Precursors of non-volatile chlorination by-products

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There has been continued concern over the health effects of chlorination by-products.[1,2] The chlorinated organic compounds that have received the most attention thus far, are the trihalomethanes (THMs).[3-6] THMs are produced by the reaction of aqueous chlorine with organic carbon in water. The source of the organic carbon has been examined by numerous workers.

Aquatic humic material is present in all waters and it is sufficiently similar in time and space that it has become the "prime suspect."[4,7,8] There are other components of total organic carbon (TOC) that are capable of THM production upon chlorination. Morris and Baum,[9] showed that chlorophyll produces THMs in its reaction with aqueous chlorine. Hoehn *et al.*,[10] demonstrated that algal extracellular products (ECP) are potent THM precursors. Briley *et al.*,[11] concluded that ECP from algal growth, as well as algae biomass, produce THM concentrations comparable to that produced from humic and fulvic acids. Phenol and ketones[12-14] and a host of other simple organic compounds are also capable of producing THMs upon chlorination. The concentrations of these compounds in tertiary-treated wastewaters or potable waters have always been deemed too low to consider them major THM precursors.

During the past several years there has been increased attention to the non-THM chlorination by-proucts. Glaze[15] found that the ratio of non-volatile to volatile chlorinated organic compounds produced from the chlorination of fulvic acids (natural carbon sources in water) to be 2:1.

Contrary to conventional belief, substances distinguished as aquatic fulvic acids but soluble in organic solvents are responsible for toxic chlorinated organic contaminants.

Non-volatile halogenated compounds can be analyzed collectively as a lump parameter by microcoulometry and labeled as total organic halogen (TOX).[16] Alternately, a subset of these compounds can be examined in detail by a chromatographic procedure. In this paper, the term "non-volatile" when applied to chlorination by-products means less volatile than THM and other purgeable compounds, but sufficiently volatile to be analyzed by gas chromatography (GC). The portion of TOX not analyzable by GC or gas chromatography/mass spectroscopy (GC/MS) is not considered in subsequent analysis.

High performance liquid chromatography (HPLC) has frequently been used as the chromatographic procedure to separate the TOX. The HPLC enables the separation and analysis of components of high molecular weight and it is potentially capable of analyzing most of the chlorination by-products. The HPLC, however, suffers from low sensitivity and poor resolution in comparison to gas chromatography. Gas chromatography and GC/MS techniques currently provide the best available techniques to identify organic compounds. Gas chromatography and GC/MS protocols are only capable of analyzing relatively light, and relatively non-polar compounds. Consequently, only a fraction (5–50%) of the components of TOX are amenable to GC analysis.

The broadest observation and probably the least debatable assessment of TOX precursors was made by Jolley[17] who noted the great variety of natural organic compounds in water, and stated that most of them are reactive with chlorine. Wachter and Andelman[18] noted that both algal biomass and ECP are as potent as humic materials in producing equivalent levels of TOX, THM, and non-purgeable TOX (NPTOX).

Other workers have attempted to narrow Jolley's observations. Wong and Oatts[19] observed that the less than 1000 molecular weight TOC fraction had the greatest chlorine demand. The results of Becher's[20] ultrafiltration work corroborate this finding. Eighty-two percent of the TOX was produced from chlorinating the portion of TOC having a molecular weight less than 1000. Reinhard[21] noted that the contribution to TOC of the less than 1000 molecular weight fraction increased from 27 to 53% after tertiary treatment. These findings imply that lower molecular weight components of TOC may be an important reactant with aqueous chlorine in tertiary-treated effluents. Other workers[22] also stressed that higher molecular weight material is more amenable to removal than the lighter components of TOC. Reckhow and Singer,[23] however, stated that humic acids are more TOX productive than fulvic acids.

This paper investigates the nature of the major precursors to the observed gas chromatographic, non-volatile chlorination by-products in a chlorinated, tertiary-treated, domestic wastewater effluent. An abundance of these compounds was observed in the plant's final effluent. It has been previously reported[24,25] that many of these non-volatile chlorination by-products are reactive with dechlorinating agents and have consequently escaped routine detection. These observations about the precursors are discussed, regarding tertiary wastewater treatment.

The overall study examined the identification of gas-chromatographable, non-volatile chlorination by-products and their reactivity with the sulfite ion. Possible treatment alternatives for the observed compounds were also studied. The results on the treatment of the unwanted, halogenated, compounds are discussed in a subsequent paper.

EXPERIMENTAL PROCEDURES

Water samples. In this work, most water samples were collected at a tertiary wastewater treatment plant in San Diego,

