



Project Summary

Analysis of Chlorinated Organic Compounds Formed During Chlorination of Wastewater Products

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Chemical by-products produced during the chlorination of municipal wastewater were examined in a study that employed several specially modified analytical methodologies. Volatile by-products were examined with the use of gas chromatography with selective detectors and gas chromatography/mass spectrometry (GC/MS). With the use of XAD resins for concentrating trace organics in the wastewater samples before and after chlorination, a number of chlorinated aromatic and aliphatic compounds were found after chlorination and superchlorination.

A rapid and convenient microextraction method was developed that is suitable for analyzing trihalomethanes and other volatile halogenated organics at the microgram-per-liter level in water. Also, a computer program was developed that may be used in conjunction with a GC/MS computerized data system to identify polyhalogenated compounds present as minor components of a complex chemical mixture. A procedure was also developed to determine the concentrations of amino acids in wastewaters, sludges, and septage before and after chlorination. Two chlorinated derivatives of tyrosine were found in a superchlorinated septage sample.

Non-volatile compounds in natural waters and municipal wastewaters, before and after chlorination, were studied with the use of high performance liquid chromatography. Fractions

collected before chlorination of the sample showed that trihalomethane formation potential was spread throughout the natural polymer. After chlorination, total organic halides of a non-volatile nature were determined by adsorption of the organics on either XAD resins or powdered activated carbon (PAC) followed by elution of the resin and combustion of the eluate or by direct combustion of the PAC. In both cases, it was found that organic halogen was spread throughout the natural polymer, although chlorination at the levels used (20-30 mg/L) did not much affect the average molecular weight of the polymer.

This Project Summary was developed by EPA's Environmental Research Laboratory, Athens, GA, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Objectives

This report describes a series of studies that examined the chemical by-products formed during the chlorination of municipal wastewater effluents. When the research began in 1974, little was known about this subject; since then, the question of by-products formed during the chlorination of all types of waters has been investigated extensively. It is now well established that by-products are produced whenever chlorine is used as a disinfectant or a biocide. Among these

are the trihalomethanes, now the subject of regulations that limit their concentration in drinking water.

The objectives of the research reported here were:

1. to develop methods for separating and identifying the types and quantities of volatile by-products produced during the chlorination of water, particularly municipal wastewater after secondary treatment. Central to this effort was the evaluation of XAD resins for concentrating trace organics in water and the use of gas chromatography with selective detectors and gas chromatography/mass spectrometry (GC/MS) for elucidating the structures of these substances.
2. to develop separation methods based on high performance liquid chromatography (HPLC) for the study of wastewater effluents and natural waters before and after chlorination. The purpose of these studies was to extend our knowledge about non-volatile compounds in water and, in particular, to determine whether halogenated non-volatile compounds are produced during chlorination of water and wastewater.
3. to investigate the chlorinated by-products produced when very large doses of chlorine (1000-3000 mg/L) are used to treat wastewaters, sludges, and septage. The use of such high doses has been proposed as a method for disinfecting and stabilizing septage and sludge and as a possible alternative wastewater treatment scheme for small systems.

Volatile By-Products of Superchlorination of Wastewater Products

Samples investigated in this study included raw municipal sewage, secondary municipal effluent, anaerobic digester supernatant, combined sludges, and septage. In most cases, by-products examined were from the chlorination of these samples using 1000-3000 mg/L chlorine, but chlorinated by-products were also found in samples chlorinated with lower doses. Volatile by-products identified included a series of polychlorinated phenols, chloroform, chlorinated benzenes and alkyl benzenes, polyhalogenated acetones, and other aliphatic halides (Table 1). In a separate study, the chlorination of amino acids in municipal wastes was also examined with emphasis on determining chlorinated by-

Table 1. Summary of Chlorinated Organics Found in Superchlorinated Municipal Wastewater

