Non-Volatile Chlorinated Organics Produced During Disinfection of Reclaimed Wastewaters

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A Final Report to the Department of Water Resources
for Contract B-54863

UCLA-Eng 87-10

April 1987

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ACKNOWLEDGMENTS

This work was supported by the California Department of Water Resources under Contract B-54863.

The authors are grateful for the help of the San Diego Aqua One treatment facility, and particularly to Mr. Greg Elliot. Mr. Ed Ruth assisted us with the GC/MS analysis. Ms. Debby Haines was particularly helpful in the preparation of this final report. Mr. Bich Huynh helped with many of the laboratory procedures.

ABSTRACT

This report describes three years of work at the San Diego Aqua One experimental wastewater reclamation facility. The project was supported by the California Department of Water Resources as a part of its efforts to encourage water reclamation in the State of California.

The original orientation of the project was to investigate the effects of fouling materials on reverse osmosis (RO) membranes. A second and lesser objective was to evaluate the selectivity of several new, low pressure membranes which were candidates for future work at the San Diego facility. As the project progressed it became obvious that the intermittent operation and daily flushing of the RO membranes precluded fouling studies.

In preparing for the investigation of fouling materials on RO membranes, several surveys or organic compounds and their removal across the treatment plant were made. These surveys indicated that the aqua culture system, sand filters, reverse osmosis unit, and activated carbon adsorber were removing the great majority of the organic contaminants. Unfortunately, the chlorination disinfection procedure was negating the positive effects of the reverse osmosis and adsorption process by producing a number of high molecular weight, non-volatile chlorinated organics. The emphasis of this project gradually changed from finding RO fouling materials to reducing chlorinated by-products.

It was observed that many of the halogenated organics formed during disinfection are reactive with dechlorinating agents (sodium sulfite). Most of these sulfite reactive compounds were found to be unsaturated halogenated molecules. Dechlorination with sulfite prior to sample extraction is consequently

only advocated in instances where the compounds of interest are known to be unreactive with the sulfite ion. Many of the observed compounds have escaped detection in the past due to laboratory dechlorination prior to sample extraction.

The major precursors to the observed halogenated compounds were found to be slightly organic solvent soluble (methylene chloride) and to have molecular weights less than 1000 daltons.

It was observed that pH, chlorine dose, contact time, as well as bromide ion concentration, greatly affect the relative distribution, as well as total amounts of chlorination by-products. To minimize the formation of the compounds observed in this study, low pH, long contact time and medium chlorine doses should be used. A general recommendation of these chlorination conditions is however intentionally not advocated. The compounds which were monitored in this work are only a fraction of the Total Organic Halogen (TOX) formed upon chlorination. A recommendation of general chlorination conditions is dependent on the minimization of the most harmful components of TOX.

The choice of chlorination conditions can potentially be tailored to minimize the most harmful components of TOX. In addition, chlorination conditions may be chosen to form components of TOX which are amenable to a subsequent treatment step.

Several treatment alternatives were screened for their ability to reduce the formation of the observed halogenated compounds. Disinfection with chloramines, carbon adsorption treatment, partial dechlorination, aeration and pre-ozonation were investigated. Carbon adsorption after chlorination was found to be the most effective treatment scheme.

I. INTRODUCTION

The use of chlorine in water treatment dates to the 1850's when it was used to deodorize London sewage. The first use of chlorine as a potable water disinfectant was 1903. In addition to disinfection, chlorine is commonly used for many other purposes including odor and taste removal, iron and manganese removal, hydrogen sulfide oxidation and prevention of biofouling on the filters and membranes used in treatment plants (White 1978).

Despite the many beneficial uses of chlorine in water treatment, there has been concern over the health effects of the chlorinated organic compounds produced during the chlorination process (Bull 1982, Cotruva 1981). These chlorinated organic compounds are produced by the reaction of aqueous chlorine with organic carbon in water. The source of the organic carbon may be naturally occurring plant and animal decay products (humic and fulvic acids), animal or bacterial metabolic products or many organic pollutants (e.g. phenols) which may be present in the chlorinated water. The chlorinated organic compounds which have received the most attention thus far, are the trihalomethanes (THM's) (Rook 1974, Rook 1976, Oliver 1979, Minear and Bird 1979).

The most commonly produced THM's in water chlorination are $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$. These compounds are also suspected carcinogens. Although it is not possible at this date to state what renders a chemical species carcinogenic, many compounds which contain carbon-halogen bonds, such as pesticides and THM's, are often implicated as possible carcinogens (Robbins and Cotran 1983).

The presence of THM's in water indicates that carbon sources in sufficient quantities to react with chlorine were present in the water prior to chlorination, which in turn implies the formation of other halogenated, oxidized and potentially harmful chlorination by-products. Since THM's are readily analyzed in the laboratory by either EPA recommended methods or other well documented techniques (US EPA 1979, Kaiser 1976, Henderson 1976, Glaze 1981, Mieure 1977, Richard 1977, Bellar 1974, Nicholson 1977), they have become "indicator compounds" for the extent of chlorination-side reactions in drinking water, in the same manner that coliforms are "indicator bacteria" for disinfection efficiency.

During the past seven years, there has been increased attention to the non-THM chlorination by-products. Glaze (1979) 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.

Volatile compounds in the water are those species with low boiling points (BP), whereas non-volatile compounds have high boiling points. There is no classical BP cutoff to distinguish between volatile and non-volatile compounds. For the purpose of this work, a volatile compound has a boiling point less than 120°C. Chloroform, a THM with a BP of 61°C is an example of a volatile chlorinated organic compound. Non-volatile Chlorinated Organics are also often labeled Non-purgeable Total Organic Halogens (NPTOX). This large group of compounds can be further divided into gas chromatographable and non-gas chromatographable compounds.

The overall goal of this research is to gain a broader understanding of the formation of gas chromatographable non-volatile halogenated organics. Currently the EPA sets standards for maximum allowable total THM's (volatile compounds) in drinking water supplies, but does not set any standards for other groups of halogenated compounds. It is quite plausible that the heavier chlorinated organics may be more harmful than THM's, and that they should be monitoried more carefully with greater attention (Cummings 1983, Coleman 1984).

In order to gain this broader understanding of gas chromatographable non-volatile chlorinated organics (NVCO), there are several basic questions that this research addresses. First, an analytical technique for extraction of NVCO and the consequent gas chromatographic separation of the extract was developed. Several interesting and significant findings were discovered during the development of the protocol for NVCO analysis. Secondly, the major organic precursors which react with chlorine to yield the gas chromatographable NVCO are classified by molecular weight and solubility and are also tentatively characterized. Third, identification and molecular characterization of some of the observed NVCO by gas chromatography/mass spectroscopy are performed. Fourth, various parameters which affect the production of NVCO upon chlorination such as pH, chlorine dose, and contact time are varied to assess their importance in producing NVCO. The final achievement of this work is the recommendation of treatment schemes and chlorination conditions which minimize the formation of the observed NVCO.

The water samples used in this work were collected at a tertiary treatment plant in San Diego, California. The examination of the chlorinated organics at the San Diego plant is part of a larger California Department of Water Resources (DWR) funded study on the presence and treatment of organic compounds at the San Diego facility. The observation that many of the NVCO seen in the treatment plant's chlorinated final effluent are also present in chlorinated drinking water and other wastewater treatment plant effluents have greatly enlarged the scope of this research.

This research intends to incorporate the concern for NVCO formation into the design of treatment plant chlorination schemes. The other novelty in this work is that unlike other research work on chlorination by-products, the premise that humic materials are the precursors to the observed halogenated compounds is not made a priori.

The achievements of this research are stated in Table 1.

Table 1

Research Goals and Achievements

1. Development of an improved analytical technique for analysis of gas chromatographable non-volatile chlorinated organics (NVCO).
2. Characterization of the major precursors for NVCO formation.
3. Identification by GC/MS of some of the formed NVCO.
4. Analysis of the effects of chlorination operating parameters on the production of gas chromatographable NVCO.
5. Recommendation of treatment schemes and chlorination conditions which would minimize the formation of gas chromatographable NVCO.

II. LITERATURE REVIEW

1. BASIC CHLORINE CHEMISTRY AND DISINFECTION

The most important use of chlorine is the disinfection of potable water. As a result of the 1972 Federal Water Pollution Control Act, all wastewater treatment plants in the United States are subject to disinfection requirements. The reactions of aqueous chlorine in potable and wastewater are very similar, but wastewater exerts a much greater chlorine demand.

1.1 Dissociation of Chlorine

Chlorine is most often applied in its elemental gaseous form. The hydrolysis proceeds according to equation (1).

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \qquad (1)$$

The hydrolysis constant is 4.0 x 10^4 mole^2/liter^2 at 25°C. The hydrolysis reaction is very rapid and goes to completion in less than one second. (Morris 1978). Hypochlorous acid is a weak acid with a dissociation constant of 3.2 x 10^4 mole/liter at 25°C.

$$HOCl \rightleftharpoons H^+ + OCl^- \qquad (2)$$

As can be seen from equation (2), pH is critical in determining the dominant species in solution (Figure 1). The time to reach equilibrium is instantaneous, being much less than one second.

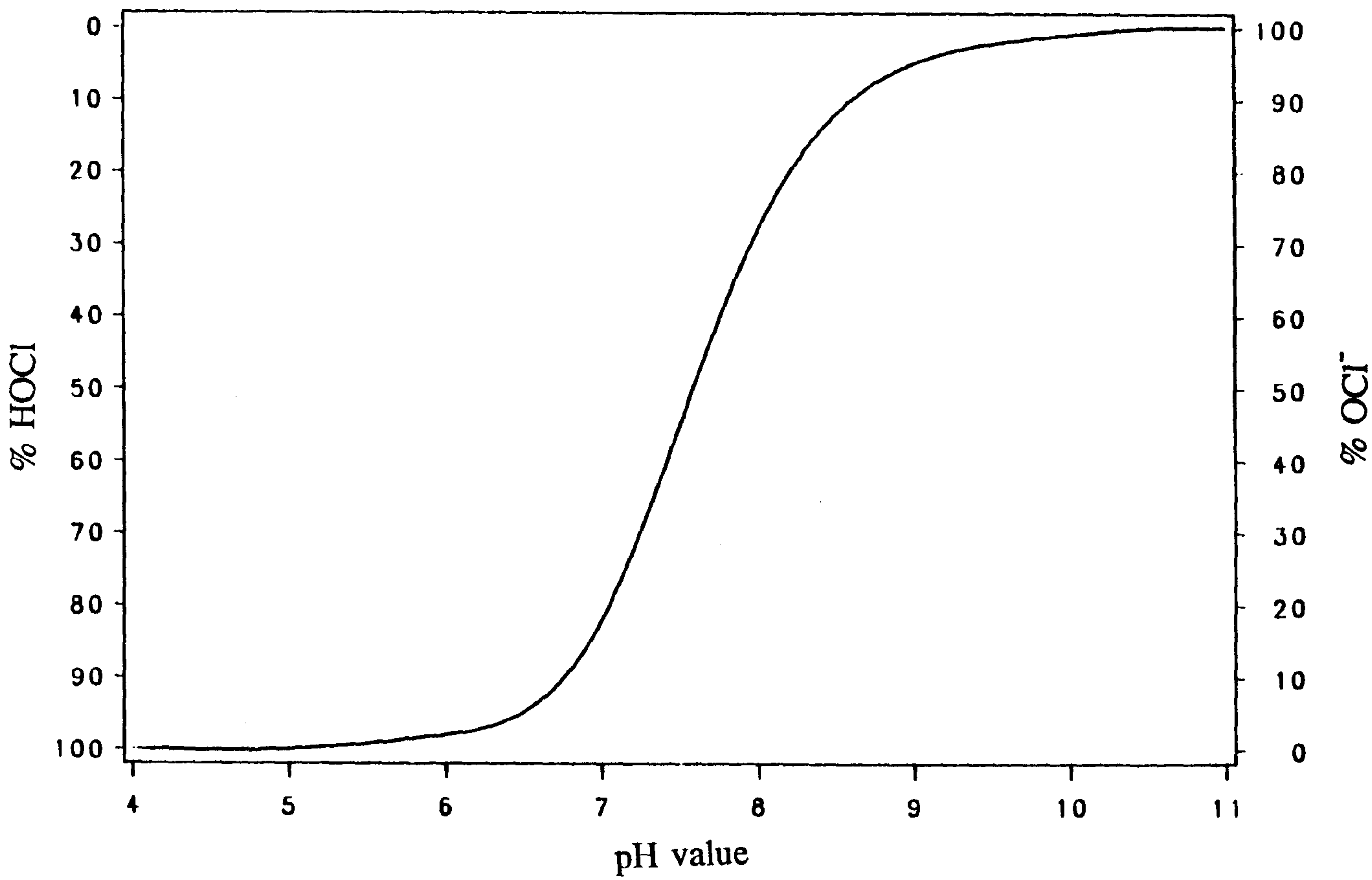


Fig. 1 Distribution of Hypochlorous Acid and Hypochlorite Ion at Different pH

1.2 Formation of Chloramines

Ammonia is commonly present in wastewater and traces often occur in many drinking water supplies. Furthermore, ammonia is often added before chlorination in order to provide stable combined chlorine residuals. Chlorine reacts with ammonia to produce chloramines. The empirical reactions of chlorine with ammonia proceed as follows:

$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^- \tag{3}$$

$$HOCl + NH_3 \longrightarrow NH_2Cl + H_2O \tag{4}$$

$$HOCl + NH_2Cl \longrightarrow NHCl_2 + H_2O \tag{5}$$

$$HOCl + NHCl_2 \longrightarrow NCl_3 + H_2O \tag{6}$$

where

NH_2Cl	=	Monochloramine
$NHCl_2$	=	Dichloramine
NCl_3	=	Nitrogen Trichloride

The products shown in equations (4), (5) and (6) represent the several forms of combined chlorine. The rates of chloramine formation and the ratio of NH_2Cl to $NHCl_2$ depend on pH and the ratio of $HOCl{:}NH_3$. High pH favors dichloramine formation and low pH favors monochloramine formation prior to the breakpoint. The addition of increasing amounts of chlorine to NH_3 free water results in a near linear increase in free chlorine residual. The first combined residual to be formed is monochloramine (Saunier and Selleck 1979). As the ratio of chlorine added to NH_3 increases, dichloramine is formed.

Increased addition of chlorine results in the breakdown of chloramines to nitrogen gas and a drop in total chlorine residual. Once the breakpoint is reached, additional chlorine produces free chlorine residuals. Figure 2 illustrates the breakpoint reactions.

The time required for chloramine formation is greater than the time required for chlorine dissociation, but is generally also rapid (Morris, 1965). The monochloramine reactions proceed most rapidly at pH 8.3 and are 99% complete in less than one second for 1 millimole NH_4^+-N and 20 millimole chlorine. At pH 2 it takes 7 minutes to complete the reactions.