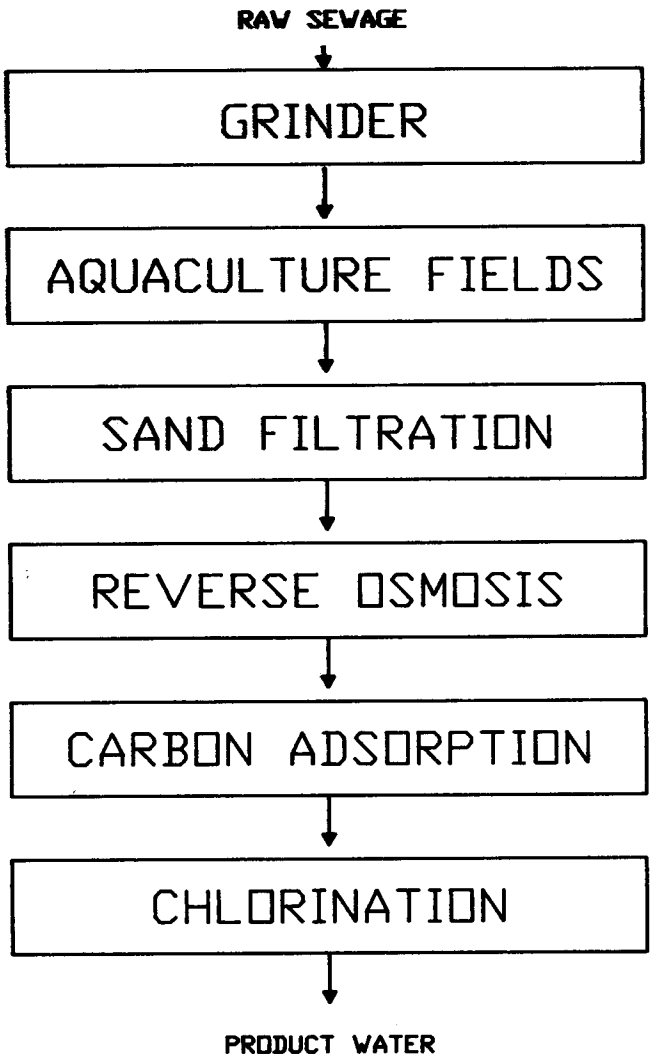

Figure 1—Schematic of the San Diego Wastewater Treatment Plant.

Calif. A schematic of the unit operations at the treatment plant is shown in Figure 1. A complete description of the plant is given elsewhere.[24,25] The most significant difference between this plant and other plants is that the secondary treatment is accomplished using water hyacinths.

Several experiments were performed to determine the nature of the observed halogenated compounds precursors. It was assumed that the precursors to these compounds are present in the aquaculture effluent, which greatly simplified the laboratory work. Working with the aquaculture effluent meant that the precursors would be found in higher concentration than in the pre-chlorination, carbon adsorption effluent. This consequently reduced the required volume of water needed to collect the precursors.

Several different fractionation schemes were used to separate the organics in the aquaculture effluent. The various fractions were subsequently chlorinated in the laboratory and the GC outputs were compared to Figure 2, which shows chlorinated San Diego effluent. The identified halogenated compounds produced during disinfection are listed in Table 1. Fractions from other treatment plants were also chlorinated in the laboratory to test whether these precursors are unique to aquaculture secondary treatment. The final experiment involved the laboratory chlorination of pure compounds that could be present in the aquaculture effluent. The GC outputs from this pure compound chlorination experiment were also compared to Figure 2. The eight experiments performed are listed in Table 2 and will each be discussed separately.

The experiments described in Table 2 have collectively provided a good description of the precursors by solubility, molecular weight, and polarity. The results from the chlorination of pure compounds reinforces these descriptions, suggesting the nature of the precursors. The analytical methods used for fractionation, solvent extraction, XAD8 resin adsorption, and GC analysis were common to most experiments in Table 2 and are described later.

XAD8 adsorption. The aquaculture effluent was adsorbed on XAD8 resin. The procedure of Thurman and Malcolm[26] for the

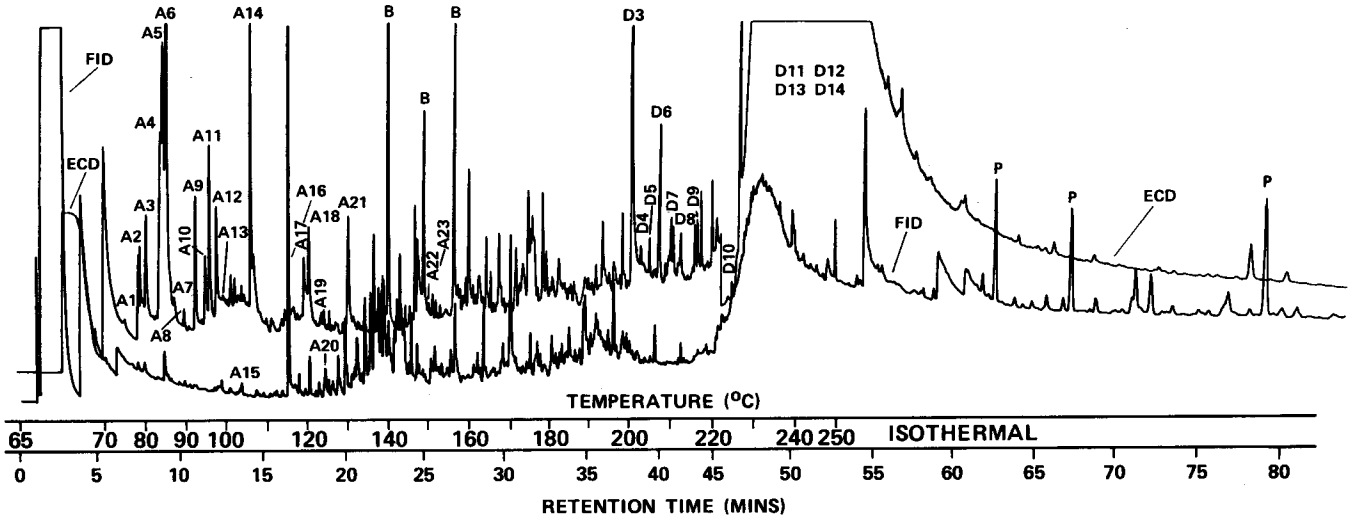

Figure 2—GC of the San Diego Wastewater Treatment Plant chlorinated final effluent. GC conditions as specified in analytical procedures. Axes are labeled for the ECD. Compound ID in Table 1.

Table 1—Halogenated compounds produced during disinfection.