Compound Number	Compound Name ^a	Identification Status	Concentration ^b µg/L
1	Chloroform	f,g	-
2	Dibromochloromethane	f,g	-
3	Dichlorobutane	d,g	27
4	3-chloro-2-methylbut-1-ene	f	285
5	Chlorocyclohexane (118)	d,g	20
6	Chloroalkyl acetate	d	-
7	o-Dichlorobenzene	f	10
8	p-Dichlorobenzene	f	10
9	Chloroethylbenzene	e	21
10	Tetrachloroacetone	e	11
11	Pentachloroacetone	f	30
12	Hexachloroacetone	f	30
13	Trichlorobenzene	f	-
14	Dichloroethylbenzene	f	20
15	Chlorocumene (154)	d,g	-
16	N-methyl-trichloroaniline (209)	d,g	10
17	Dichlorotoluene	e,g	-
18	Trichlorophenol	e	-
19	Chloro-α-methyl benzyl alcohol	e,g	-
20	Dichloromethoxytoluene	e,g	32
21	Trichloromethylstyrene (220)	d,g	10
22	Trichloroethylbenzene (208)	d,g	12
23	Dichloro-α-methyl benzyl alcohol (190)	d	10
24	Dichloro-bis(ethoxy)benzene (220)	d,g	30
25	Dichloro-α-methyl benzyl alcohol (190)	d	-
26	Trichloro-N-methylanisole	e,g	-
27	Trichloro-α-methyl benzyl alcohol	e	25
28	Trichloro-α-methyl benzyl alcohol	e	25
29	Tetrachlorophenol	f	30
30	Trichloro-α-methyl benzyl alcohol	e	50
31	Trichlorocumene (222)	d	-
32	Tetrachloroethylstyrene (268)	d	-
33	Trichlorodimethoxybenzene (240)	d	-
34	Tetrachloromethoxytoluene (258)	d	4
35	Dichloroaniline derivative (205)	c	13
36	Dichloroaromatic derivative (249)	c	15
37	Dichloroacetate derivative (203)	c,g	20
38	Trichlorophthalate derivative (296)	c	-
39	Tetrachlorophthalate derivative (340)	c	-

^aCompounds may be listed more than once if GC retention times indicate distinct positional isomers.

^bQuantitative values should only be considered as estimates, because response factors and recovery data were not available for our extraction system.

^cMass spectral information is too incomplete to propose a structure; probable molecular weight is indicated in parentheses.

^dFragmentation pattern tentatively suggests proposed compound; probable molecular weight is indicated in parentheses.

^eProbable identification is based on mass spectral interpretation.

^fCompleted identification is based on MS interpretation and confirmed by comparison with a reference spectrum.

^gCompounds were identified in runs other than November 12, 1974.

products. Chloro- and dichlorotyrosine were found in a superchlorinated septage sample, and other neutral products were also characterized.

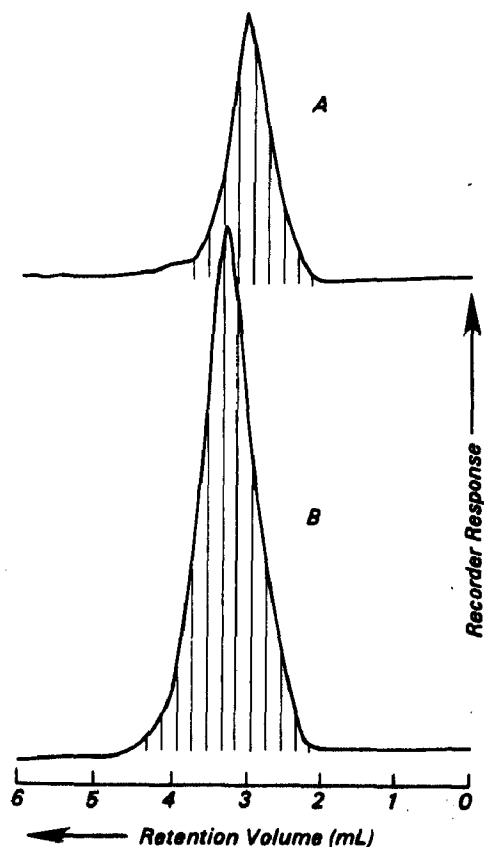


Figure 1. Size exclusion chromatograms of Cross Lake sample, freeze dried water soluble fraction. A, unchlorinated; B, chlorinated at 20 mg/L for five days.

With the exception of the studies searching for amino acid by-products, the separation procedure used in these investigations was XAD resin adsorption, followed by ether elution, evaporative concentration, and GC analysis. Selective detectors (halogen-sensitive Coulson electrolytic conductivity and electron capture) and GC/MS were used for identifying halogenated by-products.

Amino acids were concentrated by sequential adsorption/elution from DOWEX 50W-X8 and Chelex-100 resins, followed by derivatization to the N(O)-heptafluorobutyl *n*-propyl (or *iso*-amyl) esters. Identification and quantification was with GC/MS. Amino acids in raw and chlorinated municipal wastewater determined by this method, were compared with levels determined by a Beckmann amino acid analyzer with generally good agreement.