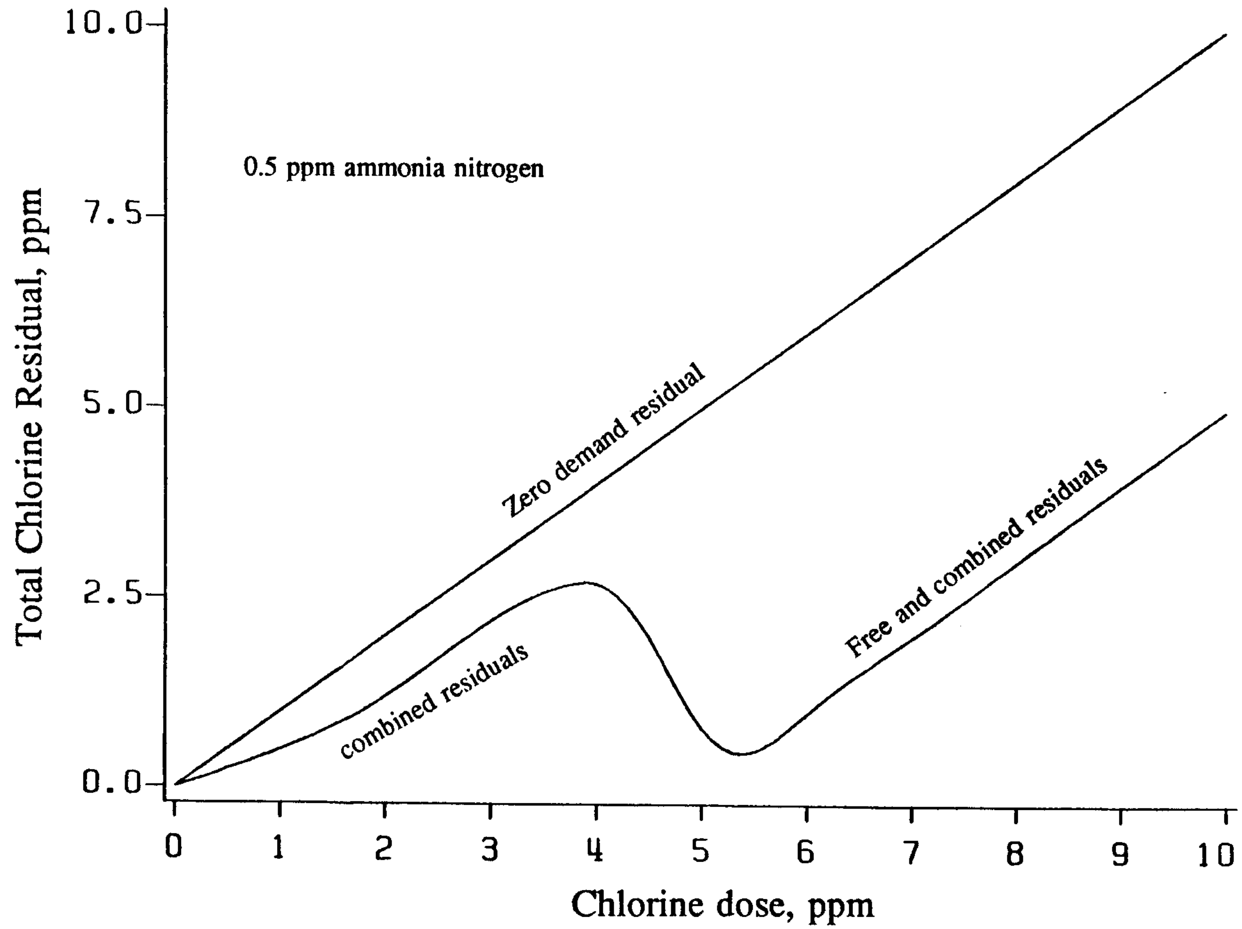


Fig. 2 Breakpoint Chlorination Curve

1.3 Disinfection Efficiencies of Chlorine Residuals

Although there is still some controversy about the disinfection efficiency of the various chlorine residuals, some generalizations can be made. Many workers have noted that hypochlorous acid is the strongest disinfectant (White 1986). Butterfield et al. (1943) noted that one hundred times more hypochlorite ion than hypochlorous acid is required to deactivate equivalent amounts of E. Coli. Chloramine residuals typically are less germicidal than hypochlorous acid, but given adequate contact time, monochloramine is nearly as effective as free chlorine in achieving disinfection of most bacteria (Collins 1971). Selleck, Saunier and Collins (1978) observed that breakpoint residuals in the pH range of 7-8 produce the most rapid disinfection. Sepp (1981) pointed out that disinfection efficiency can be improved by rapid initial mixing in the contact chamber.

1.4 Reaction of Chlorine with Inorganic Ions

The displacement of either Cl^- or OH^+ from the $HOCl$ molecule results in the oxidation of Mn^{+2} to Mn^{+3}, Fe^{+2} to Fe^{+3}, NO_2- to NO_3^- as well as many similar reactions. Equation (7) serves as an illustration

$$NO_2^- + HOCl \longrightarrow NO_2OH + Cl^- \tag{7}$$

These reactions are relatively slow and according to Kokoropoulos and Manos (1973) exhibit little reaction during the contact times used to obtain disinfection.

1.5 Reactions of Chlorine with Organic Molecules

The reactions of chlorine with organic carbon sources is the subject of this dissertation. A full discussion is presented in later sections. Chlorine may undergo oxidative reactions with organics and produce CO_2, cleave bonds, or raise the oxidation state of the compound. Substitution reactions are also very common, which lead to the production of chlorinated organics. Figure 3 shows some illustrative reactions.

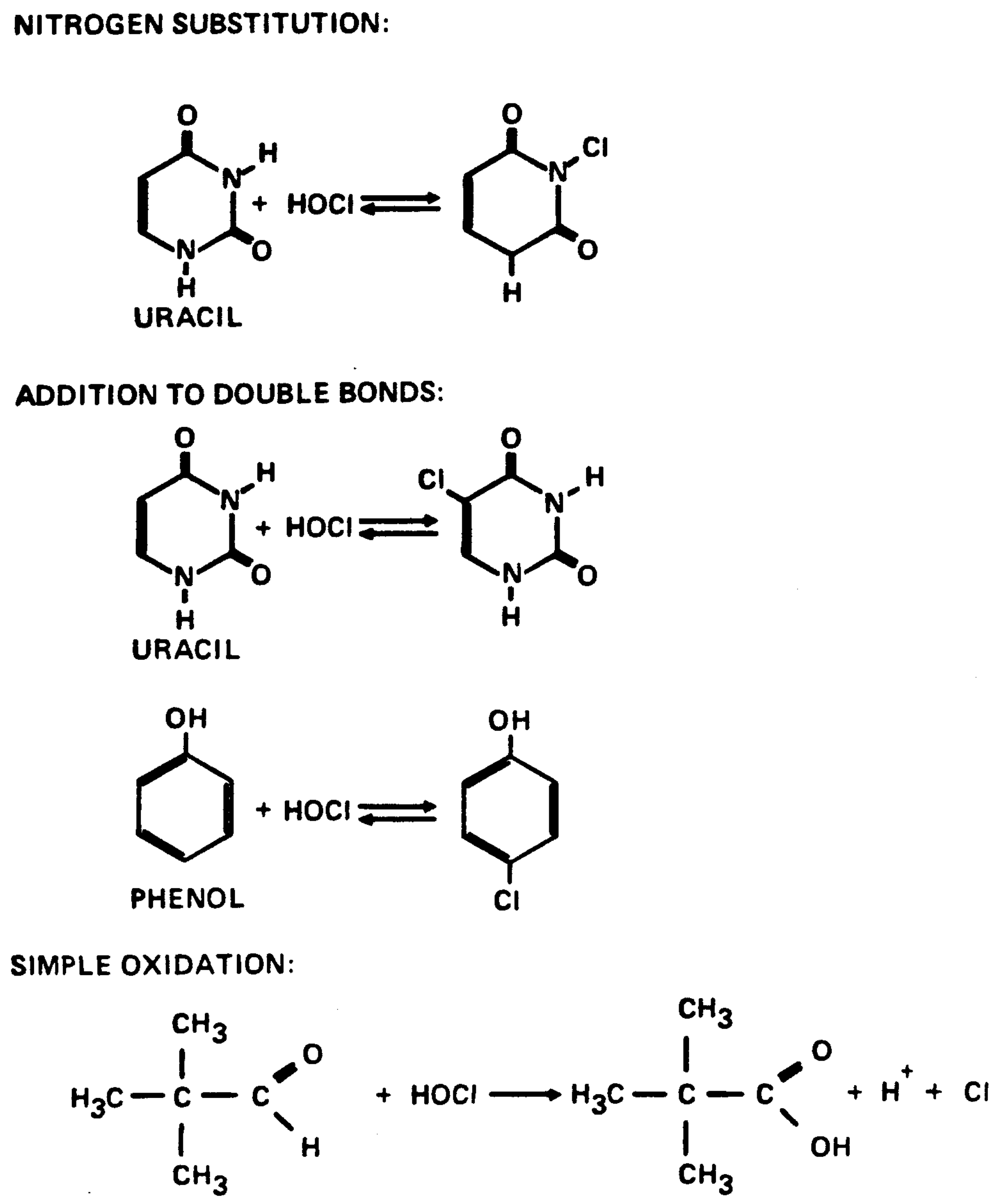


Fig. 3 Reactions of Hypochlorous Acid with Organic Compounds

2. ANALYSIS OF ORGANICS IN WATER BY GC AND GC/MS

The analysis of organic chemicals in water is becoming an increasingly important issue. Trace amounts of organics in drinking water may cause illness, cancer, taste and odor. Volatile organic compound may be collected for GC analysis by purge and trap techniques, liquid-liquid extraction, or head space methods. Non-volatile organic compounds in the aqueous phase (not adsorbed to particulates in the water) are concentrated by solvent extraction (Baker 1967, Andelman 1965, Thomas 1980), carbon adsorption, adsorption on macroreticular resins (Burnham 1972, Junk 1974, Shinohara 1981), reverse osmosis (Coleman 1980), or closed loop stripping (Coleman 1984).

The adsorption of organic contaminants from large volumes of water and their consequent desorption with small volumes of organic solvents is an attractive collection and concentration method. The use of activated carbon for this purpose has fallen out of favor because many compounds are not quantitatively desorbable from the carbon. Macroreticular resins (ex: Rohm and Hass brand XAD1-9) are effective in adsorbing many compounds. Their binding energies are small, so desorption is less problematic than with activated carbon. These resins, however, are extremely dirty and contaminated and require extensive and meticulous cleaning before use.

Solvent extraction is the most commonly used method for organics concentration. Although solvent extraction is simple and effective for numerous compounds, it suffers form many drawbacks. The distribution coefficient for the contaminants between water and the extraction solvent must be favorable, and is often unfavorable for highly polar compounds. Second, most solvents are health hazards. The most versatile extraction solvent is diethyl ether (low cost, low boiling point, high polarity, low toxicity), but its potent anesthetic effects make its use prohibitive except in hoods and well ventilated laboratories. Although dichloromethane is more toxic than ether, it has little anesthetic effect and has thus become popular with many analysts (Miller 1983, Coleman 1985, Quimby 1980). Trichlorotrifloroethane (Freon 113) is the recommended extraction solvent for oil and grease analysis due to its low toxicity *Standard Methods* (1985). The cost of Freon 113, as well as it boiling point, make it less attractive than methylene chloride and diethyl ether.

Coleman, et al. (1980) combined solvent extraction with an additional concentration step using reverse osmosis. The pre-concentration step using RO allowed for lower detection limits. The increased sensitivity of this protocol enabled the identification of four hundred and sixty organic compounds in Cincinnati, Ohio drinking water. The extract was from four hundred gallons, which were concentrated by reserve osmosis, before ether extraction. Coleman's list of organic pollutants contains chloro-phenols, chloro-aliphatic hydrocarbons, chloro-aromatic hydrocarbons, chlorinated alcohols, chlorinated ketones, chlorinated aldehydes, chlorinated ethers and acids, chlorinated esters, amides and amines. Some of these chlorinated compounds are a result of industrial dumping, but many others are chlorination by-products.

3. VOLATILE CHLORINATED ORGANICS

In 1974, Rook discovered that trace concentrations of chloroform are produced as side reactions during the chlorination of untreated river water. Since Rook's initial discovery, extensive research has been conducted on the various factors affecting THM production. Several related research areas have converged to give a nearly complete picture of haloform formation during chlorination. Work has been done on developing methods for haloform analysis (US EPA 1979, Kaiser 1976, Henderson 1976, Glaze 1981, Mieure 1977, Richard 1977, Bellar 1974, Nicholson 1977), identifying the major THM precursors (Rook 1974, Line 1984, Stevens 1976, Oliver 1979, Oliver 1980, Urano 1983, Boyce 1979, Boyce 1983, Morris and Baum 1978, Hoehn 1979), as well as efforts to reduce haloform levels by use of chloramines (Norman 1980), carbon adsorption (Rook 1974, Stevens 1976, Digiano 1983), reverse osmosis (Odegaard 1982), alum coagulation followed by sand filtration (Oliver 1979), as well as air stripping (Rook 1974).

The abundance of published literature on THM's makes it prohibitive to conduct a thorough review. Only the aspects of THM's relevant to this research are examined. Haloform precursors, the effects of pH and other variables on THM production, as well as efforts to minimize haloform formation during water chlorination, are reviewed.

3.1 Haloform Precursors

The initial observations that THM's were present in essentially every chlorinated water supply lead early researchers to conclude that the carbon source (precursor) for their production is ubiquitously present in all natural waters. Aquatic humic material is present in all waters and it is sufficiently similar in time and space that it has become the 'prime suspect' (Babcock 1979, Rook 1974, Stevens 1976). There are numerous other compounds which have been shown to be capable of THM production upon chlorination.

Morris and Baum (1978), showed that chlorophyll yields THM's in its reaction with aqueous chlorine. Hoehn et al. (1979) demonstrated that algal extracellular products (ECP) are potent THM precursors. Briley et al. (1979) concluded that ECP from algal growth, as well as algae biomass produce THM concentrations comparable to yields from humic and fulvic acids.

Phenol and ketones (Boyce and Hornig 1979, Boyce 1983, Onodera 1984), as well as a host of other simple organic compounds, are also capable of producing THM's upon chlorination. The concentrations of these compounds have always been deemed too low to consider them major THM precursors.

Due to the abundance of aquatic humic substances, rightly or wrongly, they have always been labeled the primary precursor for THM formation. Humic substances will consequently be described in some detail before discussing chlorination experiments of humic materials.

Christman (1981, 1983), as well as Gjessing (1976) have done extensive research on the nature of aquatic humic substances. Humic substances are a complex assemblage of decayed plant and soil materials and of the polymeric compounds produced by the random combination of these various biomonomers (Gilliam 1982). As can be inferred from such a broad and vague definition, the nature of humic material is at best poorly understood.

The substances which are collectively called humic material can be further separated and classified. In 1919 Oden described a classification system which is still the most commonly used today (Table 2). The differentiation criteria used in this system are the varying solubilities of aquatic humic fractions in acids and bases.

Oden's classification system, as well as several other fractionation schemes in use today, should be regarded more as operative than absolute definitions. Some of the other classification systems can separate humic materials into thirteen chemically and spectroscopically different fractions using adsorption column chromatography (Dragunev 1969).

Table 2

Classification of Humic Materials

Group	Description
Humas coal	insoluble in base and acid
Fulvic acid	soluble in base and acid
Hyatomelanic acid	soluble in base, insoluble in acid, soluble in alcohol
Humic acid	soluble in base, insoluble in acid and alcohol

In addition to their solubility differences, the humic material fractions also contain differing percentages of elemental carbon, oxygen, nitrogen, sulfur and hydrogen. Although humic and fulvic acids vary slightly from location to location, the following generalizations are made. Aquatic humic acid contains larger amounts of hydrogen and lower amounts of carbon and nitrogen than aquatic fulvic acid. Additionally, aquatic humic materials are mostly fulvic acid (60-90%) with smaller amounts of hyatomelanic acid (9-30%) and humic acid (1-20%) and even smaller amounts of humas coal (Christman 1981).

X-ray crystallography and chemical degradation of the large humic molecules and the consequent gas chromatographic analysis of the breakdown products by Christman (1981) and others (Liao 1982, Gilliam 1982) has lead to the formulation of several models of the structure of these humic macromolecules. Figure 4 is a model proposed by Christman of a structure which is capable of producing most of the observed degradation products. It should be emphasized that this is only a model and it is likely that no such exact entity exists in nature.

Humic materials have been implicated as sinks and chelating agents for volatile chlorinated compounds as well as for their role as chlorination precursors (Gabitta, et al. 1985; Gabitta, 1986). Calloway, Gabitta and Vilker (1984) also noted that low molecular weight halocarbons exhibit greater solubility in humate solutions than in distilled water. These observations indicate that humic materials may contribute to elevated halocarbon levels in water supplies in numerous ways.

