 275; those of both dichlorobisphenol A dimethyl ether isomers were 324 and 309; those of trichlorobisphenol A dimethyl ether were 358 and 343; and those of tetrachlorobisphenol A dimethyl ether were 392 and 377. A pure standard of tetrachlorobisphenol A was commercially available, as it is apparently used as a flame retardant. The mass spectrum of its methylated derivative is compared with

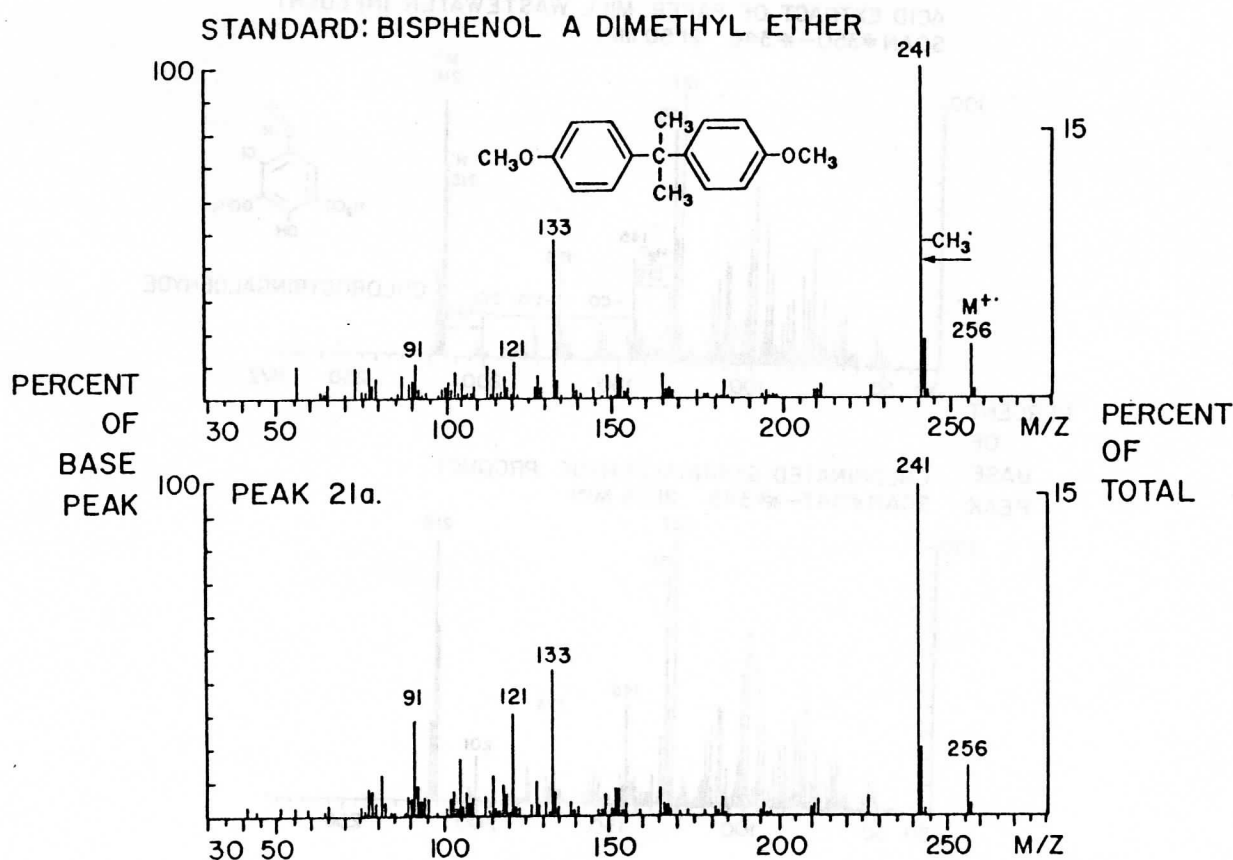
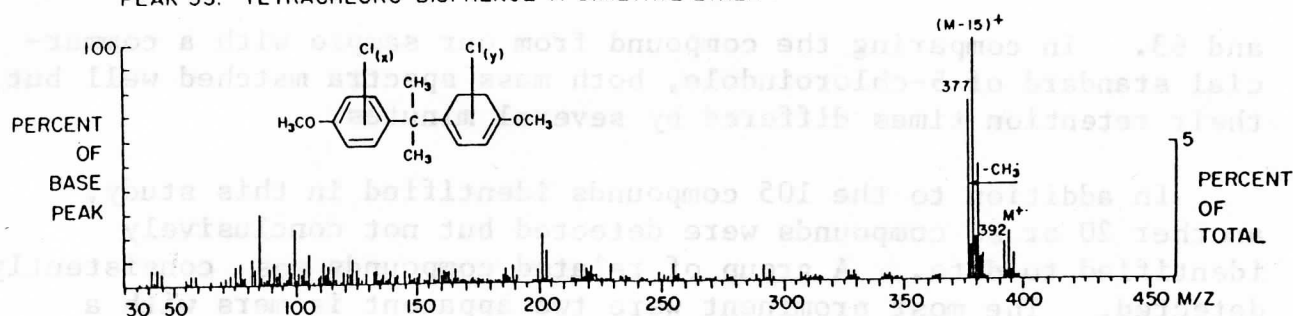