Identification	RT, min	Method of ID[a]	Percent confidence in ID	Reference number	Concentration in chlorinated[b] SD final effluent average, μg/L
Chloroform	—	1, 2, 3	>95	E1	ND
Chloro-bromomethane	—	1, 2, 3	>95	E2	ND
Dichloro-propane	—	1, 2	90	E3	ND
Dichloro-cyclohexane	5.52	1, 2	60	A1	3.1
Unknown unsaturated chlorinated compound	6.39	—	—	A2	5.0
Unknown	6.67	—	—	A3	0.5
Chloro-iodo methane	7.80	1	>95	A4	0.8
2-Propanone 1,1 dichloro	8.00	1, 2	90	A5	5.7
2-Propanone 1,1,1 trichloro	8.28	1, 2	90	A6	10.0
C_3NCl_3	9.17	1	60	A7	0.7
1-Propene 1,2,3,3 tetrachloro	9.46	1, 2	80	A8	<0.5
Unknown	9.85	—	—	A9	<0.5
Unknown	9.91	—	—	A10	0.4
$C_4H_6Cl_3N$	10.64	1	60	A11	1.0
$C_5H_8Cl_2$	11.17	1	90	A12	2.9
MW 152, 2 chlorines $C_4H_2O_2Cl_2$	11.94	1	60	A13	0.3
$C_5H_3Cl_3O$	13.25	1	70	A14	4.6
Cyclopentanol 1,2 methyl	14.24	1, 2	90	A15	1.5
$C_5H_5Cl_3O$	15.25	1	90	A16	<0.5
Pentachloropropene	15.83	1	90	A17	1.5
$C_5Cl_3H_5O$	16.49	1	90	A18	3.3
MW 146, 1 chlorine	17.21	1	60	A19	3.1
Benzaldahyde	17.63	1, 2	90	A20	1.2
Unknown	19.36	—	—	A21	4.2
1-Hexanone,5 methyl,1-phenyl	22.48	1, 2	70	A22	3.1
Unknown halogenated aliphatic acid	22.64	—	—	A23	<0.5
Unknown	23.43	—	—	A24	<0.5
Unknown halogenated aliphatic. Formed mostly at high pH and low chlorine dose	25.54	—	—	A25	<0.5
$C_4H_4Cl_4O$ (may be fragment of larger molecule) molecule	36.23	1	60	D1	ND
$C_4H_2Cl_4O$ (may be fragment of larger molecule)	36.25	1	60	D2	ND
C_4Cl_4O (may be fragment of larger molecule)	36.55	1	80	D3	8.9
2,4, Dichloro-6-methyl phenol	37.43	1, 2	90	D4	<0.5
$C_8Cl_2OH_{14}$	38.60	1	30	D5	1.9
$C_8H_9Cl_2NO_2$	38.87	1	30	D6	7.6
$C_{10}Cl_2H_{12}NO_2$	39.55	1	30	D7	1.0
2,4,6 trichlophenol	40.61	1, 2, 3	>95 70	D8	2.8
Dichloro-propyl phenol	41.61	1		D9	0.6
Trichloro benzoic acid	42.89	1	60	D10	33.2
MW 232, 3 chlorines	44.12	1	60	D11	0.8
MW 230, 3 chlorines	45.15	1	60	D12	5.1
Trichloro-phenol ethoxy	46.03	1	80	D13	5.8
Unknown	47.59	—	—	D14	<0.5

[a] 1 = manual interpretation of MS scan; 2 = computer-matched interpretation of MS scan; and 3 = GC retention time match with known standard.

[b] Concentration is based on 10 000 area counts/ng for flame ionization detector (FID) area. Concentration is the average for all samples collected at the San Diego plant. Concentration values should be regarded as ±100%.

collection of fulvic and humic acids, modified with additional resin cleaning steps, was used. No humic/fulvic split was made. Details are provided elsewhere.[24]

Extractable organics analysis. A modification of an extraction procedure previously developed to quantify total extractable organics in run-off waters was used.[27] A large volume of water (1 to 4 L) was acidified to pH 2 with concentrated sulfuric acid. Sodium chloride (5 g/L water) was added to the extraction vessel before extraction. The sample was then extracted with three successive portions of methylene chloride (60 mL CH_2Cl_2/L water) for 5 minutes. Standards composed of 1-bromohexadecane, hexadecene, tetradecane, *m*-cresol, or *o*-chlorophenol were used

Table 2—Experiments to fractionate the precursors.

Experiment	Description
1	Chlorination of XAD8 extract
2	Chlorination of CH_2Cl_2 total and silica gel fractions
3	Solvent extraction versus XAD8 adsorption for precursors collection
4	Chlorination of organic solvent fractions eluted from XAD8 columns
5	Chlorination of humic/fulvic fractions
6	Chlorination of ultrafilter separated fractions
7	Chlorination of fractions from other treatment plants.
8	Chlorination of pure compounds

to determine recovery efficiency depending on the chromatographic pattern of the sample. All of these standards interfered with some of the peaks to a certain extent due to the complexity of the chromatograms. The areas of these standards were subtracted prior to all quantitative calculations. No other corrections were made to any of the GC results. If a sample showed low recovery (less than 90%), then the experiment was repeated. The recovery standards were used only as a check that the extractions were of high efficiency.

GC analysis was performed with an instrument equipped with both a flame ionization and an electron capture detector (FID and ECD) in a splitless mode. The two detectors work in parallel by means of an SGE fused silica splitter.

All GC and GC/MS samples were run using a 30-m Supelcowax 10 (0.25 mm inside diameter) fused silica column. Helium was used as the carrier gas at a pressure of 103 kPa (15 psig). The initial column temperature was 65°C with an initial 4-minute hold. The oven temperature was then programmed to 250°C at 4°C per minute. The column temperature was held at 250°C for 30 to 55 minutes. The injection port was set at 250°C and the detector oven maintained a 280°C temperature. Peak areas were integrated electronically. The integrated area report was stored on floppy disks by a personal computer (PC) connected to the integrator. All calculations and data analysis were performed on the PC using the stored data. GC/MS samples were run at an initial 25°C with all other variables as previously mentioned.

Chlorination of extracts. Solvent extractable and XAD8 adsorbable organic compounds from the aquaculture effluent were chlorinated in concentrated, 15-mL solutions. The extract was added to an appropriate amount of distilled water so that after addition of chlorine solution, the total volume was 15 mL. Chlorine was added as a 4 mg/mL solution followed by pH adjustment. The 25-mL flask was then stirred for the appropriate time before extraction (usually two hours).