Reinhard (1984) used ultrafiltration to show that the molecular weight ranges of dissolved organic carbon can range from less than 500 to greater than 10,000. It is generally believed that the color humic macromolecule's molecular weight may range from 500 to an excess of 100,000. There are conflicting reports in the literature and little, or no, agreement on the MW of the fulvic vs. humic vs. hyatomelanic fractions. It is generally agreed upon however, that fulvic acids are of lower MW (500-20,000) and that humic acids cover the larger MW range (10,000-200,000).

Rook (1974) postulated the importance of aromatic carbon rings with two OH groups in the meta position as precursors for haloform formation (Figure 5).

Resorcinol (Fig. 5) is considered to be a building block of the humic and fulvic acids as can be seen by comparing Figs. 4 and 5. Rook chlorinated fulvic acid samples, as well as solutions of resorcinol, other diols and di-ketones and showed them to be capable of significant $CHCl_3$ production.

Boyce and Hornig (1983), using isotopically labeled resorcinol, elegantly showed the production of isotopically labeled chloroform. In later work, Boyce and Hornig also showed that aromatic di-ketones are also capable of $CHCl_3$ formation upon chlorination (1979). In similar experiments, Secholing (1984) also chlorinated model aqueous humus compounds which resulted in significant THM production. Stevens (1976) conducted bench and pilot scale chlorinations on humic materials (humic and fulvic acids) as well as low molecular weight compounds containing the acetyl moeity (C = 0), and concluded that both classes of compounds are capable of THM formation.

Oliver, Simon and Visser (1980) fractionated humic and fulvic acids into different molecular weight ranges by ultrafiltration. The fractionated material was then redissolved in high grade water and chlorinated with sodium hypochlorite (15 mg/L) at pH 11 for 72 hours. After quenching the residual chlorine, the chloroform concentrations were determined by GC analysis following an extraction step using pentane. They observed that 72-80% of the chloroform came from the fulvic acid rather than the humic acid components. They also noted that the 1,000-10,000 MW fulvic acid fraction was the most $CHCl_3$ productive component.

3.2 Effects of pH, and other Parameters on THM Production

Stevens et al. (1976) conducted bench and pilot scale experiments to determine the effect of humic acid concentration, pH, temperature, free vs. combined chlorine and reaction time on THM production. They observed an increase of THM concentration with time at a given chlorine dose and found high pH to yield greater amounts of haloforms. Free chlorine produced four times more haloforms than combined residuals. Higher temperatures also greatly increased haloform production. After 100 hours of contact time 225 μg/L chloroform were produced from 10 mg/L free chlorine, 1 mg/L humic acid at pH 7 and 40°C. Only 45 μg/L of chloroform were produced at 3°C. Oliver (1979) also observed similar results. Figure 6 summarizes the trends in their observations.

Peters, Young and Perry (1980) also examined the reactions of free chlorine at varying pH's and temperatures with humic and fulvic acids extracted from the Thames River. They observed similar trends to those observed by Stevens et al. Peters et al. however, made the further distinction between chloroform which was formed directly from humic molecules and chloroform which was formed from a non-volatile chlorinated organic intermediate. The NVCO would be semi-stable chlorinated molecules produced

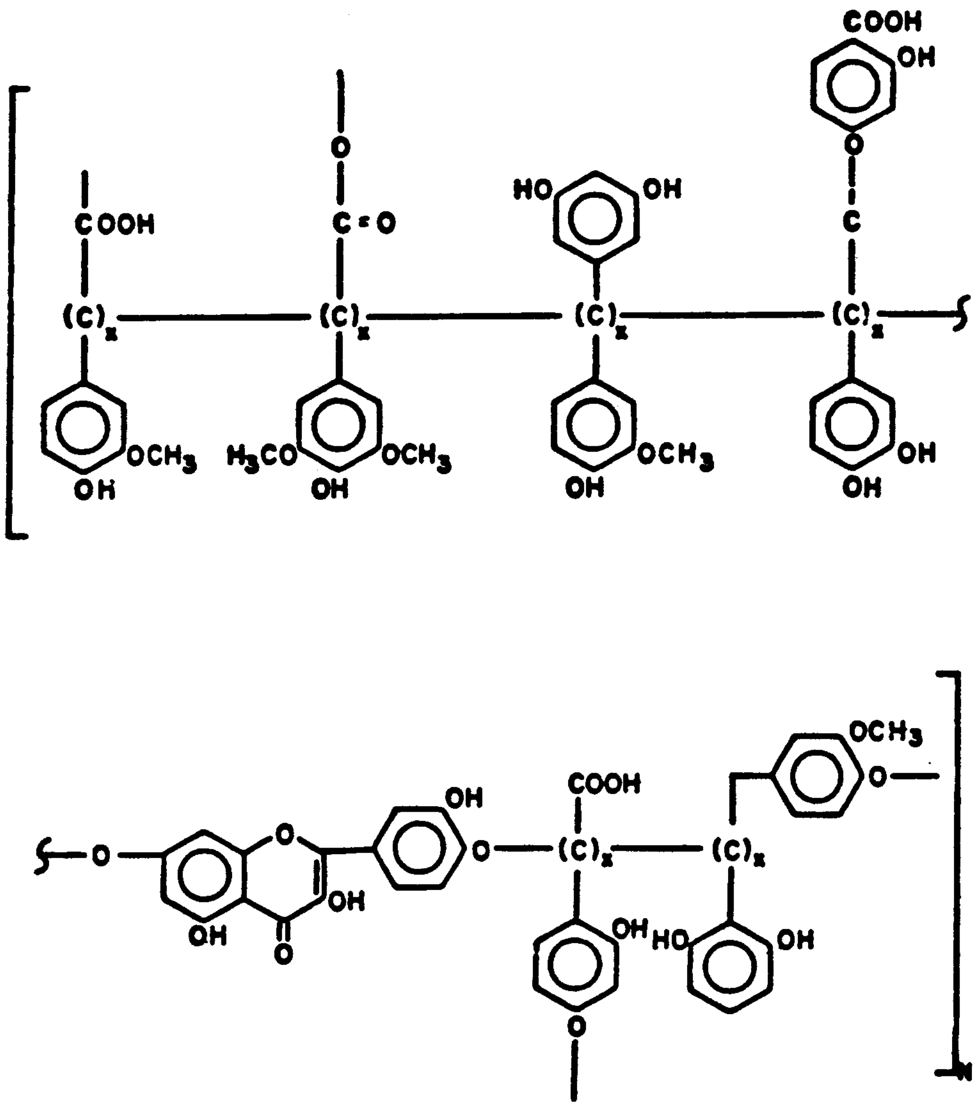


Fig. 4 Model of Aquatic Humic Macromolecule; reproduced from Christman, et al. 1981.

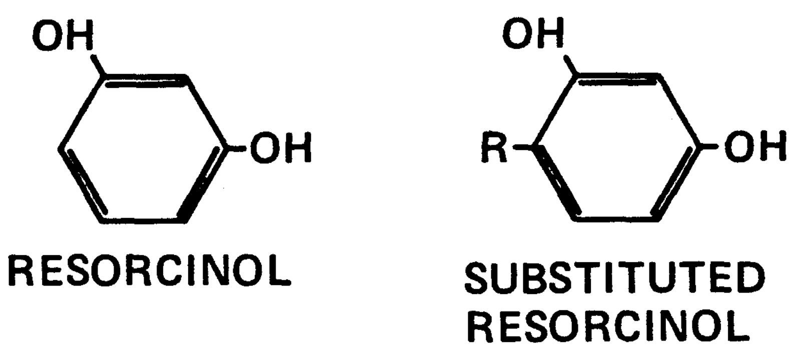


Figure 5: Molecular Structure of Resorcinol

by the chlorination of humic acid.

They were able to make the distinction between the two sources of chloroform by stripping the chlorinated water with nitrogen gas (the stripped water should contain no chloroform) and the consequent direct aqueous injection of a water sample in the GC. The high temperature of the GC injection port accelerates the breakdown of $CHCl_3$ from the NVCO. This chloroform was termed residual $CHCl_3$. Total chloroform was measured without stripping the chlorinated sample. Dissolved chloroform, resulting from the immediate breakdown of humic materials, is calculated as a difference between total and residual chloroform. Figure 7 is a schematic of these two reaction paths.

Urano et al. (1983) observed the increasing haloform production with increasing chlorine dose while chlorinating humic substances with free chlorine. They observed similar pH, temperature and time relations as previously discussed increased THM formation at high pH, high initial chlorine concentrations, long contact times and higher temperatures. They consequently derived the following empirical rate equation, which summarizes the various parameter effects on haloform production.

$$[THM] = 3.5 \; x \; 10^3 e^{-4.47x10^3/T}(pH - 2.8)[TOC][Cl_2]_o^{.25} \; t^{.36} \tag{8}$$

where

[THM]	=	trihalomethane concentration
T	=	temperature (°C)
[TOC]	=	total organic carbon concentration
$[Cl_2]_o$	=	initial free chlorine concentration
t	=	time (hours)

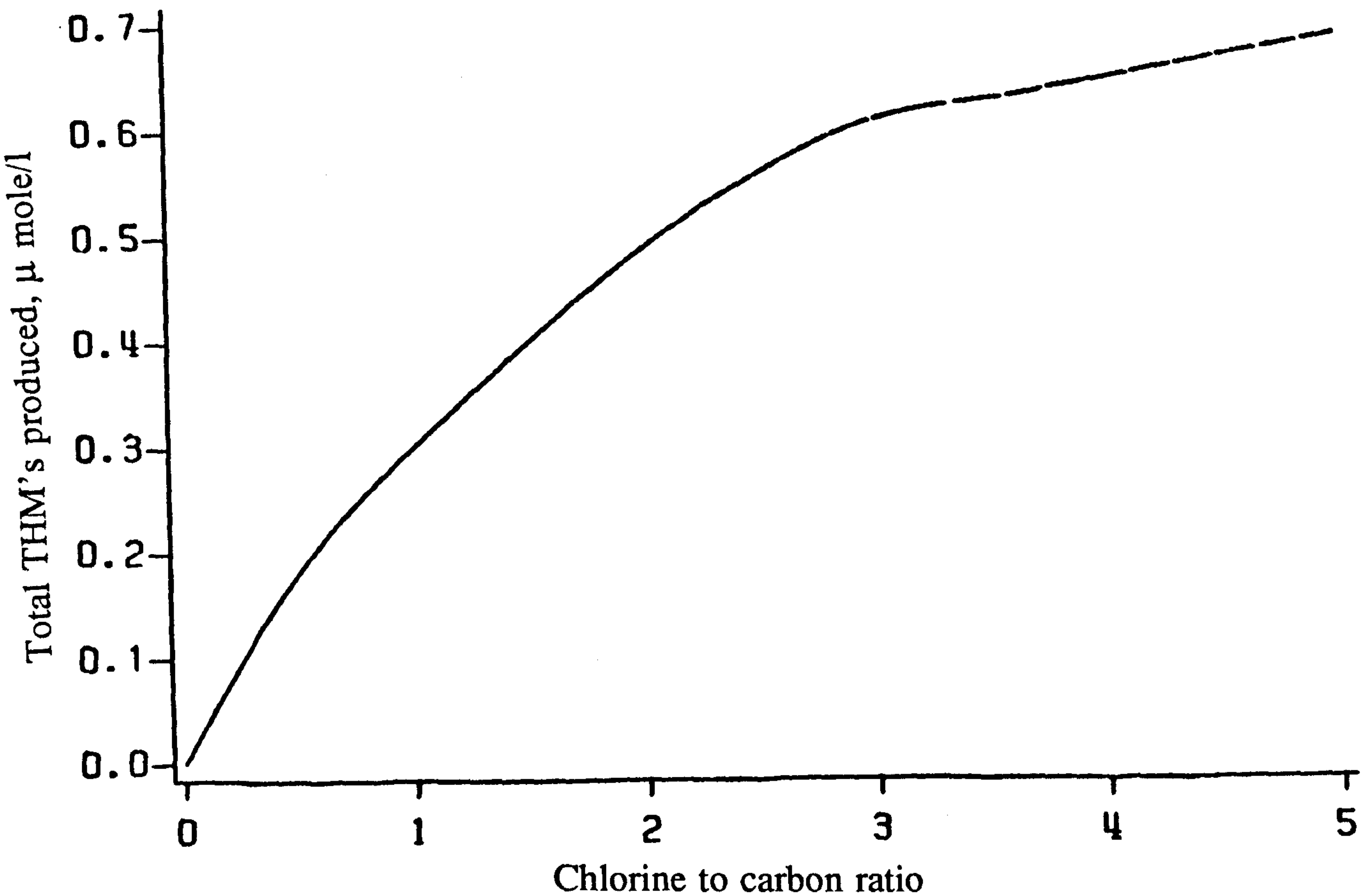


Fig. 6a Effect of Chlorine Dose on THM Formation

After Stevens et al. (1976)

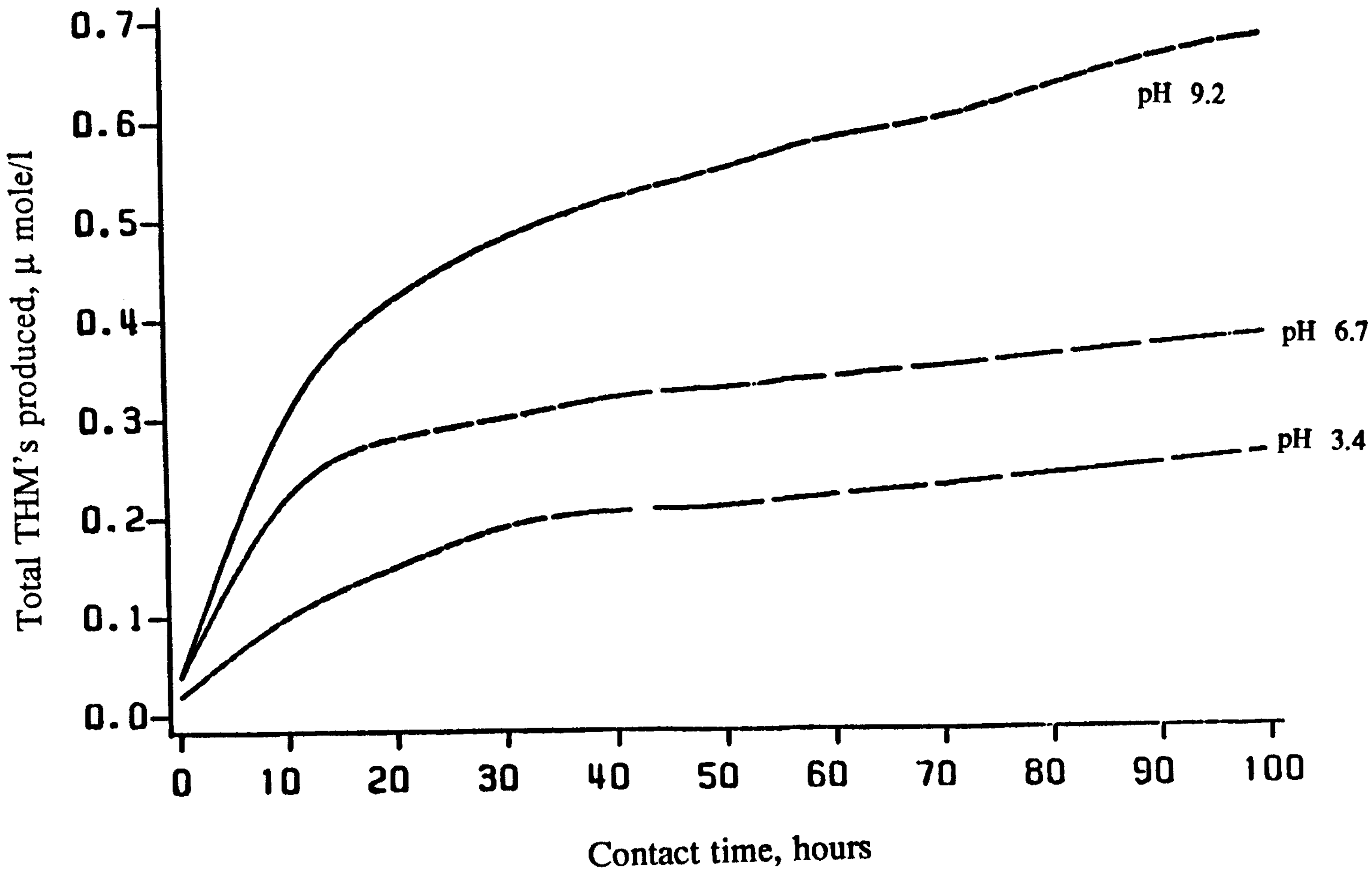


Fig. 6b Effects of Contact Time and pH on THM Formation
After Stevens et al. (1976)