Figure 6. Mass spectra of bisphenol A dimethyl ether.

PEAK 33. TETRACHLORO-BISPHENOL A DIMETHYL ETHER



STANDARD: TETRACHLORO-BISPHENOL A DIMETHYL ETHER

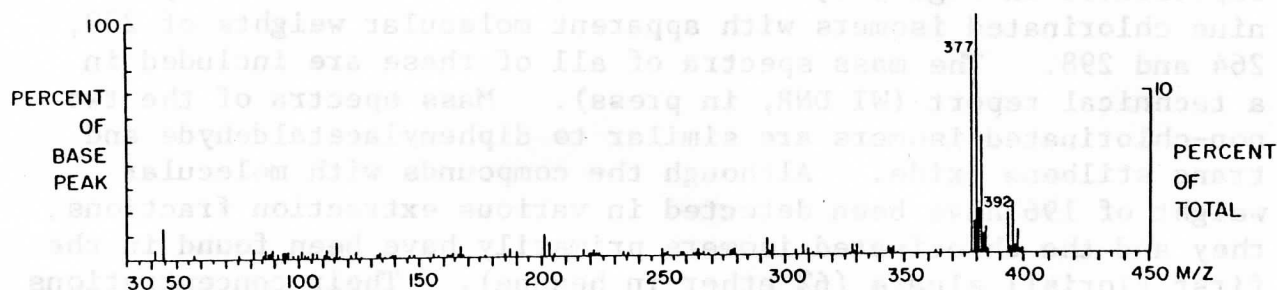


Figure 7. Mass spectra of tetrachlorobisphenol A dimethyl ether.

that of peak 33 (Figure 3) in Figure 7. In a laboratory chlorination of bisphenol A performed similarly to that of syringaldehyde, it was shown that 2,4,6-trichlorophenol was the main product formed, although various chlorinated bisphenol A isomers having 1-4 chlorines were also formed.

Trichloro-dimethoxyphenol was tentatively identified in the acid extract (Figure 3). Its methylated derivative was peak 11 which eluted just after a close congener, trichloroveratrole (peak 10). Trichloro-dimethoxyphenol was another compound which was detected in the acid extract chromatographed directly without derivatization on an Ultra-Bond 20M column. It eluted just after tetrachloroguaiacol. Its mass spectrum showed abundant molecular ions at m/z 256-260 consistent for 3 chlorine atoms, a similar cluster at ions m/z 241-245 ($M-15$)⁺ and m/z 198-202, ($M-58$)⁺. The mass spectrum of the methylated derivative, peak 11 (Figure 3) showed abundant isotopic molecular ions now at m/z 270-274 with subsequent fragments ($M-15$)⁺, ($M-43$)⁺ and ($M-58$)⁺.

Chloroindole apparently has not been previously detected in wastewaters, but it has been isolated from a bacterium (*Pseudomonas pyrocinia*) (Neidleman, 1975) and from an acorn worm (*Ptychodera flava laysanica*) from the Pacific Ocean (Higa and Scheuer, 1975). In our study of untreated wastewater from a municipal sewage treatment plant, this compound was detected in the 20% ether in hexane Florisil eluate at a concentration of ca. 30 $\mu\text{g/L}$. The mass spectrum showed abundant isotopic molecular ions m/z 151 and 153, base peak of m/z 89, and less abundant ions at m/z 124, 116

and 63. In comparing the compound from our sample with a commercial standard of 5-chloroindole, both mass spectra matched well but their retention times differed by several minutes.