Non-Volatile By-Products of Chlorination of Natural Waters and Wastewaters

Two methods were used to investigate non-volatile by-products: an adsorption-combustion-microcoulometric procedure, which sought to measure total organic halides (TOX), and a series of HPLC-based procedures with various detectors, including manual collection of fractions for TOX, dissolved organic carbon (DOC), and trihalomethane formation potential (THMFP) measurements. (THMFP measures the potential of naturally occurring organics to form trihalomethanes upon chlorination. The ratio of THMFP to DOC is a measure of this potential normalized to the organic content of the sample.)

Samples included a secondary municipal wastewater effluent and water from a reservoir in western Louisiana (Cross Lake). The non-volatile organic compounds were isolated by freeze drying and redissolved to obtain fractions soluble in neutral, acid, or base solutions. Further fractionation of the neutral fraction by size exclusion HPLC showed that chlorination changes the molecular weight profile of the natural polymer only slightly (Figure 1). Moreover, before chlorination, trihalomethane formation potential is spread through the molecular size range of the polymer (Table 2). Fractionation of the polymer after chlorination showed that the non-volatile organic-bound halogen (NVTOX) is also spread throughout the polymer (Table 3). These results show that the potential for forming THMs and other halogenated by-products is most likely a characteristic of the organics in natural waters, and moreover, that flocculation techniques are not likely to remove THMFP entirely.

Fractionation of the freeze-dried acid soluble fraction of the natural polymer with a weak anion exchange resin with pH gradient elution produced fractions in three separate pH regions (Figure 2). Model compound studies suggest that one of these fractions has a pK_a value similar to that of phenols, and another, the pK_a value of hydroxybenzoic acids. The nature of the third fraction, which occurs to various extents in waters from different sources, is unknown.

Table 2. Characteristics of the Water Soluble Fractions of Cross Lake Water Collected by Size Exclusion HPLC (Unchlorinated)

Fraction Number	Molecular Weight Range	Molecular Weight at P_k Maximum	DOC ^a (mg/L)		THMFP ^c (μ g/L)		THMFP ^d /DOC	
			\bar{x}	S^b	\bar{x}	S^b	\bar{x}	S^b
1	$31.6 \times 10^3 - 15.9 \times 10^3$	22.4×10^3	0.63	0.04	31	7	.049	.011
2	$22.3 \times 10^3 - 7.9 \times 10^3$	14.2×10^3	0.93	0.00	73	2	.078	.002
3	$19.1 \times 10^3 - 7.1 \times 10^3$	10.3×10^3	1.28	0.04	95	10	.074	.008
4	$15.9 \times 10^3 - 5.1 \times 10^3$	7.9×10^3	1.22	0.20	43	5	.035	.004
5	$6.3 \times 10^3 - 0.2 \times 10^3$	3.9×10^3	0.91	0.20	62	2	.068	.002
Average Sum	10.5×10^3		4.97		304 (262 as Cl)		.061	.005

^aDOC = Dissolved Organic Carbon.

^bS = Standard Deviation.

^cTHMFP = trihalomethane formation potential using a chlorine dose of 20 mg/L, 3 days, pH 6.5.

^dUnits of THMFP/DOC in mg THMFP/mg C.

Table 3. Characteristics of the Water Soluble Fractions of Cross Lake Water Collected by Size Exclusion HPLC (Chlorinated^a)

Fraction Number	Molecular Weight Range	Molecular Weight at Pk Maximum	DOC \bar{X}	(mg/L) S^b	NVTOX ^c \bar{X}	($\mu\text{g/L}$) S^b	NVTOX/DOC ^d \bar{X}	S^b
1	$31.6 \times 10^3 - 14.2 \times 10^3$	19.1×10^3	1.04	0.48	65	11	.063	.010
2	$19.1 \times 10^3 - 6.9 \times 10^3$	12.6×10^3	0.98	0.16	47	8	.048	.008
3	$15.9 \times 10^3 - 6.3 \times 10^3$	7.1×10^3	1.00	0.36	86	13	.086	.013
4	$12.6 \times 10^3 - 2.2 \times 10^3$	3.9×10^3	0.64	0.08	20	9	.031	.014
5	$7.1 \times 10^3 - 0.15 \times 10^3$	2.5×10^3	0.52	0.04	42	8	.081	.015
Average	8.2×10^3						.062	.012
Sum			4.18		260			

^aOriginal sample chlorinated at 20 mg/L for five days before freeze-drying and redissolving.