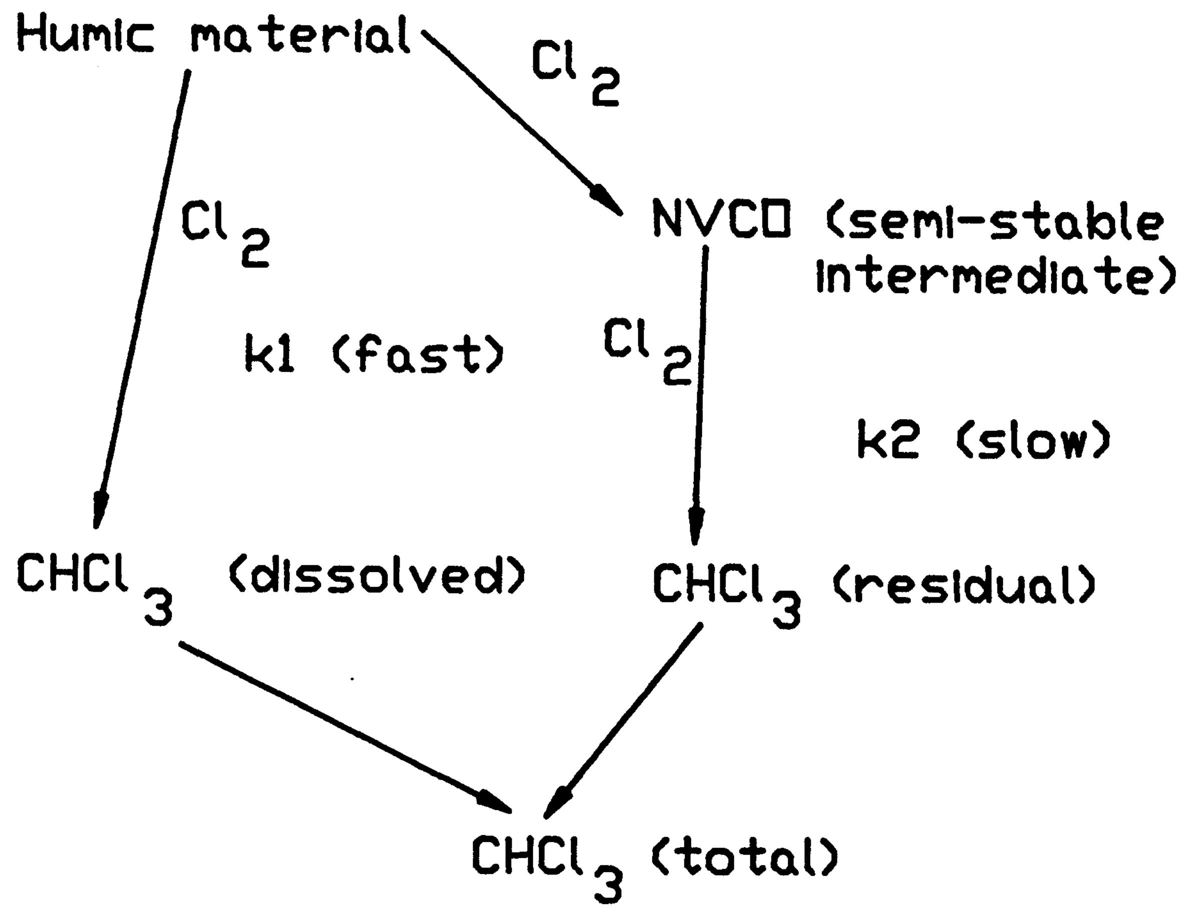


Fig. 7 Reaction Pathways for THM Formation

3.3 Efforts to Minimize Haloform Production

The efforts to minimize the THM levels in chlorinated waters include alternate forms of disinfection, precursor removal prior to chlorination or removal of the THM's after their production.

Norman et al. (1980) investigated the use of chloramines at the Huron, South Dakota treatment plant in order to reduce their high THM levels (137 μg/L). Ammonium sulfate was added at a location which would allow 30 minute contact time with free chlorine before the formation of chloramines. The free chlorine contact period was a compromise in order to allow maximum disinfection with minimum THM formation. This practice resulted in a 75% reduction in the THM levels (37 μg/L).

Oliver and Lawrence (1979) observed that filtering with a 0.45 micron prior to chlorination only marginally reduced THM formation. Alum coagulation and flocculation followed by filtration through a sand filter caused a 67% reduction in THM formation and a 34% drop in TOC. They reasoned that the most likely explanation for the drop in haloform production is the removal of humic materials (precursors) by the coagulation flocculation step. The authors had previously observed that about half of commercially purchased humic and fulvic acids are removed from a 5 mg/L aqueous solution with their alum treatment.

Rook (1976) used several pilot scale treatment schemes to reduce haloform formation. Under his reaction conditions 65 μg/L of chloroform were produced without treatment. Coagulation prior to chlorination reduced the levels of chloroform to 28 μg/L. Coagulation followed by sorption on anion exchange resins reduced the levels even further (9 μg/L). The use of this anion resin however, is costly and its regeneration is an added source of contamination to the environment.

Rook also used ozonation in conjunction with chlorination in order to reduce haloform levels. The ozonation was supposed to render the precursors unreactive to the consequent chlorination. Only slight improvement was observed using this technique.

In another series of experiments, Rook studied the removal of haloforms following their formation. Carbon adsorption, as well as air stripping, were tested. Activated carbon was found very effective for THM removal, but the haloforms broke through in a relatively short time (2 weeks) even though the carbon was still very effective in removing other larger molecules. As would be expected, air stripping of the haloforms is a successful technique.

Odegaard and Koottatep (1982) used reverse osmosis to remove the humic precursors prior to chlorination. 80-100% color removal was achieved using small pore membranes. No data however, were given for haloform reduction.

McCreary and Snoeyink (1980) used activated carbon for the removal of different MW fractions (separated by gel filtration and ultrafiltration) of humic material in an effort to remove haloform precursors. They found the lower MW fractions of the humic macromolecule to be better removed by carbon adsorption. Additionally, functional group analysis of the fractionated humics showed that activated carbon treatment efficiency decreases with increasing total carboxyl groups (polar moiety) in the particular fraction.

They were unable to correlate haloform production with total carboxyl groups however. As has been previously stated, the lower molecular weight fractions have a higher THM formation potential (THMFP) than the higher MW humic fractions. Despite the higher removal efficiency of the lower molecular weight fractions by the activated carbon, THM formation is only moderately reduced by carbon treatment, since the high MW fractions react with chlorine to a greater extent in the absence of the lighter MW fractions.

4. NON-VOLATILE CHLORINATED ORGANICS (NVCO)

Non-volatile chlorinated organic compounds (NVCO) have not been extensively studied for a variety of reasons. Rook's initial finding of chloroform in chlorinated water in 1974 set a trend for analysis of volatile compounds, which has only recently been revised. Secondly, non-volatile compounds are more difficult to analyze chromatographically because of column and temperature requirements. The low concentrations of individual NVCO (collectively the total NVCO may be greater than THM's however) may have prevented their detection by some researchers. Furthermore, the bulk of the organic matter in water is non-volatile, which makes identification and separation more difficult.

Non-volatile halogenated compounds can be analyzed collectively as a lump parameter by microcoulometry and labeled as total organic halogen (TOX) (Glaze 1977). Alternately, a subset of these compounds can be examined in detail by a chromatographic procedure.

High pressure liquid chromatography (HPLC) has frequently been used as the chromatographic procedure to separate the TOX. HPLC enables the separation and analysis of components of very large molecular weight. HPLC is consequently potentially capable of analyzing most of the chlorination by-products. HPLC however suffers from low sensitivity and poor resolution in comparison to a GC system. In addition, HPLC retention times may be very long and peak width may exceed several minutes, which makes matching to known standards difficult.

Gas chromatography (GC) and gas chromatography/mass spectroscopy (GC/MS) techniques provide the best available techniques for positive identification of organic compounds. GC 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 GC analysis.

4.1 Measurement of NVCO as TOX

The parameter TOX has recently been standardized as a US EPA procedure (US EPA 1980). The method often involves an adsorption concentration step with the subsequent combustion of the organic halides in an organic halide analyzer. The analysis is done in a gaseous stream and a titration by silver of the hydrogen halide generated (ASTM 1981). The measurement of TOX includes volatile and non-volatile halogenated compounds. Glaze, Peyton and Rawley (1977) demonstrated the utility and accuracy of the TOX parameter using both volatile and non-volatile halogenated compounds. Their test solutions included THM's and chlorophenols.

Jenkel and Roberts (1980) provide examples of the utility of the TOX parameter for the examination of chlorinated wastewater.

In a recent review publication Johnson and Jensen (1986) point out that pH and chlorine dose affect the extent of oxidation and substitution reactions of chlorine with organic matter in water. In summarizing the work of others, they note that large chlorine doses increase the percentage of TOX that is THM's. Low pH favors the formation of Non-purgeable TOX (NPTOX), whereas high pH favors THM formation.

Fleischacker and Randtke (1983) chlorinated extracted fulvic acids, a commercially available humic acid and municipal secondary effluent extract (XAD8 adsorption). They observed that under most chlorination conditions chloroform represents only a small fraction of TOX. If chlorination is performed at high pH, chloroform becomes a sizeable amount of TOX. The authors also note that chloroform production is more strongly influenced by temperature than NPTOX.

Reckhow and Singer (1984) extracted lake fulvic acids by adsorption on XAD8 macroreticular resins. 320 ml solutions of 4.1 mg/L TOC were chlorinated at various pH, chlorine dose, and reaction times. Chloroform, Dichloroacetic acid (DCAA), Trichloroacetic acid (TCAA), and TOX were monitored. Alum coagulation and ozone treatment were evaluated for effectiveness in reducing the levels of the four measured parameters. Reckhow observed an increase in TOX, chloroform, DCAA, and TCAA as HOCl dose was increased. Longer reaction times also resulted in higher levels for all of the measured components. High pH favors light species, and chloroform levels become a smaller fraction of TOX at low pH. Surprisingly, humic acid fractions had higher yields than fulvic acid fractions for all species. The effectiveness of alum and ozone in reducing organic halides is discussed in a later section.

Wachter and Andelman (1984) chlorinated algal extracellular products as well as chlorophyll and measured TOX, Purgeable Organic Halide (POX), as well as NPTOX. The molecular size distribution of NPTOX was determined by HPLC, followed by TOX detection of the effluent. pH had the same effects on organohalide distribution as previously mentioned. As contact time increased, the ratio TOX/TOC increased as well as the ratio $CHCl_3/TOC$. The results of their size exclusion analysis point out that the majority of NPTOX has a MW greater than 1000 Daltons.

Chow and Roberts (1981) also observed that longer reaction times and higher chlorine doses tended to favor THM production and reduced levels of NPTOX. These workers chlorinated three liter volumes of secondary municipal effluents.

Norwood et al. (1983) extracted fulvic and humic acids and chlorinated concentrated samples in their laboratories. Their 1000 mg TOC samples were chlorinated with 4000 mg of free chlorine. The residual chlorine was then quenched after 24 hours. TOX and acid extractable organics were analyzed. Extraction efficiency was quite high for the produced TOX. 29.9 mg of organic halide were present in the unextracted sample. After ether extraction only 7.8 mg of TOX were measured representing a 74% extraction efficiency. This indicates that the majority of their observed TOX is relatively non-polar or slightly polar.

Bean, Mann and Neitzel (1983) analyzed chlorinated effluents from nuclear power station cooling waters. THM's, TOX and phenols were analyzed. Chlorophenols were a large portion of TOX (12-37%). THM's also represented a significant portion of TOX (up to 71%). The differences from previously mentioned values emphasize the point that chlorination by-products are very dependent on the source water as well as the chlorination conditions.

4.2 Analysis of NVCO by HPLC

Jolley (1978) identified several carbohydrates, polyols, organic acids, amides, amino acids, indoles, pyridine derivatives, purine derivatives and pyrimidine derivatives in domestic wastewater effluent. He observed chlorinated derivatives of many of these compounds in the chlorinated effluents. His laboratory chlorination was done with Cl^{36} tagged chlorine gas. His detector was a Cl^{36} radio counter using HPLC separation.

Jolley's HPLC output consisted of peaks with half hour widths and a total run time of sixty hours. These chromatogram characteristics make positive identification of compounds a difficult task. Jolley calculated that 0.5 to 3.1 percent of the applied chlorine is incorporated in the observed chlorinated organics.

Glaze et al. (1979) note that the reduced MW of extracted fulvic acids after chlorination (from 10.5×10^3 to 8.2×10^3). Using TOC, TOX and average molecular weight data, the authors estimate that the broken down fulvic polymer molecule contains 7 chlorine atoms.

Saleh and Mokti (1983) used three HPLC separation modes to fractionate both chlorinated and unchlorinated fulvic acids extracted from Texas, Oklahoma and Louisiana reservoirs. They discerned the formation of new compounds, most likely halogenated fulvic acids by the dual use of UV and fluorescence detectors.

Becher, Gjessing et al. (1985) fractionated natural humic water (no extraction) into seven fractions by high performance size exclusion chromatography (HPSEC). The seven fractions were chlorinated and TOX was measured. Each of the seven fractions was TOX productive. The lightest MW fraction produced the highest TOX values upon chlorination. In a parallel analytical route, ultrafiltration of the original water sample lead to the observation that 82% of the TOX resulted from chlorination of the less than 1,000 MW fraction. The authors commented that the ultrafilter MW readings were slightly lower than the values given by the HPSEC.

4.3 Analysis of NVCO by GC and GC/MS

In a recent publication, Miller and Uden (1983) discussed their studies on the effects of reaction time, NaOCl dose, pH and source of humic material with respect to the quantitative formation of chloroform and three non-volatile chlorinated organics. The three NVCO were dichloroacetic acid, trichloroacetic acid and chloral hydrate. They also followed the formation of seventeen other unidentified NVCO.

Humic and fulvic acids were isolated by adsorption on XAD resins. The extracted humic material (mostly fulvic acid) was redissolved in 40 ml of distilled water in an air tight container for chloroform quantification. One hundred ml volumes were used in the NVCO studies. 5 mg/L of fulvic acid (measured as TOC), 25 mg/L NaOCl, pH 7 phosphate buffer, and 24 hour reaction time were the base parameters for the experimental work. Four to five variations of chlorine dose, reaction time and pH were used while maintaining the other parameters constant in their quantitative studies.

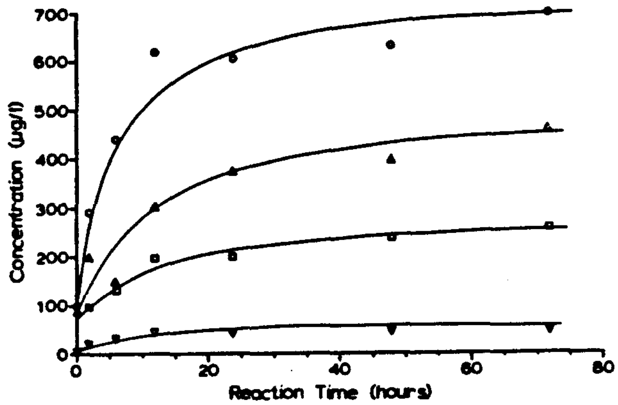
Sodium thiosulfate was added to quench residual chlorine before all analyses. Haloforms were measured by purge and trap techniques and the NVCO were extracted with diethyl ether. The NVCO extract was chromatographed with and without diazomethane derivitization. The reaction of diazomethane with the ether extracts results in the formation of methyl esters from the corresponding acids and yields methyl ethers from phenols. These non-polar derivatives are more amenable to gas chromatographic analysis. More peaks were observed after derivatization than before, indicating the presence of acids, alcohols and phenolics in the original ether extract. Figures 8a, 8b and 8c show the quantitative trends of their observations.