Extractions were done in 60-mL separatory funnels. After the addition of NaCl and sulfuric acid, the reaction flask was rinsed with 25 mL of methylene chloride. The wash was added to the separatory funnel. Samples were extracted for 1 minute. The combined three extracts were evaporated and dried as previously described.[24]

Silica gel chromatography. A 14-cm, silica gel packed column (1.9 cm diameter) was used to separate the methylene chloride extracted organics into three fractions. The silica gel was cleaned by extracting in a Soxhlet device with methylene chloride overnight prior to use, and rinsing with two column lengths of each solvent used. An aliphatic, non-polar fraction was eluted with two column lengths of hexane. An aromatic, non-polar fraction was eluted with two column lengths of benzene and a third polar fraction was collected with two column lengths of 1:1 methylene chloride:methanol and two column lengths of methanol.

Reagents. All reagents were analytical grade or better. All solvents were distilled before use. The sodium chloride and sodium sulfate were baked at 550°C for at least 4 hours before use. All aqueous reagents were prepared in distilled water. Polytetraflourethylene tape was used in place of stopcock grease at all times.

RESULTS

XAD8 chlorination extracts from the aquaculture effluent. It was initially conjectured that humic and fulvic acids were the major precursors to the observed halogenated organics. It has been shown that XAD8 resins are effective in the concentration of these natural acids.[26] Several other researchers have shown that chlorinated XAD8 extracts yield an abundance of halogenated compounds.[28,29] Therefore, XAD8 resin was chosen to concentrate these precursor compounds from the aquaculture effluent. It should be noted that XAD8 resin is fully capable of adsorbing a host of compounds contained in treated wastewaters and that humic and fulvic acids are only a small fraction of the different adsorbed organics.[30,31]

Carbon adsorption effluent prior to chlorination at the San Diego treatment plant typically had a TOC of 0.5 to 1.0 mg/L. Therefore, it was decided that a laboratory chlorination with 1.0 mg TOC of XAD8 extract should be performed. Figure 3 compares favorably to Figure 2, showing that chlorination of the XAD8 extracts reproduced most of the halogenated compounds observed at the San Diego plant. Figure 3 does not contain compounds present prior to chlorination because they are not collected by the XAD8 adsorption/desorption protocol (they are only desorbed by an organic solvent). The total ECD area produced upon chlorination of 1.0 mg XAD8 TOC with 2.5 or 10.0 mg free chlorine is almost identical to the total ECD area produced by the halogenated compounds in 1 L of chlorinated San Diego effluent. This implies that our choice of chlorination conditions are representative of actual conditions.

The results of this experiment indicate that the precursors are collectible by XAD8 adsorption. This implies that the precursors are acidic compounds found in the aquaculture effluent (adsorbable in acid solution, but desorbable with alkaline solution).

Laboratory chlorination of CH_2Cl_2 extracts. Total methylene chloride extractable organics from the aquaculture effluent, as well as the silica gel fractionated extract, were redissolved in distilled water and chlorinated as concentrated 15-mL solutions (Fractions 1 and 2 were dissolved in 2.0 mL of methanol before addition of water; blanks demonstrated that methanol addition does not affect any of the GC results. Aquaculture extract (1.5 mg, by weight) was used and a chlorine dose of 2.5 mg was applied at pH 7 for a 2-hour contact period.

The resultant chromatographs were compared to Figure 2. The chlorinated total extract, and the chlorinated third fraction (methanol:methylene chloride elutable) gave very similar chlorination patterns to Figure 2. Fraction 1 (hexane eluate) and Fraction 2 (benzene eluate) were basically not affected by the

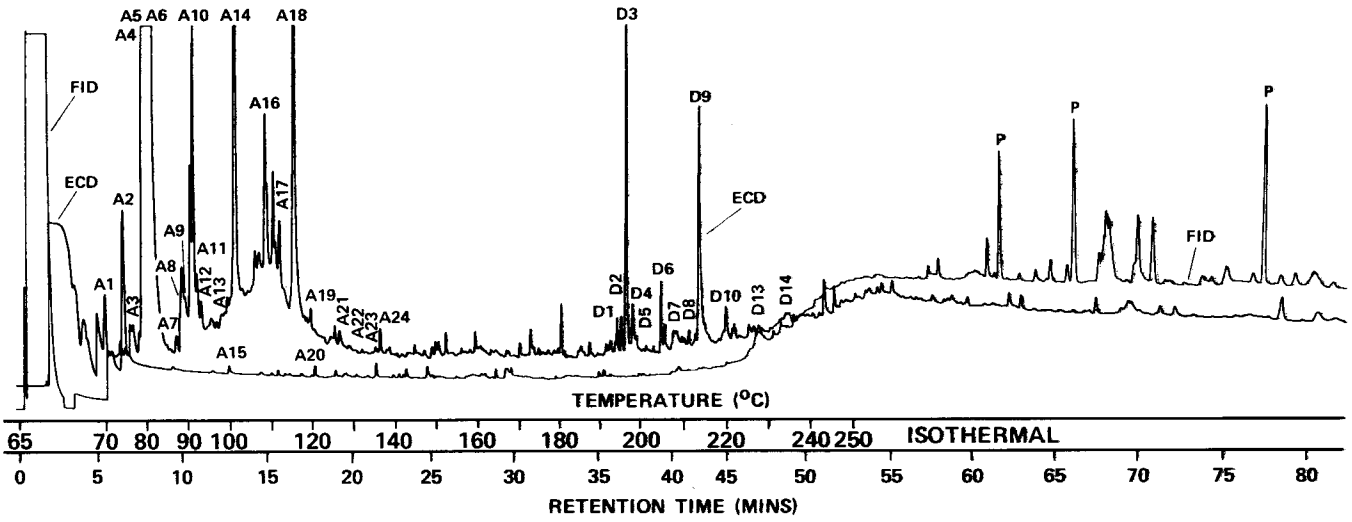

Figure 3—GC of chlorinated XAD8 aquaculture extract. Chlorination conditions: 1 mg TOC, 10 mg chlorine, pH 7, contact time 2 hours. GC conditions as previously specified. Axes are labeled for the ECD. Compound identified in Table 1.

addition of chlorine. Compounds in the third fraction caused an increase of 66% in ECD area. In the total extract, 30% of the increased ECD area could not be accounted for in the three collected fractions. This implies that compounds too polar to elute from the silica gel column were responsible for the difference.