In addition to the 105 compounds identified in this study, another 20 or so compounds were detected but not conclusively identified to date. A group of related compounds was consistently detected. The most prominent were two apparent isomers with a molecular weight of 196. In wastewater samples of the paper mill represented in Figure 3, these two isomers were followed by about nine chlorinated isomers with apparent molecular weights of 230, 264 and 298. The mass spectra of all of these are included in a technical report (WI DNR, in press). Mass spectra of the two non-chlorinated isomers are similar to diphenylacetaldehyde and trans stilbene oxide. Although the compounds with molecular weight of 196 have been detected in various extraction fractions, they and the chlorinated isomers primarily have been found in the first Florisil eluate (6% ether in hexane). Their concentrations have been sufficiently high to mask some of the PCB peaks detected with GC/EC. This mill's extensive deinking, recycling and bleaching processes could conceivably release the compounds with molecular weight 196 which ultimately become chlorinated.

This GC/MS study was aided by the use of a low-loaded, Ultra-Bond 20M column packing (ca. 0.3% Carbowax 20M) similar to that first discovered by Aue (1973). Elutions were characteristically sharp, with polar phenolic compounds eluting quite well. Baseline separation of pentachloroanisole from tetrachloroveratrole was achieved, contrary to the case for 3% SP-2100, 3% OV-17, or the mixed phase packing 4% SE-30/6% OV-210 designed for pesticide analyses. Very low bleed on temperature programmed analyses aided background subtraction resulting in optimum mass spectra.

The fate and long-term health and ecological implications of many of the 105 compounds identified requires further research. For PCBs and some other chloro-organics, sampling data and laboratory experiments show a direct correlation of their concentrations in wastewaters with suspended solids concentrations. Suspended solids reduction in wastewater treatment plant also reduces the chloro-organic concentration in the final effluent (WI DNR, in press). For example, the untreated wastewater of a paper mill which deinks and recycles paper contained 25 $\mu\text{g/L}$ PCBs and 2,020 mg/L suspended solids. Following primary clarification, concentrations were reduced to 2.2 $\mu\text{g/L}$ PCBs and 72 mg/L suspended solids. After secondary treatment the final effluent contained only 1.4 $\mu\text{g/L}$ PCBs and 10 mg/L suspended solids. Now the final disposal of the treatment plant sludge containing PCBs must be resolved.

ACKNOWLEDGEMENTS

This study was supported in part by a contract from the U.S. EPA Great Lakes National Program Office, Region V, (EPA Contract No. 68-01-4186). Additional support was provided by the Wisconsin Department of Natural Resources and the Wisconsin Laboratory of Hygiene.

REFERENCES

- Aue, W.A., C. Hastings, and S. Kapila. 1973. J. Chromatog. 77, 299-307.
- Brownlee, B., and W.M.J. Strachan. 1977. J. Fish Res. Bd. Can. 34, 838-843.
- Carter, M.H. March, 1976. EPA Report No. 600.4-76-004.
- Donaldson, W.T. 1977. Environ. Sci. & Technol, 11, 348.
- Fox, M.E. 1977. J. Fish Res. Bd. Can. 34, 798-804.
- Higa, T., and P.J. Scheuer. 1975. Naturwissenschaften, 62, 395-396.
- Jolley, R.L. (Ed.) 1976. Proceedings of the 1975 Conference on the Environmental Impact of Water Chlorination, ORNL CONF 751096, Oak Ridge, Tennessee.
- Keith, L.H. (Ed.) 1976. Identification & Analysis of Organic Pollutants in Water. Ann Arbor Science Publishers, Inc., Ann Arbor, MI, 718 p.
- Leach, J.M., and A.N. Thakore. 1977. Prog. Water Tech., 9, 787-798.
- Lindström, K. and J. Nordin. 1976. J. Chromatog., 128, 13-26.
- Mass Spectrometry Data Centre. 1974. Eight Peak Index of Mass Spectra. 2nd ed., Mass Spectrometry Data Centre, Aldermaston, U.K., 2933 p.
- Matsumoto, G., R. Ishiwatari, and T. Hanya. 1977. Water Res. 11, 693-698.
- Merck and Co., Inc. 1976. The Merck Index, 9th ed., Merck and Co., Inc., Rahway, N.J.
- Neidleman, S.L. 1975. CRC Critical Reviews in Microbiology 3 (4), 333-358.

Rogers, I.H. Sept. 1973. Pulp Paper Mag. of Can., 74 (9).

Rogers, I.H., and L.H. Keith. 1974. "Organochlorine Compounds in Kraft Bleaching Wastes. Identification of Two Chlorinated Guaiacols", Environment Canada, Fisheries & Marine Service, Res. & Dev., Technical Report No. 465.

USEPA. 1973. Fed. Reg. Part II, Vol. 38, Nov. 28.

USEPA. 1977. "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants", EMSL, Cincinnati, Ohio, 69 p.

WI DNR, "Investigation of Chlorinated and Nonchlorinated Compounds in the Lower Fox River Watershed". EPA Contract No. 68-01-4186 (in press).