In an earlier publication, Quimby, along with Uden, Delaney and Barnes (1980), using a very similar experimental protocol to Uden's previously described work, identified the chlorinated compounds listed in Table 3. This list of compounds contains both volatile and non-volatile chlorinated organics. Figures 8d and 8e show the gas chromatographs of some of these compounds.

Coleman et al. (1984) identified many NVCO produced by the chlorination of aquatic humic material. Many of these identified compounds had previously been observed in chlorinated drinking waters and are suspected mutagenic agents. It is worthy to note that these workers did not add any dechlorinating agents before extraction, but allowed the chlorine to be fully consumed by the humic macromolecules (reaction times in excess of ninety hours). The significance of this point shall be discussed in a later section.

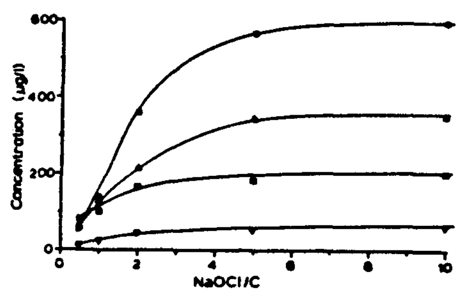
Table 3 Halogenated Compounds Observed by Quimby, et al.

1 - chloroform	8 - 2-chlorophenol
2 - trichloroacetic acid	9 - pentachloro-phenol
3 - dichloroacetic acid	10 - bromodichloromethane
4 - chloral hydrate	11 - chlorodibromomethane
5 - 1-chlorophenol	12 - 3-bromophenol
6 - 2,4,6 trichlorphenol	13 - bromoform
7 - 2-chlorobenzoic acid	14 - 1-bromobenzoic acid



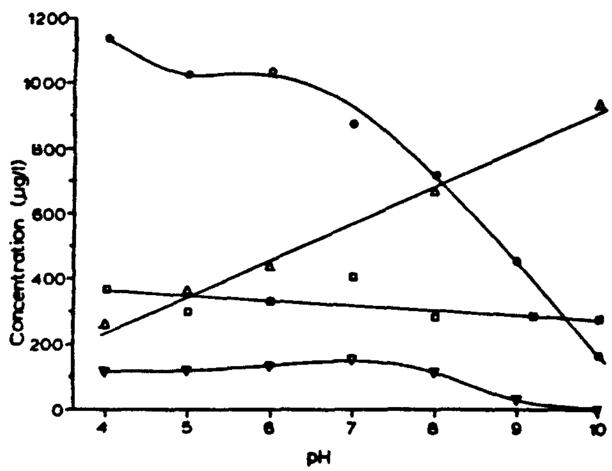
Formation curves with respect to reaction time of the four major aqueous chlorination products of fulvic acid: (O) TCAA; (□) DCAA; (Δ) chloroform; (∇) chloral hydrate.

Figure 8a



Formation curves with respect to the NaOCl to C ratio of the four major aqueous chlorination products of fulvic acid: (O) TCAA; (□) DCAA; (Δ) chloroform; (∇) chloral hydrate.

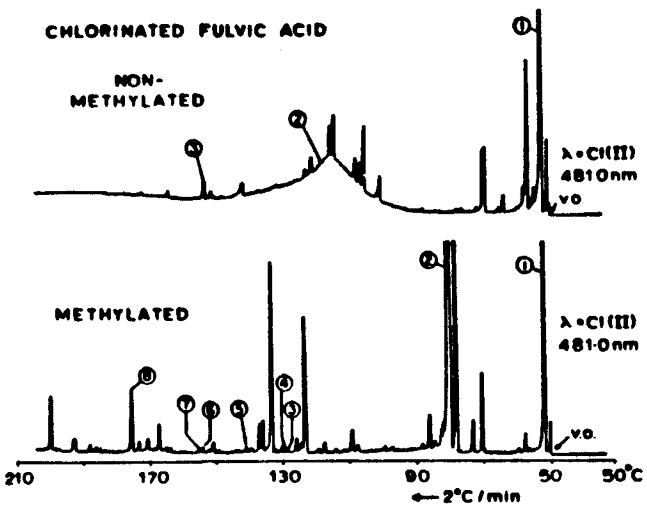
Figure 8b



Formation curves with respect to pH of the four major aqueous chlorination products of fulvic acid: (O) TCAA; (□) DCAA; (Δ) chloroform; (∇) chloral hydrate.

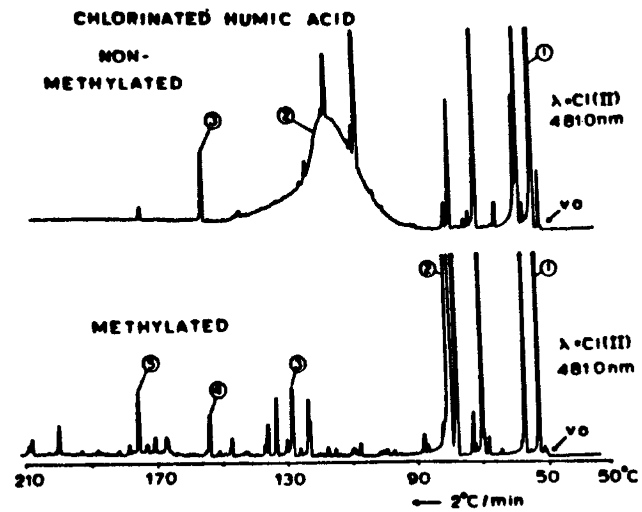
Figure 8c

Figs. 8a, 8b, 8c: Formation of halogenated compounds with respect to contact time (8a), chlorine dose (8b) and pH (8c). Reproduced with permission from Env. Sci. and Tech., Vol. 17, p. 153, 1983. Copyright 1983, American Chemical Society. Article authored by J.W. Miller and P.C. Uden.



Chlorine selective capillary gas chromatogram of non-methylated chlorinated fulvic acid extract (above) and chlorinated fulvic acid extract methylated with diazomethane (below). Peak identities: (above) (1) chloroform, (2) trichloroacetic acid, (3) 1-chlorophenol; (below) (1) chloroform, (2) trichloroacetic acid methyl ester, (3) 2,4,6-trichlorophenol methyl ester, (4) 2-chlorobenzoic acid methyl ester, (5) 3,5-dichlorobenzoic acid methyl ester, (6) 1-chlorophenol, (7) 2-chlorophenol, (8) pentachlorphenol methyl ether. Column 100 m X 0.4 mm i.d. OV 225 glass support coated open tubular (SCOT) column

Figure 8d



Chlorine selective capillary gas chromatogram of non-methylated chlorinated humic acid extract (above) and chlorinated humic acid extract methylated with diazomethane (below). Peak identities: (above) (1) chloroform, (2) trichloroacetic acid, (3) 1-chlorophenol; (below) (1) chloroform, (2) trichloroacetic acid methyl ester, (3) 2,4,6-trichlorophenol methyl ether, (4) 1-chlorophenol, (5) pentachlorophenol methyl ether.

Figure 8e

Figs. 8d, 8e: GC's of chlorinated fulvic acid (8d) and humic acid (8e) breakdown products. Reproduced with permission from Analytical Chemistry, Vol. 52, p. 261, 1980. Copyright 1980 American Chemical Society. Article authored by B.D. Quimby, M.J. Delaney and P.C. Uden.

The work of Coleman et al. is impressive in many ways. Two different extraction solvents were used (dichloromethane and diethyl ether), as well as closed loop stripping (CLS), a relatively new analytical method for non-volatile organics analysis were compared. Derivatization of the extracts was employed prior to GC/MS using state of the art fused silica capillary columns. Mutagenic assays (Ames tests) were performed on the NVCO extracts. In summary, the work was broad in its scope and combined to yield interesting and significant results.

They observed that the methylene chloride extract contained the most compounds, but that the ether extract was more mutagenic. They interpreted this to mean that the ether extract contained highly polar compounds that were not suitable for gas chromatography, but that these polar compounds result in the increased mutagenic activity. It was also observed that the gas chromoto-graphable NVCO account for only 25% of the total organic halogen (TOX) measured by coulometry. Table 4 contains some of the NVCO observed by Coleman et al.

The authors conclude that much research remains to be done on NVCO and that it is likely that most of the mutagenic activity observed in the extracts was not represented by resolved GC peaks. They imply that much work remains to be done on developing and validating practical techniques for uncovering highly polar compounds from chlorinated water. Christman et al. (1981) had previously noted that humic breakdown products are extremely polar di and tri acids.

In a 1985 publication, Kringstad, Sousa and Stromberg (1985) observed the similarity between chlorination by-products of humic materials and bleaching liquors in the pulp industry. These extracts were found to be Ames test mutagenic. Many of these NVCO were aromatic and included several chlorophenols. No chemical dechlorinating agents were used to arrest the chlorination reaction. Excess residual chlorine was removed by rotoevaporation at 25°C. Table 5 lists some of the NVCO which were identified.

Christman et al. (1979, 1981), chlorinated extracted humic materials and identified the breakdown products by GC/MS. Excess chlorine was quenched with sodium arsenite before ether extraction. Derivatized methyl esters were then prepared before GC/MS analysis. An abundance of non-chlorinated breakdown products were observed which frequently contained an aromatic ring. No aromatic chlorinated products were observed however. Most of the identified NVCO were aliphatic acids including dichloroacetic acid and trichloroacetic acid. Miller (1983), Coleman (1984), Kringstad (1985), Quimby (1980), Snoeyink (1981) and McCreary (1981) on the other hand, observed several aromatic NVCO. This point is currently unclear in the literature. Clarifying this point is important because aromaticity often implies increased health risk.

Leer (1985) discovered the presence of highly chlorinated ethers in river sediments near an epichlorohydrin production plant. These compounds are formed during the aqueous chlorination of allyl chloride. Although the production of these chloroethers is a purely industrial problem, it points out that new classes of chlorinated compounds are continuous being discovered. All the chloroethers observed by Leer had not been previously identified.

Table 4 Halogenated Compounds Observed (by Coleman, et al.)

trichloracetonitrile	1,1,1 trichloro-2-butanone
dichloroacetonitrile	hexachloroethane
1,1 dichloro-2-propanone	pentachloropene
3,3 dichloro-2-butanone	1,1,1,3,3 pentachloropropanone
3,3 dichloropropenal	tetrachlorothiophene
dichloropropenenitrile	bromotrichlorothiophene
1,1 dichloro-2-butanone	tetrabromothiophene
bromochloroacetonitrile	tetrachlorocyclopropene
1,1,1 trichloro-2-propanone	pentachloro-3-buten-2-one
2,2 dichloro-3-pentanone	hexachlorocyclopentadiene
trichloropropenitrile	bromodichlorophenol, acetate ester
tribromophenol, acetate ester	dichlorodihydroxybenzene
dibromodihydroxybenzene, acetate ester	
trichlorodihydroxybenzene, acetate ester	

Table 5 Halogenated Compounds Observed by Kringstad, et al.

2,4,5 trichlorophenol	3,4,5 trichlorocatechol
2,3,4,6 tetrachlorophenol	tetrachlorocatechol
pentachlorophenol	3,4,5 trichloroguaicol
3,4,5 trichlorocatechol	2-chloropropenal
pentachloroacetone	hexachloroacetone
1,3 dichloroacetone	1,1,3,3 tetrachloroacetone

4.4 Summary of Effects of Chlorine Dose on NVCO Formation

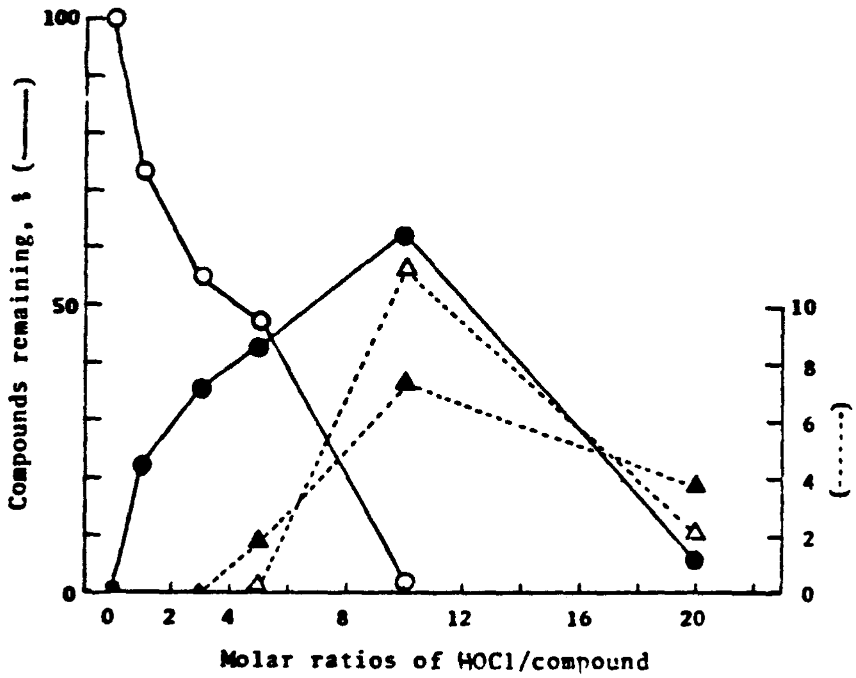
As previously discussed, the chlorination of humic materials at low pH favors the formation of heavier products. Low chlorine doses also favor the formation of high MW components. Several workers have observed the same trends in the chlorination of pure compounds. Norwood et al. (1980) made these observations while chlorinating resorcinol. Rook (1979) observed an increase in $CHCl_3$ concentrations, but a decrease in the larger chloro-resorcinol molecule. Onodera et al. (1984) observed the formation of chloro-phenols and polychlorophenols upon the chlorination of aqueous solutions. These chlorophenols however, were further oxidized upon increased chlorine dosages (Fig. 9).

The results from the chlorination of these pure compounds may serve to illustrate the point that an optimum dose of chlorine exists, which would minimize the harmful products (possibly a choice between less toxic and very toxic).

4.5 Precursors to NVCO

The notion that one precursor is responsible for all NVCO formation is as fruitless as the idea that only one precursor is responsible for THM formation. It now becomes a question of what is the major component that is most reactive with aqueous chlorine and is most responsible for the observed halo-organics.

The broadest observation and probably the least debatable assessment is made by Jolley. Jolley (1978) noted the great variety of natural organic



Residual amounts of reaction products in aqueous phenol solutions (50 µmol/l) after treatment with hypochlorite at various equivalents of chlorine per mole of compound and 20°C for 1 h. Yields derived from GC peak areas, relative to the peak area of starting material. ○, Phenol; ●, chlorophenols; △, polychloropolyhydroxyphenols; ▲, chlorophenol dimers.

Fig. 9: Chlorination of phenol at various chlorine doses. Reproduced with permission from Journal of Chromatography, Vol. 288, p. 98, 1984. Copyright 1984 Elsevier Science Publishers. Article authored by S. Onodera, K. Yamada, Y. Yamaji and S. Ishikura.

compounds in water and stated that most of them are reactive with chlorine.

Other workers have attempted to narrow Jolley's observations. Wong and Oatts (1984) filtered Chesapeake Bay water using ultrafilters with nominal MW cutoffs of 1000, 10,000, 30,000, and 100,000. They stated that ten to thirty percent of the chlorine demand was attributable to fractions with nominal MW above 10,000. The less than 1000 MW fraction had the greatest chlorine demand. The authors interpret the results to mean that fulvic acids are the most responsible for aqueous chlorine demand.

The results of Becher's (1985) ultrafiltration work corroborate Wong and Oatts' results. 82% of the TOX was from the less than 1000 MW fraction.