The results from this experiment show that the precursors are polar compounds (third fraction and nonelutable polar fraction). This conclusion concurs with the results of Experiment 1. More significant, however, is the observation that the precursors are solvent extractable. This implies that they are only moderately polar, because if they were very polar, they would not be solvent extractable. Although this observation is highly qualitative it is also highly significant. Humic and fulvic acids are not generally solvent extractable. Indirectly, therefore, this experiment implies that the precursors do not fit the classic definitions of humic and fulvic acids.

Solvent extraction versus XAD8 adsorption for precursors collection. The experiments discussed in Sections 1 and 2 indicate that the precursors to the observed, non-volatile, chlorinated organics can be collected by either XAD8 resin adsorption or by methylene chloride extraction. An experiment was designed to determine which method is more efficient for the collection of the alleged precursors.

Two 1-L samples of reverse osmosis (RO) effluent were chlorinated in the laboratory with 10 mg/L NaOCl at pH 7 for 2 hours. Another duplicate set of RO effluent samples were chlorinated under the same conditions except that the samples were passed over XAD8 (at pH 2) resin before chlorination. A third set of samples was extracted with CH_2Cl_2 and the methylene chloride was discarded before chlorination at pH 7. The resultant total ECD areas from each set of samples were then compared.

The XAD8 treated samples showed an average 70% reduction in total ECD area, whereas the methylene chloride extracted samples showed only an average 33% reduction in total ECD area. This shows that the XAD8 resin is more effective in removing the precursors to the observed gas chromatographable non-volatile chlorinated organics. This is quite fortunate because XAD8 adsorption is simpler and cheaper to perform than solvent extraction (once the resin has been cleaned). It was decided that XAD8 resin be used for all future precursors collection protocols.

Chlorination of organic solvent eluted fractions from XAD8 columns. To better understand the solubility properties of the precursors the following experiment was performed. Sixteen liters of aquaculture effluent at pH 2 were passed through a cleaned XAD8 column. The adsorbed organics then were eluted with a series of increasingly polar solvents. The first fraction was collected with 35 ml of diethyl ether. The second fraction was collected with 35 mL of methylene chloride and a third fraction was collected in the same volume of methanol. The fourth fraction was eluted with an identical volume of 0.1 *N* NaOH.

Each fraction was analyzed by GC before and after chlorination with 10 mg/L NaOCl at pH 7 for 2 hours. As would be expected, many of the solvent extractable compounds in the aquaculture effluent were collected by XAD8 adsorption and appeared in both the ether and methylene chloride fractions. These fractions consequently contained background organics that gave a sizeable ECD response. The solvent extractable compounds are not collected in the Thurman/Malcolm XAD8 adsorption procedure because the XAD8 adsorbed organics are collected with 0.1 *N* NaOH instead, and these gas chromatographable compounds are not elutable with this alkaline solution.

Table 3—Organic solvent fractionated XAD8 extract.

Fraction number	Solvent	Total ECD area before chlorine addition	Total ECD area after chlorine addition	Net percent increase in total ECD area due to chlorine
1	Ether	3.38×10^7	3.22×10^8	952
2	CH_2Cl_2	5.73×10^7	1.53×10^8	267
3	Methanol	2.54×10^6	7.61×10^7	2996
4	0.1 *N* NaOH	5.83×10^5	2.32×10^6	398

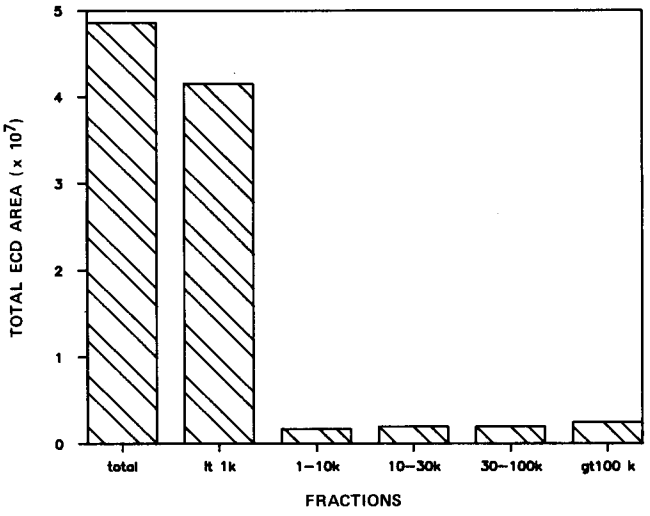

Figure 4—Total ECD areas of chlorinated UF fractions from the San Diego Wastewater Treatment Plant XAD8 extract. It = less than, gt = greater than, k = 1000 daltons.

No effort was made to translate the ECD total areas into concentrations, because the desired results can be obtained by comparing the raw, total areas. Table 3 shows the total ECD area before and after chlorination (the ether, methylene chloride, and methanol were evaporated and the residues were redissolved in distilled water before chlorination).

The precursors to the observed gas-chromatographable, halogenated compounds are apparently easily elutable with organic solvents (ether, methylene chloride, and methanol). This experiment again suggests that these precursors do not fit the classic definitions of humic and fulvic acids because humic compounds are not ether or methylene chloride soluble (fulvic acids are elutable with methanol to a certain extent). Although this experiment points out that the precursors are ether elutable, it is a cleaner separation to collect them with 0.1 *N* NaOH because the background chromatographable compounds are not collected with the sodium hydroxide solution.