^bS = Standard deviation.

^cNVTOX = non-volatile TOX determined by the XAD procedure after purging sample to remove THMs and other purgeable organohalides.

^dNVTOX/DOC in mg Cl/mg C.

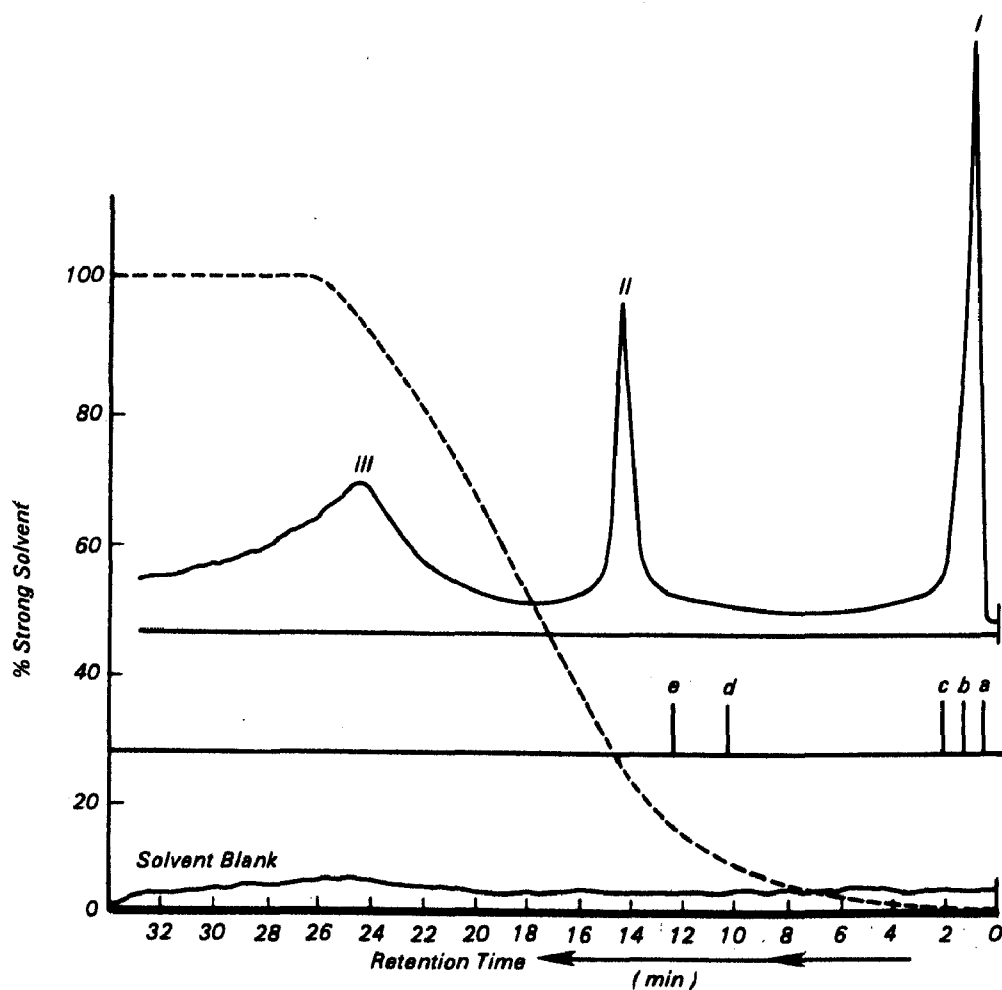


Figure 2. Weak anion exchange HPLC chromatogram of Cross Lake water, acid soluble fraction of freeze dried sample (unchlorinated). Reference compound code: a-phenol; b-3-methylcatechol; c-vanillic acid; d-2,4-dihydroxybenzoic acid; e-2,4,6-trihydroxybenzoic acid. Dotted line: solvent gradient (100%=pH 6.2; 0%=pH 3.2)

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A. W. Garrison is the EPA Project Officer (see below).

The complete report, entitled "Analysis of Chlorinated Organic Compounds Formed During Chlorination of Wastewater Products," (Order No. PB 83-144 444; Cost: \$17.50, subject to change) will be available only from:

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