The findings of Reckhow and Singer (1984), however, contradict these claims. Reckhow asserts that humic acids are more TOX productive than fulvic acids. The discrepancy may lie in the difference of the water samples. In addition, Reckhow was working with concentrated extracts, whereas Becher and Wong and Oatts were using unextracted water. Reckhow's extraction methods may not have been effective for the low MW components.

Reinhard (1984) states that the less than 1000 MW fraction increases from 27% to 53% of TOC after tertiary treatment. This implies that the higher MW fractions are well removed by lime clarification, filtration, ozonation, biological activated carbon and a second filtration step at the Palo Alto, California water reclamation plant. These findings mean that lower MW TOC may be a very important reactant with aqueous chlorine in tertiary treated effluents.

Wachter and Andelman (1984) note that both algal biomass and algal extracellular products (ECP) are as potent as humic materials in producing equivalent levels of TOX, THM and NPTOX.

Jolley (1978) had stated that carbohydrates are oxidized by chlorine and yield no chlorinated organics. Malcolm, Thurman et al. (1981) observed that the amount of carbohydrates associated with aquatic humics and fulvics changed significantly after chlorination. The carbohydrate content is reduced by 50% after chlorination. No work was done on the nature of the breakdown products.

The amino acids proline, analine (Stanbro 1979) and tryptophan yield chlorinated derivatives upon chlorination (Ingols 1954). In their work at the Yuma Desalting plant, Malcolm and Thurman (1981) observed changes in the concentrations of several amino acids after chlorination, implying their reaction with chlorine.

4.6 Efforts to Minimize NVCO Formation

The efforts to minimize NVCO formation due to water chlorination are very similar to the efforts to combat THM production. One may remove the NVCO precursor before chlorination or remove the NVCO in the post chlorination water.

McCreary and Snoeyink used activated carbon to successfully reduce NVCO levels after chlorination. Johnson and Randtke (1983) used coagulation to decrease NVCO levels in chlorinated waters. Johnson and Randtke found the coagulation-flocculation scheme capable of removing both NVCO precursors and the formed NVCO. Both workers used total organic halogen (TOX) as the parameter to measure NVCO.

Reckhow and Singer (1984) found alum coagulation to remove THM, TOX, trichloroacetic acid, dichloroacetic acid and dichloroacetonitrile precursors to a significant extent. Ozone treatment in conjunction with alum treatment sometimes reduced treatment efficiency (compared to alum coagulation alone), presumably by breaking up larger molecules which were more amenable to coagulation.

Fleischacker and Randtke (1983) recommend low chlorine doses, high pH and the use of chloramines in order to minimize TOX levels. NPTOX levels were reduced by 79% by the addition of ammonia prior to chlorination.

Chow and Roberts (1981) found chlorine dioxide to produce only 17% of the TOX levels produced by free chlorine. The authors chlorinated secondary municipal wastewater effluent from Palo Alto, California. 20 mg of residual were applied for a 24 hour contact period. The TOX produced from the chlorination of another California treatment plan was reduced by 99% by using chlorine dioxide instead of free chlorine.

5. LITERATURE REVIEW SUMMARY

Chlorination by-products can be subdivided into volatile (THM's) and non-volatile components. Volatile halogenated organics are best analyzed by GC. The non-volatile fraction (NPTOX) can be analyzed by GC, HPLC or TOX.

Volatile chlorinated organics (THM's) are formed upon the chlorination of most drinking waters. Humic acids, fulvic acids, algal biomass and algal extracellular products were shown to be THM precursors. High pH, high chlorine dose, long contact time and elevated temperature maximize THM formation. Carbon adsorption, aeration, and disinfection using chloramines are viable THM remediation techniques.

NPTOX is also formed during the disinfection of water. Most organic carbon is reactive with chlorine to a certain extent leading to NPTOX formation. Some workers, with disagreement from others, state that the low MW fractions of TOC (in the water) are the most NPTOX productive upon chlorination. Carbon adsorption, chlorination with chloramines and alum coagulation followed by sand filtration have been shown to reduce NPTOX levels.

The formation of THM's and NPTOX during the chlorination of water are intimately related. Often the levels of one of the components of TOX is reduced, while the concentration of the other component is raised by varying chlorination parameters (chlorine dose, pH and contact time).

In the upcoming chapter (Results and Discussion), a similar relationship and dependence on chlorination parameters for the light and heavy components of gas chromatographable non-volatile chlorinated by-products is discerned. The precursors to these gas chromatographable halogenated compounds are characterized by MW and solubility. In addition, the treatment alternatives discussed in this chapter are examined for the reduction of this sub-group of TOX. An improved analytical protocol is also introduced for the analysis of the observed halogenated organics.

III. OVERVIEW AND PROCEDURES

1. OVERVIEW OF EXPERIMENTAL TECHNIQUES AND EXPERIMENTS

This research work has involved the development of an analytical technique for the analysis of gas chromatographable non-volatile chlorinated organics (NVCO), and the use of the developed protocol in a variety of experiments. Some of these experiments examined the nature of the NVCO. Another set of experiments focused on the identity of the precursors to the formation of these halogenated compounds. A third group of experiments were designed to assess the effect of chlorination parameters on the formation of the NVCO. The last group of experiments screened several treatment schemes to quantify their ability to reduce the levels of these chlorination by-products.

The experimental procedures used to achieve these goals can be divided into four broad categories. The ultimate sample analysis was always done using GC or GC/MS of a solvent extract. The sample extract, however, came from different origins. First, water from a tertiary wastewater treatment plant in San Diego, California was extracted with methylene chloride and the extract was analyzed gravimetrically, by GC and by GC/MS. This first category of experiments studied the nature of the extractable organics at the San Diego facility. Extractable organics were analyzed at various locations along the plant's treatment scheme. The results from the first category of experiments pointed out that chlorination produces an abundance of halogenated organic compounds in the plant's effluent.

The second category of experimental procedures involves laboratory chlorination of the pre-chlorination water from the San Diego facility. This category of experiments studied the effects of chlorination parameters, such as chlorine dose, pH and contact time on the production of the halogenated organics observed at San Diego facility. These experiments also confirmed that chlorination is the cause of the produced halogenated organics. Laboratory chlorination experiments were also used to assess the utility of various treatment schemes to reduce NVCO levels.

The third category of experimental procedures is laboratory chlorination of extractable (solvent extractable and XAD8 adsorbable) organics from the San Diego treatment plant. These experiments were used to assess the effect of chlorination parameters on the production of NVCO, and examine various treatment schemes. Fractionation of the organic extracts and the consequent chlorination of the various fractions yields information on the nature of the organic precursors which react with chlorine.

The last category of experimental procedures involved work with pure compounds. Various pure compounds were chlorinated as aqueous solutions in the laboratory and the breakdown products were analyzed by GC. In addition, sodium sulfite was added to pure compounds (as aqueous solutions) to assess the reactivity of the compounds with the $SO_3^=$ ion.

Table 6 lists the experiments which will be discussed, classifies the experiments by one of the above mentioned categories and references the reader to the appropriate sections in the procedures description. Table 6 also indicates the research goal (goals listed in Table 1) that the experiment sup-

Table 6 List of Performed Experiments

Experiment Number	Description of Experiment	lab procedure category	goal experiment supports	reference sections in procedures
1	Extractable organics at the San Diego treatment plant. 15 sampling dates; 6/84-3/86	1	1,3,B	1,4,5
2	Solvent extraction vs. XAD8 adsorption for collection of NVCO precursors	2	2	1,2,4,5
3	Organic solvent elution of XAD8 extract and chlorination of the fractions	3	2	1,3,5,9
4	Humic/Fulvic split of XAD8 extract and chlorination of the fractions	3	2	1,3,5,9
5	Elution of XAD8 extract by pH gradients and chlorination of the fractions	3	2	1,3,5,9
6	Separation of XAD8 extract on enzacryl gel and chlorination of the fractions	3	2	1,3,5,9
7	Ultrafiltration of XAD8 extract and chlorination of the fractions	3	2	1,3,5,6
8	NVCO precursors in other treatment plants and other water samples	1,2,3	2	1,3,4,5,6,9
9	Chlorination of pure compounds	4	2	1,7
10	Addition of sodium sulfite to pure compounds	4	1,2	1,8
11	Chlorination of carbon adsorption effluent from San Diego Wastewater Treatment Plant	2	4	1,2

Table 6 (continued)

Experiment Number	Description of Experiment	lab procedure category	goal experiment supports	reference sections in procedures
12	Chlorination of XAD8 extract	3	2,3,4	1,3,4,5
13	Effect of bromide ion on NVCO formation	3	4	1,3,5
14	Treatment of NVCO by activated carbon	2	5	1,2,9
15	Treatment of NVCO by use of chloramines	3	4,5	1,3,5
16	Treatment of NVCO by use of ozone	3	5	1,3,5,9
17	Treatment of NVCO by 2 stage chlorination	2,3	5	1,2,3,5

Key: Category No.

1. analysis of solvent extracts
2. chlorination of water samples
3. chlorination of extracts
4. work with pure compounds

Goal No. (see Table 1)

B = background information

ports.

2. DESCRIPTION OF THE SAN DIEGO WASTEWATER TREATMENT PLANT

The majority of the water samples used in this work were collected at the San Diego water hyacinth tertiary wastewater treatment plant named "Aqua I". The treatment plant is a pilot testing and demonstration facility. It is the first step in the City of San Diego's plan to build a large (MGD scale) aquaculture based treatment facility.

Raw sewage (85% domestic, 15% industrial) is first subjected to mechanical grinding. The sewage, free of large debris, next passes to several mildly aerated aquaculture fields. Water hyacinth, small fish and other aquatic organisms provide the secondary treatment. The aquaculture effluent next passes through UV sterilizers en route to a sand filter. Before entering a reverse osmosis (RO) unit, UV sterilization is again performed. The pH also is lowered to 4-5 in order to preserve the membranes. The RO unit operates at 400-600 psi with a permeate flow of 50 gpm. Cellulose acetate membranes are used in conjunction with other thin layer composite membranes that the treatment plant is testing. The RO effluent next passes over activated carbon before final chlorination at pH 5.

The chlorination is done using sodium hypochlorite (NaOCl). A free chlorine residual of 1.0 to 1.5 mg/L is maintained in the 10,000 gallon chlorination tank. The chlorination procedure is non-standard. The chlorine residual is periodically checked and always maintained above 1 mg/L. New (unchlorinated) water is only added to the tank when the water level drops below 3000-4000 gallons. The chlorinated product water is used to feed animals kept at the plant, and for irrigation around the plant. Most of the plant's effluent is discharged after reverse osmosis. Water passes through the carbon adsorption columns and is chlorinated only when the water level in the chlorination tank drops. Figure 10 provides a schematic of the treatment plant.

The schematic shown in Figure 10 represents the treatment process train which was selected by the City of San Diego for its ultimate MGD scale expansion. Other unit operations including ultrafiltration and ozonation exist at the plant but were tested and not selected for the eventual expansion.

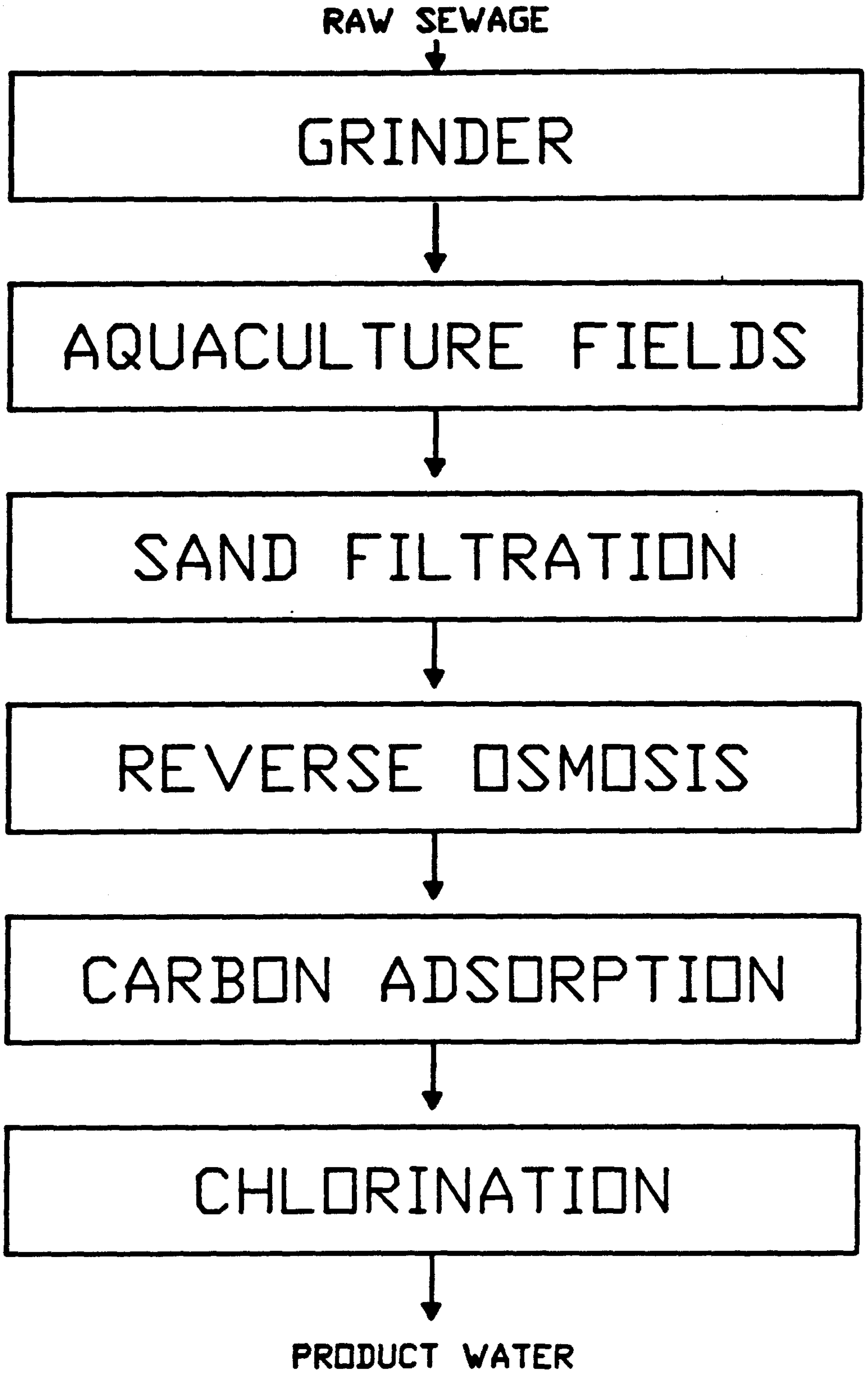


Fig. 10 Schematic of the San Diego Wastewater Treatment Plant

3. ANALYTICAL PROCEDURES

3.1 Extractable Organic Analysis

A modification of an extraction procedure previously developed to quantify total extractable organics in runoff waters was used (Stenstrom, Fam, Silverman, 1984). Using the automated shaker/stirrer shown in Figure 11, up to four liters of water may be easily extracted. This methodology enables the extraction of large amounts of extractable organics for accurate gravimetric analysis. Gravimetric analysis was used in the preliminary screening of the extractable organics present in the San Diego plant.