Chlorination of humic/fulvic fractions. A humic/fulvic split of the XAD8 extract was made by centrifugation at pH 1. The soluble fraction is fulvic acid and the residue is labeled the humic fraction. The humic and fulvic fractions were analyzed by gas chromatography before and after chlorination, with 10 mg NaOCl at pH 7 for 2 hours. The total ECD response was compared with the unfractionated sample. The fulvic fraction produces 98% of the total ECD area produced by the unfractionated sample (identical GC pattern), whereas the humic fraction only accounts for 6% of the total area of the unfractionated sample. The additional 4% in total area must be attributed to experimental error.

The results of this experiment conclusively demonstrated that humic acid is not the major precursor to the observed compounds. The precursors are present in the fraction that Thurman and Malcolm[26] have labeled fulvic acids. Operationally, this fraction contains acidic compounds that are base soluble. Many workers have chosen to label these compounds fulvic acids for a lack of a better name. It is felt that this label is too broad especially since the precursors of interest have been shown to be organic solvent soluble and classically, fulvic acids are only water soluble.

Chlorination of ultrafiltration fractions. The XAD8 adsorbed organics from the aquaculture effluent were (40 mL from 2000 mL of concentrated extract collected from 360 L; TOC concentration of 1 mg/10 mL concentrated extract) separated into five molecular weight (MW) ranges by ultrafiltration. Ten milliliters (1 mg TOC) of the greater than 100 000 MW, the 100 000 to 30 000 MW, the 30 000 to 10 000 MW and the 10 000 to 1 000 MW fractions were chlorinated with 10 mg chlorine at pH 7 for 2 hours before extraction. Thirty milliliters of the less than 1 000 MW fraction were chlorinated under the same conditions. Thirty milliliters were used because the solution was diluted threefold by the filter washings. GC analysis was performed before and after chlorination for each fraction. All samples were run in duplicate.

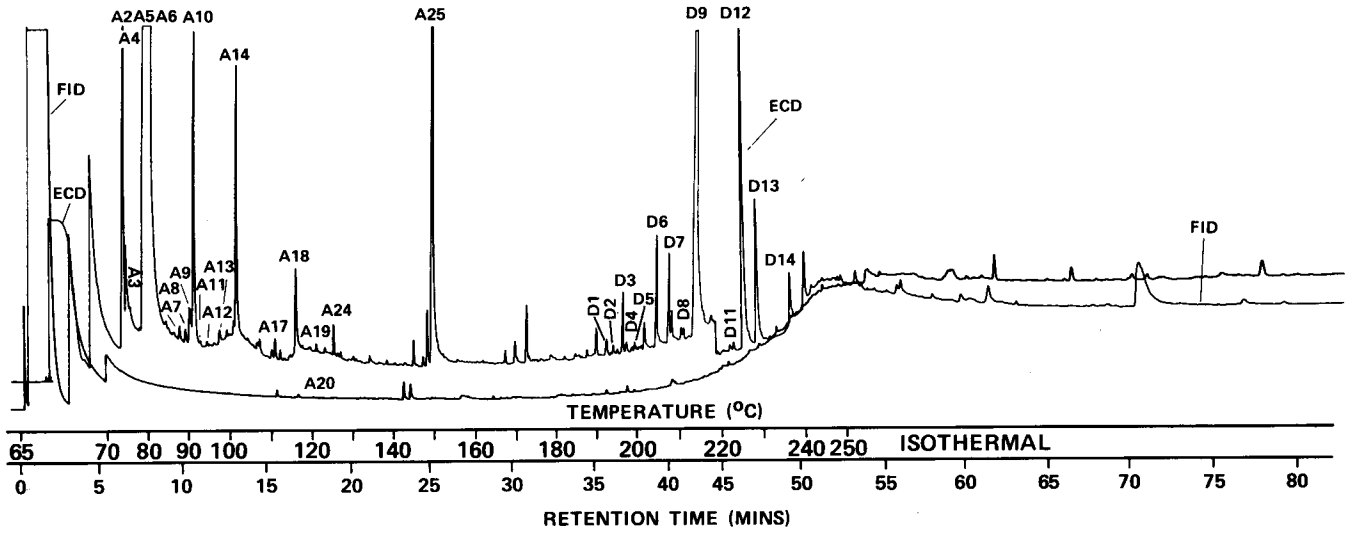

Figure 5—GC of chlorinated XAD8 extract from Whittier Narrows Wastewater Treatment Plant. GC conditions as previously specified. Axes are labeled for the ECD.

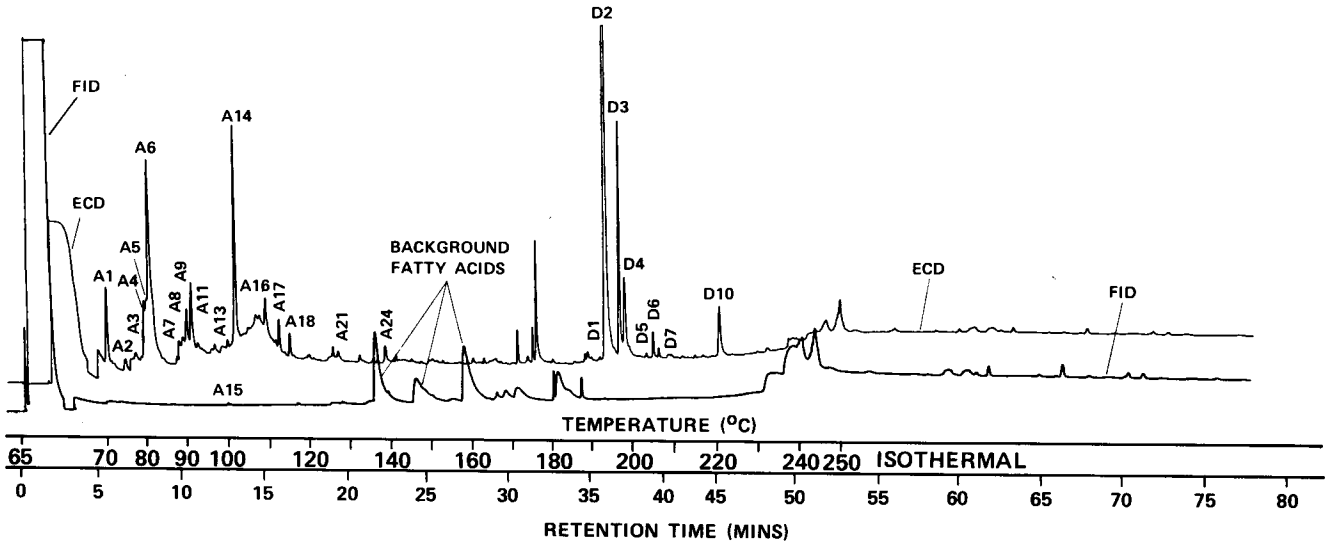

Figure 6—GC of chlorinated XAD8 extracts. GC conditions as previously specified. Axes are labeled for the ECD. Compound identified in Table 1.

Figure 4 shows the total ECD area attributable to chlorination from each fraction. The unchlorinated fractions gave virtually no ECD peaks. No effort was made to translate total ECD areas into concentration because only a relative comparison between the fractions was required. The sum of the total ECD areas for the five fractions was slightly greater than the area of the unfractionated extract (103%), but lies within the range of probable experimental error.

Chlorination of XAD8 extracts from other treatment plants. XAD8 extracts were collected from two other wastewater treatment plants and chlorinated in the laboratory. This experiment was done in order to investigate whether the observed halogenated organics in the San Diego plant are unique to water hyacinth based secondary treatment.

One plant used activated sludge secondary treatment (Whittier Narrows Wastewater Treatment Plant, Whittier, Calif.), while the other plant used water hyacinth fields for secondary treatment (Orlando, Fla). Figure 5 is the GC output for the chlorinated Whittier Narrows XAD8 extract. Figure 6 is the similar output from the Florida water hyacinth treatment plant. A comparison of Figure 3 to Figures 5 and 6 shows that the halogenated organics observed in San Diego are also common to the latter two wastewater treatment plants. The axes in Figures 5 and 6 are labeled for the ECD. The FID axis is slightly offset to the left. The various MW fractions (of the XAD8 extract) of the two treatment plants were chlorinated. Again, the less than 1000 MW fraction accounted for nearly 85% of the total ECD areas of the total unfractionated extract.

In summary, the two wastewater treatment plants show similar halogenated organics profiles upon laboratory chlorination to the San Diego plant. This similarity shows that the precursors are not unique to the San Diego plant nor to water hyacinth based secondary treatment.

Chlorination of pure compounds. Twenty-four pure compounds that are likely to be present in the aquaculture effluent were purchased from various chemical distributors and chlorinated in the laboratory. The compounds were chosen so as to represent an assortment of natural organic compounds. Carbohydrates, lipids, amino acids, metabolic acids, as well as plant pigments were chosen. The resultant gas chromatographs after chlorination were compared to the San Diego chlorinated effluent, as well as the chlorinated aquaculture XAD8 extract. Because only retention time matches (not MS comparisons) were used for comparison, the identifications must be regarded as possible but not positive. The chosen list of compounds is by no means exhaustive and is only meant to give ideas about the halogenated organics formation potential of the chosen classes of compounds.

Table 4 lists the compounds that were chlorinated, the class and amount of the compound that was chlorinated, as well as the applied chlorine dose (if the initial chlorine dose was productive, other doses were attempted). The reference numbers (see Table 1 for reference numbers) for the compounds that were produced during chlorination are also included. Examination of Table 4 shows that carbohydrates, lipids, and fatty acids are not likely to be precursors to the observed compounds. Amino acids, as well as the fatty acids, produce a few halogenated organics upon chlorination, but do not produce the wide spectrum of compounds seen upon chlorinating the XAD8 aquaculture extract.

Figure 7 is a chromatogram of chlorinated Morin, a plant flavonol. Flavones and flavonols are the most widely distributed of all the yellow plant pigments. The deeper yellow colors of plants are normally due to carotenoids. Figure 7 resembles the chromatograms of the chlorinated aquacultures XAD8 extracts (Figure 2). The axis labeled in Figure 7 is for the ECD. The FID is slightly offset to the left.

Flavones and flavonols were chosen as model compounds for chlorination for a variety of reasons. Their MW is less than 1000 (typically 220 to 400). They are soluble in water and organic solvents depending on the extent of hydroxylation. Flavones and flavonols are moderately polar, as well as acidic. These compounds are also widely distributed in the plant kingdom. Lastly, their pale yellow color matches the color of the XAD8

Table 4—Chlorinated pure compounds.

Compound name	TOC mg used	Chlorine added, mg	Reference number produced in trace amounts[a]	Reference number produced in large amounts	Other halogenated compounds produced[b,c]
			Carbohydrates		
Cellulose	10.2	20.4	NP[d]	NP	Low
Corn starch	9.9	19.8	NP	NP	NP
Fructose	5.9	11.8	NP	NP	NP
Levan	4.5	9.0	NP	NP	NP
Pectin	5.8	11.6	NP	NP	NP
			Amino carbohydrates (found in bacterial cell walls)		
N-acetyl-muramic acid	2.5	5.0	NP	NP	NP
N-acetyl-neuramic acid	5.0	10.0	NP	NP	NP
			Aromatic carbohydrate		
Tannic acid	6.0	12.0	NP	A10	Low
			Amino acids and proteins		
Pepsin	5.0	10.0	NP	A14	Low
Proline	5.0	10.0	NP	A12	Low
Tryptophan	4.3	8.6	D7	A14	Low
			Lipids and cholesterol		
Cholesterol	6.3	12.6	NP	NP	Low
Psychosine	2.5	5.0	NP	NP	Low
Sphingosine	2.5	5.0	NP	A2	Low
			Unsaturated hydrocarbon		
Squalene	5.0	10.0	A1, A2	A16	Low
			Fatty acids		
Lactic	5.0	10.0	NP	NP	High
Pyruvic	5.0	10.0	NP	NP	High
Malic	5.4	10.8	NP	NP	High
Oleic	5.0	10.0	NP	NP	High
			Flavone type plant pigments		
Catechin	8.8	20.0	A1, A2, A4, A8, A9, A10, A11		High
Flavone	6.5	13.0	A1, A2, A4, A16, A17, A23, A24, D3, D8, D10		High
Kaempherol	2.5	5.0, 10.0, 20.0, 40.0	A1, A2, A4, A6, A8, A10, A14, A16, A17, A18, A23, A24, D8		High
Morin	2.5	5.0, 10.0, 20.0, 40.0	A1, A2, A4, A6, A8, A9, A10, A14, A16, A17, A18, A23, A24, D3, D8		High

[a] Trace amounts indicate that ECD area for that compound is less than 5% of the ECD response produced by the chlorination of 1 mg XAD8 resin extract.