A large volume of water (1 to 4 liters) was acidified to pH 2 with concentrated sulfuric acid. Sodium chloride (5 g/l of 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 per liter of water) for five minutes. 1-bromohexadecane, hexadecene, tetradecane, m-cresol, or o-chlorophenol was used as a recovery standard 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 chromatographs. The areas of these standards were subtracted prior to all quantitative calculations. No corrections were made to any of the GC results. If a sample showed low recovery (<90%) it was repeated. The recovery standards consequently were used only as a check that the extractions were of high efficiency. Most of the GC's shown in this dissertation were chosen without internal standards to minimize interference with the sample peaks. The combined methylene chloride extract was then reduced to approximately 40 ml by rotoevaporation

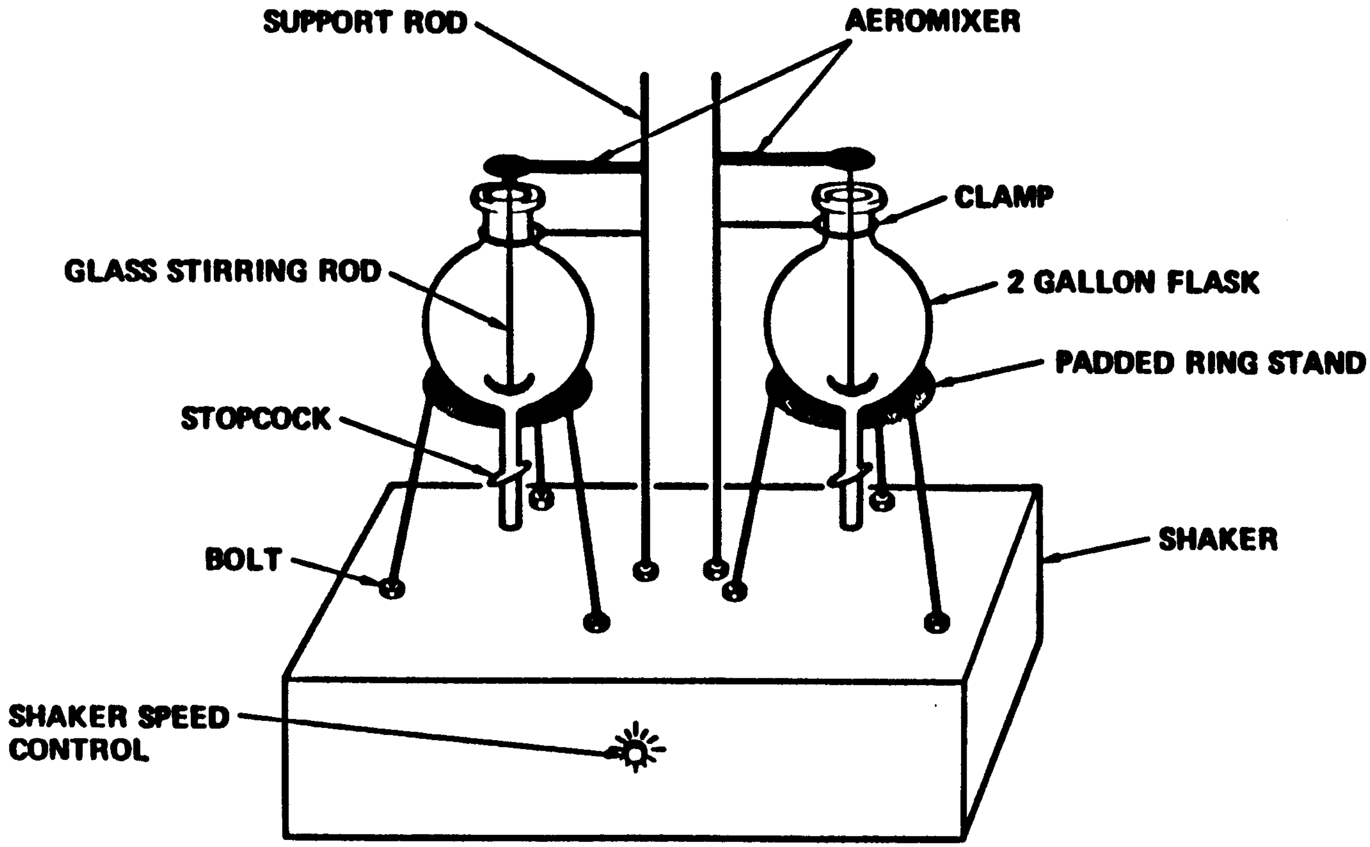


Fig. 11 Extraction Apparatus

at 32°C. The concentrated extract was then dried with sodium sulfate to adsorb any remaining water. The water free samples were stored in 5 to 10 ml of methylene chloride in a stoppered 25 ml round bottom flask at 2°C until they were analyzed (storage period was usually less than four hours).

GC analysis is performed with a Varian Vista 6000 instrument equipped with both a flame ionization and an electron capture detector in a splitless mode. The two detectors work in parallel by means of an SGE fused silica splitter.

A fused silica column (30m) wall coated with Carbowax 20M (.25 mm id) and a 22 meter fused silica SP2100 column were used for the initial chromatograms. Neither column performed optimally, the SP2100 provided a high temperature capability, but poor resolution. The Carbowax column provided good separation of the light compounds, but was unable to handle the heavier components. A Supelcowax 10, 30 meter fused silica column was finally chosen. The resolution is as good as the Carbowax column and the maximum safe operating temperature is 260°C which is almost as good as the SP2100. All chromatograms discussed henceforth are produced using the Supelcowax column, unless specifically stated otherwise.

Extracted samples were very gently evaporated to near dryness (one drop left) at 32° and low evaporator pressure. The sample residue was then redissolved (no visible, undissolved residue was observed) in an appropriate amount of methylene chloride (usually 1.0 ml) to render a good chromatogram at range 10^{-12} and an attenuation of 16 or 32 (about 5 ng/ul injected). Helium was used as the carrier gas at a pressure of 14-16 psig. The initial column temperature was 65°C with an initial four minute hold. The oven temperature was then programmed to 260 at 4° per minute. The column temperature was held at 260 for 30-55 minutes. The injection port was set at 250°C and the detector oven maintained a 280°C temperature. Peak areas were integrated using a Hewlett Packard model integrator. 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 using the Supelcowax 10 column. The MS instrument is a Finnigan 4000 series. Table 7 shows the extraction efficiency of this procedure for a variety of compounds and points out the reproducibility of the method.

3.2 Laboratory Chlorination of Water Samples

One liter volumes were used for all chlorinations. The appropriate amount of calcium hypochlorite solution is added from a prepared and calibrated solution. A 4 mg/ml stock solution of $CaOCl_2$ was prepared in distilled Arrowhead water. The pH of the chlorinated water is then immediately adjusted with 1N HCl or 1N NaOH to the desired acidity. The pH adjustment is done in less than one minute. In the instance where ammonia or bromide ion was added, the addition was done before pH adjustment. The ammonia solution was prepared as 70 mg $N\text{-}NH_4$/ml from NH_4Cl in distilled Arrowhead water

Table 7

Method Extraction Efficiency

Compound	Area of Standard ($x10^{-3}$)	Extract 1 Area	Extract 2 Area	% Recovery (Average)
2-octanone	54.9	50.6	50.9	92.4
2-nonanone	67.8	65.4	66.7	97.3
tridecane	95.1	90.2	87.2	93.2
1-tridecene	86.6	80.1	82.5	93.7
hexadecane	55.1	54.5	56.5	100.7
1-hexadecene	79.0	78.9	81.8	101.6
decanol	49.7	51.7	55.7	108.0
octadecane	65.4	68.8	71.0	106.0
1-octadecene	91.5	94.4	97.1	104.0
1-chloro-phenol	27.5	21.3	23.2	80.7
phenol	52.6	22.6	20.1	40.4
2,5 dimethylphenol	49.7	48.8	48.4	97.7
m-cresol	76.6	62.8	59.0	79.5
hexadecanone	78.3	83.6	83.6	106.0
O-N-propylphenol	67.7	67.2	69.4	101.0
2,3 dimethylphenol	97.6	96.5	96.5	98.8
4-t-butylphenol	162.2	162.8	162.8	101.0
2,4,5 trichlorophenol	9.9	9.7	10.0	100.0
1-hexadecanol	41.1	44.6	43.8	107.0
1-octadecanol	18.0	17.9	16.1	95.0

The chlorinated solution was stirred in a constant temperature (25°C) bath for the appropriate time before extraction. The extraction and GC analysis proceeded as previously described. Sodium sulfite was only added in experiments where sodium sulfite dose was used as a variable. In such instances a 6 mg/ml solution was used.

3.3 Chlorination of Extracts

Solvent extractable organics and XAD8 adsorbable organics from the aquaculture effluent were subjected to chlorinations as concentrated 15 ml solutions. One mg (measured as TOC) of XAD8 extract (procedure described below) was added to an appropriate amount of distilled Arrowhead water so that after addition of chlorine (and ammonia) solution, the total volume is 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.

The aquaculture effluent solvent extractable organics were extracted as previously described. The aquaculture solvent extract was consequently fractionated into three fractions by silica gel column chromatography (described below). Each of these three fractions, as well as the total extract, were chlorinated. It was found necessary to add 2 ml of methanol to dissolve some of the extracts. Procedural blanks using methanol showed that addition of alcohol does not introduce any new variables. The chlorination of the organic extracts was identical to chlorination of the XAD8 extracts except for the initial solubilization of the organic solvent extract in 2 ml of methanol.

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. The funnel was violently shaken by hand for one minute. The combined three extracts were evaporated and dried as previously described.

3.4 Silica Gel Column Chromatography

A 14 cm silica gel packed column (1.9 cm diameter) was used to separate the extracted organics into three fractions. The silica gel was soxhlet extracted with CH_2Cl_2 overnight prior to use as well as being rinsed 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 CH_2Cl_2:methanol and two column lengths of methanol.

3.5 XAD8 Adsorption

The water samples were adsorbed on XAD8 resin purchased from Rohm and Haas. The procedure used was a modified version of a protocol described by Malcolm (Thurman and Malcolm 1981) for the collection of fulvic and humic acids.

The resin was washed in .1N NaOH for six days with daily change of the wash solution or until the TOC of the wash solution drops below 10. The NaOH washed resin was then washed in diethyl ether (soxhlet extracted) for 24 hours followed by extraction in methanol for 24 hours. The resin was then packed onto a glass column and rinsed with distilled water until the TOC drops below 1 (about 3 gallons of water). The packed column was then alternately rinsed with .1N NaOH and .1N HCl 3 times.

The filtered (.45 micron) pH 2 sample was then passed onto the cleaned XAD8 column. The adsorbed organics were desorbed with three bed volumes of .1 N NaOH. The extract was reacidified to pH 2 and consequently readsorbed onto a smaller XAD8 column in order to concentrate the solution. It was desorbed with .1N NaOH. No fulvic/humic split is made. The solution was adjusted to an appropriate volume to yield the desired TOC level.

3.6 Ultrafiltration

40 ml of the XAD8 (4 mg TOC) adsorbable extract were fractionated into five nominal molecular weight ranges by four ultrafilters. The ultrafilters have nominal MW cutoffs at 100,000, 30,000, 10,000 and 1,000 and were purchased from Millipore Inc. High purity nitrogen gas at 110 psi was used to force the pH 7 extract through the membranes. Each membrane was rinsed with two 10 ml aliquets of high purity water (distilled Arrowhead water) and the wash was combined with the filtrate for passage through the next smaller membrane size. The residue from the 100,000 MW, the 30,000 MW and the 10,000 MW filters was desorbed by overnight stirring in 40 ml of .1N NaOH. The residue from the 1,000 MW filter was stirred overnight in pH 9 water. The less than 1,000 MW fraction was collected as a 120 ml solution, which is 40 ml of the original solution, plus 80 ml of washes. The solution was not reconcentrated.

3.7 Chlorination of Pure Compounds

Approximately 5 mg TOC of several pure compounds were chlorinated as concentrated 10 ml solutions in water. The TOC was calculated theoretically and was consequently measured gravimetrically. The chlorination procedure is identical to the chlorination of the XAD8 extracts. A chlorine dose giving a 2:1 Cl:C ratio was applied. All chlorinations were done at pH 7 for two hours.

3.8 Addition of Sodium Sulfite to Pure Compounds

Approximately 5 mg of each pure compound was dissolved in 2.5 ml of water. Water insoluble compounds were dissolved in methanol and methanol solutions yielding 5 mg of the compound (usually 20 µl) were added to the water. A control (no SO_3^-) sample was extracted with 5.0 ml CH_2Cl_2 for compounds eluting at temperatures higher than 75°C or 5.0 ml of pentane for early eluting compounds. The extraction was done in a 10 ml vial.

Sodium sulfite (excess) was added to an identical sample vial and the vial is allowed to stand at room temperature for 15 minutes before extraction. The control and sulfite containing sample were gas chromatographed at the previously described conditions. All samples were analyzed in triplicate.

3.9 TOC and Gravimetric Analysis

TOC measurements were run in triplicate using an Ionics TOC analyzer (Model 1270) which employed a combustion-infrared method for the analysis of soluble and purgable TOC. Acetic acid was used to prepare standards for each analytical run. Gravimetric analysis was performed using a Mettler

Electrobalance.

3.10 Other Procedures

There are several other procedures which were used. These procedures were not used routinely and will be described when the appropriate experiment is discussed. Table 8 is a list of these protocols.

Table 8

Other Procedures

1. Elution of XAD8 adsorbable organics by organic solvents.
2. Elution of XAD8 adsorbable organics by pH gradients.
3. Fractionation of XAD8 extract by enzacryl gel.
4. Humic/fulvic split of XAD8 extract.
5. Treatment of NVCO by powder activated carbon.
6. Treatment of NVCO by ozone.
7. Treatment of NVCO by aeration.

3.11 Reagents

All reagents were analytical grade or better. All solvents were distilled before use. The sodium chloride and sodium sulfate are baked at 550°C for at least four hours before use. All aqueous reagents were prepared in distilled Arrowhead brand water. Arrowhead brand drinking water was found to be superior to the laboratory distilled tap water and Sparkletts brand drinking water (contained fewer GC peaks). The Arrowhead brand water was distilled in glass in the laboratory before use. Teflon tape was used in place of stopcock grease at all times.

IV. RESULTS AND DISCUSSION

1. SOLVENT EXTRACTABLE ORGANICS AT SAN DIEGO (BACKGROUND ORGANICS)

Solvent extractable organics were collected at the San Diego Wastewater Treatment Plant on fifteen different dates. Initially, both acid and base neutral extracts were analyzed (separately, not successively). It was found that the GC output was similar, but not identical, for both extracts. Gravimetric and GC analysis (total FID area) showed that the Base Neutral extract was roughly about 65% of the acid extract. Consequently, only acid extractables were analyzed after the 3/85 sampling date. Some of the data from eight of these sampling dates are presented in this section as background information on the nature and concentration of organics in the secondary effluent, as well as the treatment efficiency of the various unit operations. The other seven sampling dates do not provide information on background organics at the treatment plant.

The treatment scheme at the San Diego plant has been previously described. Table 9 is a summary of the gravimetric data accumulated during 1984-1986 at the San Diego plant.

It is quite apparent from Table 9 that the treatment scheme at San Diego is quite effective in reducing the extractable organic levels from the secondary effluent. The reduction in treatment efficiency from 97 to 93 percent after chlorination indicates that chlorination has broken down organic carbon which prior to chlorination was not solvent extractable. This assertion is validated by gas chromatography of the extracts.

Table 9 Gravimetric Data for Total Acid Extractable Organics

Date	Aquaculture Effluent mg/L	Sand Filter Effluent mg/L	% Reduction	RO Effluent mg/L	% Reduction	Carbon Adsorption Effluent mg/L	% Reduction	Chlorinat. Product mg/L	% Reduction
11/84	4.04	ND		ND		ND		0.22	
	4.48	ND		ND		ND		0.34	
avg	4.26	ND		ND		ND		0.28	93
1/85	6.51	ND		0.55		ND		0.34	
	5.55	ND		0.61		ND		0.18	
avg	6.03	ND		0.58	90	ND		0.26	96
3/85	6.10	ND		ND		ND		0.46	
	6.62	ND		ND		ND		0.69	
avg	6.36	ND		ND		ND		0.57	91
4/85	ND	3.18		0.41	ND		ND		
5/85	3.71	ND		ND		ND		ND	
6/85	4.88	4.45	9	0.52	89	0.21	96	0.31	94
7/85	5.22	3.88	25	0.27	95	0.14	97	0.34	93
4/86	3.33	ND		ND		ND		ND	
Total									
avg	5.04	3.84	24	0.47	91	0.18	97	0.36	93

key
avg = average of duplicate values
ND = not determined

% reduction is based on aquaculture effluent value

The aquaculture effluent from 5/85, 7/85, as well as 4/86, was fractionated by silica gel column chromatography into three fractions of increasing polarity. The first fraction generally contains aliphatic hydrocarbons. The second fraction contains aromatic hydrocarbons, cyclic unsaturated hydrocarbons, as well as alkyl benzene and alkyl phenolic surfactants. Fraction three contains polar compounds such as phenols, acids and alcohols. Some compounds are not elutable from the silica gel column and are thus called non-elutable polars (NEP). Table 10 points out that gravimetrically, the extract is mainly composed of polar compounds, but that gas chromatographically (based on total areas from the FID detector) the non-polar fractions represent a sizeable percentage of the gas chromatographable compounds. This is not surprising since polar compounds are less amenable to gas chromatography.