[b] Low indicates that the ECD area of the compounds is less than three times the background ECD noise blank level.

[c] High indicates compounds are greater than three times background levels.

[d] NP means not productive.

aquaculture extract. In summary, this list of properties closely matches the properties of the precursors in the San Diego XAD8 extract discussed previously.

The similarity of the chlorination products of the flavones and the aquaculture XAD8 extract, as well as the matching of their respective solubility, MW, color, and acidity properties is an appealing match, but admittedly may only be coincidental. Furthermore, it is highly unlikely that these flavone compounds remain unchanged after secondary treatment. It is more plausible that a modified plant pigment may be the reactant with aqueous chlorine.

SUMMARY AND CONCLUSIONS

The major precursors to the observed halogenated compounds were found to be slightly organic solvent soluble and to have MW less than 1000 daltons. The precursors were found to be collectible in the fraction that many researchers call aquatic fulvic acid; however, the fact that these compounds are organic solvent soluble makes it difficult to continue to call them fulvic acids. It is hoped that deviation from traditional nomenclature will stimulate research to better classify aquatic fulvic acids. Humic acid was shown to definitely not be the major precursor to the

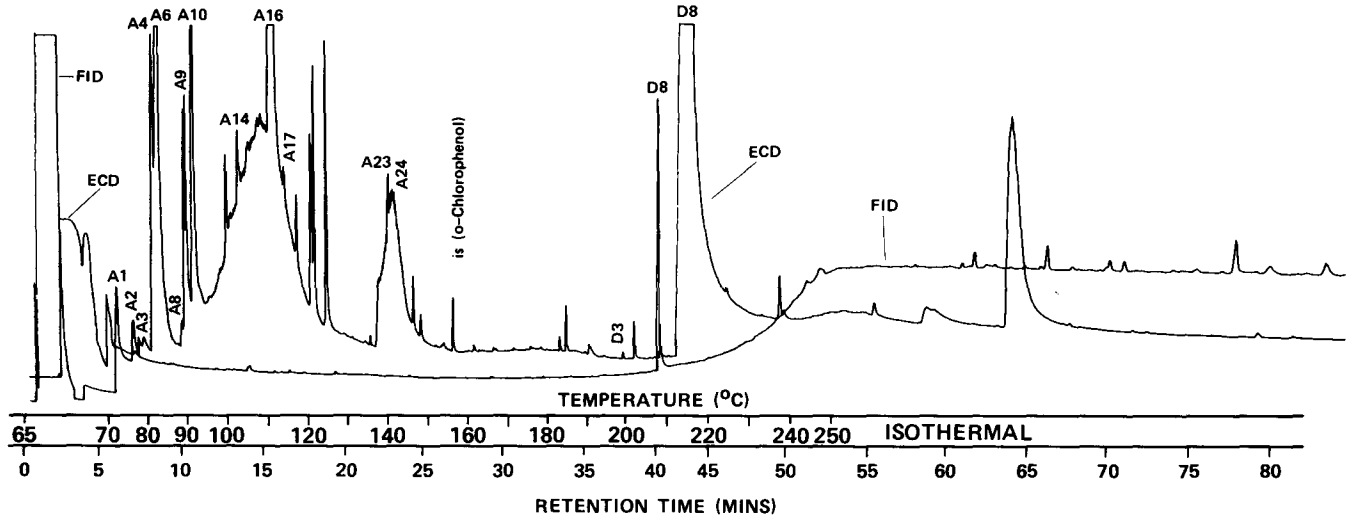

Figure 7—GC of the breakdown products of chlorinated morin. GC conditions as previously specified. Axes labeled for the ECD. Compound identified in Table 1.

observed compounds. Table 5 summarizes the characteristics of the precursors and cites the relevant experiment to support the conclusion.

Flavones and flavonols provide good laboratory models of the precursors because they give similar chlorination patterns upon chlorination to the observed non-volatile chlorinated organics at the San Diego plant. The tested flavone compounds also possess similar MW and solubility properties to the precursors. It is unlikely, however, that the tested flavones are the exact precursors. The precursors are more likely to be modified plant pigments due to secondary treatment and other biological and chemical alteration that the molecules may undergo.

Our findings about the size and solubility of the precursors have several implications for tertiary wastewater treatment. Other workers[21,22] have shown that the larger hydrophobic components of TOC are more easily removed. The smaller, polar components that are least likely to be removed were found to be the most reactive with chlorine for the examined subset of TOX.

Table 5—Precursors characteristics.

Observation	Reason	Experiment supporting conclusion
1. Precursors are acidic	XAD8 adsorbable in acid	3.1
2. Precursors are polar	Column chromatography polar fraction	3.2
3. Precursors cannot be too polar; organic solvent soluble.	They are CH_2Cl_2 extractable and desorbable by ether from XAD8 columns	3.2, 3.3, 3.4
4. Precursors have MW less than 1000 daltons	Ultrafiltration of XAD8 extract	6
5. Precursors are common to many wastewaters	Present in tested water samples	7
6. Precursors may be colored	All productive fractions were pale yellow to bright yellow	1, 3, 8
7. Flavenols and flavones provided good precursor models	Similar properties, similar GC pattern	1–8

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