Table 10

General Makeup of Aquaculture Effluent Extract

Date	% grav. frac. 1+2	% GC(FID) frac. 1+2	% grav frac. 3+NEP	% GC(FID) frac. 3+NEP
5/85	25.5	72.0	74.5	28.0
7/85	27.4	79.0	72.6	21.0
4/86	42.3	57.0	57.7	43.0

It is possible to estimate the percentage of the gravimetric extract that is represented by gas chromatographable peaks. Different compounds give a different area response count by the FID detector to the same amount (by mass) injected into the same column under identical chromatographic conditions. An estimate of 5,000 (acids) to 15,000 (hydrocarbons) area counts per nanogram of compound can be used as "ballpark estimates" which should give a range for the concentrations given by the total FID area counts.

Table 11 provides a comparison of the treatment of organics using gravimetric data, total FID areas and total ECD areas. A percentage of the gravimetric value that is represented by the FID areas is also estimated. The treatment of non-gas chromatographable compounds is slightly better than treatment of the smaller gas chromatographable compounds. This fact is also reflected in the percentage of the gravimetric weight that is represented by FID peak areas. This percentage is higher for the carbon adsorption effluent (15-44% in 6/85) than for the aquaculture secondary effluent (8-24% in 6/85).

Table 11 also clearly illustrates the dramatic effects of chlorination. The increase in total FID (decrease in treatment) area indicates the breakdown of larger molecules which prior to chlorination were not amenable to gas chromatography. The increase in total ECD area indicates that many of these breakdown products are halogenated.

The aquaculture effluent extracts from 11/84 and 4/86 were analyzed by GC/MS for positive identification of some of the compounds in the extract. The GC/MS in 11/84 was run by James Montgomery Engineers Laboratory. The results from Montgomery Engineers are of poor quality and will not be discussed. The 4/86 GC/MS was run at UCLA and provided for tentative identification of numerous compounds. The sparse use of MS data is due to the unavailability of a quality Mass Spectrophotometer on a routine basis at the time that the experimental work was done.

Table 11 Comparison of Reduction Efficiencies

Sampling	%Reduction Gravimetric		% Reduction FID area		% Reduction ECD area		% of grav. that is in FID	
	6/85	7/85	6/85	7/85	6/85	7/85	6/85	7/85
Aquacult.	-	-	-	-	-	-	8-24	4-12
Sand Filt.	9	25	23	24	18	27	7-21	4-12
RO	89	95	82	78	47	79	14-42	12-36
Carbon	96	97	93	96	78	95	15-44	14-42
Chlorinated Effluent	94	93	63	80	25	80	48-145	40-120

Key:

% Reduction based on aquaculture effluent values

% of grav. that is in FID = % of the gravimetric weight that can be accounted for by FID peak areas.

The GC data collected during and after 7/85 was saved on floppy disks. It was consequently possible to match retention times of the aquaculture effluent GC extracts form 7/85 and 4/86. This was done in order to assess the reduction of the individually identified peaks from 4/86 with the complete treatment plant sampling done in 7/85. It was not possible to do a complete plant monitoring in 4/86 because the RO unit was not operable.

Figure 12 is the GC output for the aquaculture effluent (4/86) showing both ECD and FID detectors. Figure 13 is the reconstructed chromatogram from the GC/MS of the same sample. Table 12 lists the compounds in the extract which were tentatively identified and their approximate concentrations. Table 13 shows how well some of these compounds were treated along the plant's treatment train during the 7/85 sampling.

It is interesting to note that the RO unit is ineffective in removing nonyl-phenol and its related compounds. These compounds are effectively removed after carbon adsorption. Figure 14 is fraction 1 (aliphatics) from the aquaculture effluent. This extract greatly resembles motor oil extracts previously analyzed (Stenstrom, Fam, Silverman 1984). Figure 15 is the chromatogram of fraction 2 of the aquaculture effluent. The nonyl-phenol series of compounds is clearly visible in this chromatogram. Figure 16 is the total RO extract chromatogram. One observes that the surfactant series comprises a large portion of the extract (compare Figures 15 and 16).

Examination of the ECD peaks form the 7/85 sampling date points out that 109 new halogenated compounds were formed after chlorination (this analysis is not easily performed for samples collected prior to 7/85, since the output was not saved on disks). In addition, several compounds which were present in the aquaculture effluent showed significant increases (greater than 500%) after chlorination. This is quite expected since the water entering the treatment plant had previously been chlorinated by the City of San Diego. The halogenated organics are apparently well treated by the aquaculture fields, but reappear after chlorination.

In summary, the aquaculture effluent is mainly comprised of fatty acids (human waste), hydrocarbons (refined oils and biogenic (C_{31} n-alkane)), surfactants (from household detergents), pthalate compounds (plasticizers), cholesterols (human waste) and low amounts of halogenated compounds (industrial use and chlorination by-products). The RO unit effectively removes most of these compounds except for the detergents. Carbon adsorption provides final polishing for nearly 97% overall treatment of these compounds. The non-gas chromatographable compounds are also well treated as can be seen from the gravimetric data. Chlorination results in the production of an abundance of gas chromatographable halogenated compounds and is the problematic treatment step at the San Diego Treatment plant.

A mixture of 23 compounds of different polarity and MW was passed through the RO unit (4/17/86) to assess its selectivity towards the various organics. This data is presented in tabular form in Appendix 1. As expected the RO unit treats less polar large MW compounds more effectively. Figure 17 illustrates the effect of MW on the treatment of C12, C14, C16 and C18 straight chain fatty acids (from the 7/85 sampling date).

Table 12 Compounds Identified in the Aquaculture Effluent During the 4/86 Sampling by GC/MS

Scan No.	Compound Name or Structure	Method of ID	Approximate Conc. μg/L	% Confidence in ID
243	decane (is)	1,2,3	10.0	>95
251	C_{11} *aliphatic*	1,2	0.5	70
291	CH_2ClBr	1,2,3	2.5	>95
447	CH_2ClI	1,2	2.5	>95
461	chloro-benzene	1,2,3	2.3	>95
476	C_{12} aliphatic	1,2	0.4	70
586	C_9 alcohol	1,2,	1.8	60
597	3-heptanol 3,6 dimethyl	1,2	0.6	70
614	C_9 alcohol	1,2	0.6	70
660	tetradecane (is)	1,2,3	9.4	>95
709	1,4 dichlorobenzene	1,2,3	0.5	>95
754	1,3 dichlorobenzene	1,2,3	3.1	>95
897	cyclohexanone 4-(1,1 dimethyl ethyl)	1,2	1.3	80
915	1-hexanone 1-phenyl	1,2	0.6	90
1146	tetradecanal	1,2	1.4	80
1152	benzene (1-pentyl-heptyl)	1,2	1.4	>95
1178	C_{19} aliphatic	1,2	6.5	80
1196	hexanoic acid 3,5,5 trimethyl	1,2	3.6	90
1277	m-creosol (is)	1,2,3	10.8	>95
1312	hexadecanal	1,2	3.7	80
1346	2-chloro benzeneamine	1,2	5.1	90
1409	$C_8H_{12}O_2Cl_2$	2	10.2	90
1481	1-hexadecanol	1,2,3	8.9	95
1562	1-dodecanoic acid	1,2,3	8.2	>95
1616	1-octadecanol	1,2,3	26.5	95
1642	2,3 dichlorobenzeneamine	1,2	4.5	90
1663	branched C_{14} acid	1,2	15.3	95
1682	4-nonylphenol	1,2	5.6	95
1692	1-tetradecanoic acid	1,2,3	28.1	>95
1701	long chain alkyl phenol	1,2	4.2	95
1713	long chain alkly phenol	1,2	4.4	95
1725	1-pentadecanoic acid	1,2	38.9	95
1736	branched C_{15} acid	1,2	28.4	95
1755	branched C_{15} acid	1,2	14.9	95
1814	1-hexadecanoic acid	1,2,3	85.4	>95
1824	branched C_{16} acid	1,2	72.8	95
1870	branched C_{16} or C_{17} acid	1,2	21.9	90
1915	C_{31} n-alkane	1,2,3	35.5	>95
1962	1-octadecanoic acid	1,2,3	97.5	>95
1990	1-nonadecanoic acid	1,2	52.7	95

Table 12 Compounds Identified in the Aquaculture Effluent During the 4/86 Sampling by GC/MS (Continued)

Scan No.	Compound Name or Structure	Method of ID	Approximate Conc. µg/L	% Confidence in ID
2044	branched C_{19} or C_{20} acid	1,2	43.6	
2110	pthalate compound	1,2	ND	90
2146	pthalate compound	1,2	ND	90
2221	pthalate compound	1,2	ND	90
2297	pthalate compound	1,2	ND	90
2324	pthalate compound	1,2	ND	90
2380	pthalate compound	1,2	ND	90
2509	pthalate compound	1,2	ND	95
3351	cholesterol isomer	1,2	ND	95

Key:

1. manual interpretation of MS data
2. computerized matching of MS data
3. GC retention time matched with known standards

ND not determined because peaks are too broad
% confidence in ID is a personal judgement
\- concentrations evaluated based on area response of similar classes of compounds.
(is) internal standard

Table 13 Treatment of Some of the Identified Compounds in the Aquaculture Effluent during the 7/85 Sampling

Compound	scan No. (4/86 Sample)	% Treatment After RO	Carbon
1,3 dichlorobenzene	754	99.5	100.0
tetradecanal	1146	56.0	100.0
C_{19} hydrocarbon	1178	83.2	100.0
C_9 branched acid	1196	86.0	100.0
2,propenal 3,phenyl	1247	91.3	100.0
hexadecanal	1312	58.6	98.4
2 chloro-benzeneamine	1346	46.6	97.3
C_{22} hydrocarbon	1354	85.8	100.0
$C_8H_{12}O_2Cl_2$	1409	88.7	100.0
1-hexadecanol	1481	73.1	100.0
1-dodecanoic acid	1562	47.0	81.5
2,3,dichlorobenzamine	1642	98.1	98.7
branched C_{14} acid	1663	57.2	89.5
4-nonyl phenol	1682	39.1	100.0
long chain alkyl phenol	F2	31.1	100.0
long chain alkyl phenol	F2	12.4	91.3
long chain alkyl phenol	F2	7.6	100.0
long chain alkyl phenol	F2	34.8	93.5
1-tetradecanoic acid	1692	50.2	95.1
long chain alkyl phenol	F2	49.2	100.0
1-pentadecanoic acid	1725	74.6	100.0
long chain alkyl phenol	F2	38.5	100.0
long chain alkyl phenol	F2	17.2	92.9
long chain alkyl phenol	F2	4.0	100.0
branched C_{15} acid	1755	72.8	100.0
1-hexadecanoic acid	1814	94.8	100.0
C_{31} n-alkane	1915	92.2	97.4
1-octadecanoic acid	1962	94.7	83.0
pthalate compound	2110	100.0	74.1
pthalate compound	2146	100.0	100.0
pthalate compound	2221	52.4	100.0
pthalate compound	2297	72.2	100.0
pthalate compound	2324	100.0	100.0
pthalate compound	2380	100.0	100.0
pthalate compound	2509	100.0	100.0

Key: F2 - compound not clearly identified in the 4/86 MS output but was present in the 7/85 sample as a fraction 2 compound eluting near nonyl phenol (see Figure 16).

Compounds not listed in this table but listed in Table 12 were not present in the 7/85 sample.

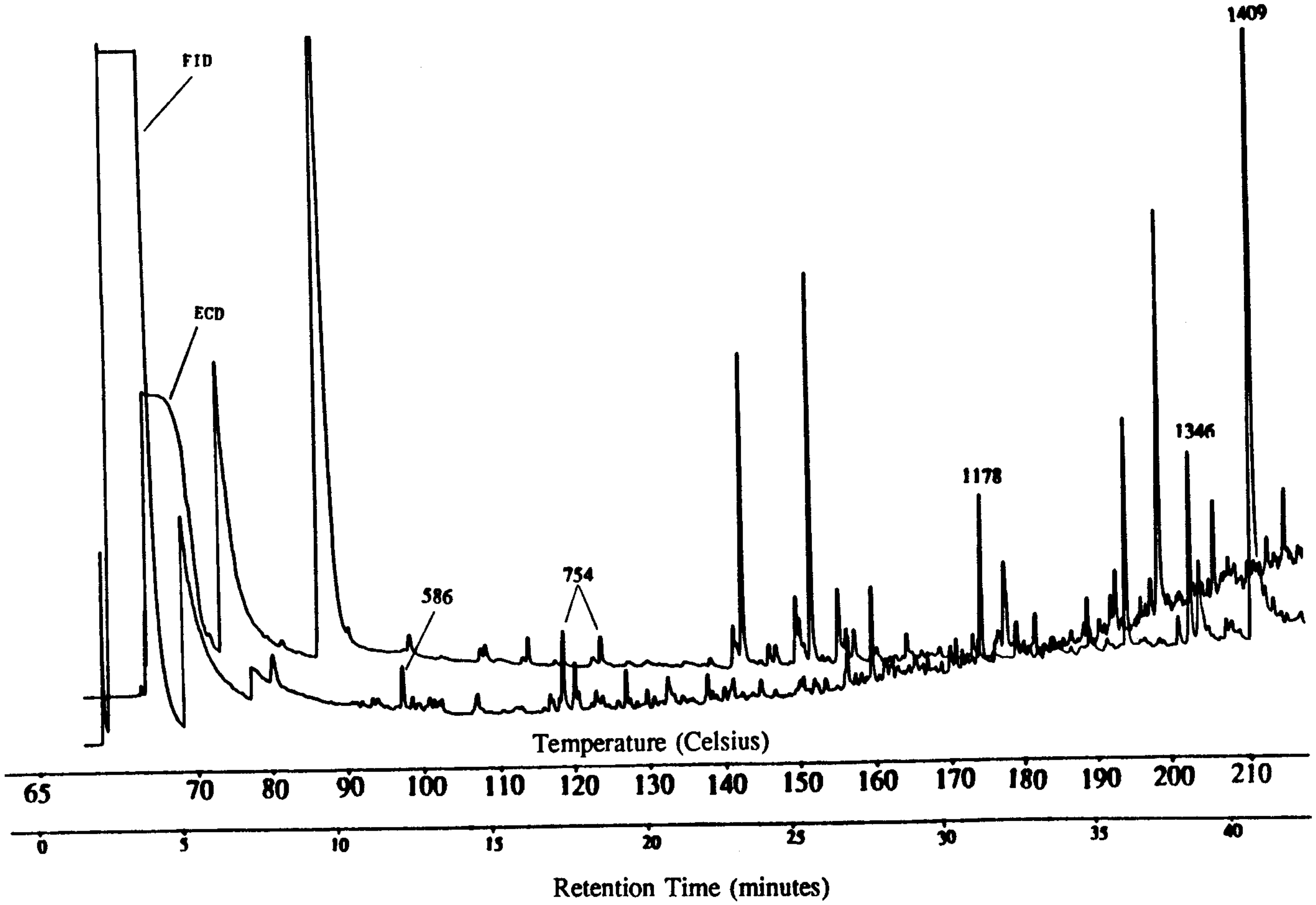


Fig. 12: GC of the aquaculture effluent total extract. GC conditions as specified in analytical procedures. Some MS scans are labeled. See Table 12 and Fig. 13 for complete listing. Axes are labeled for the FID.

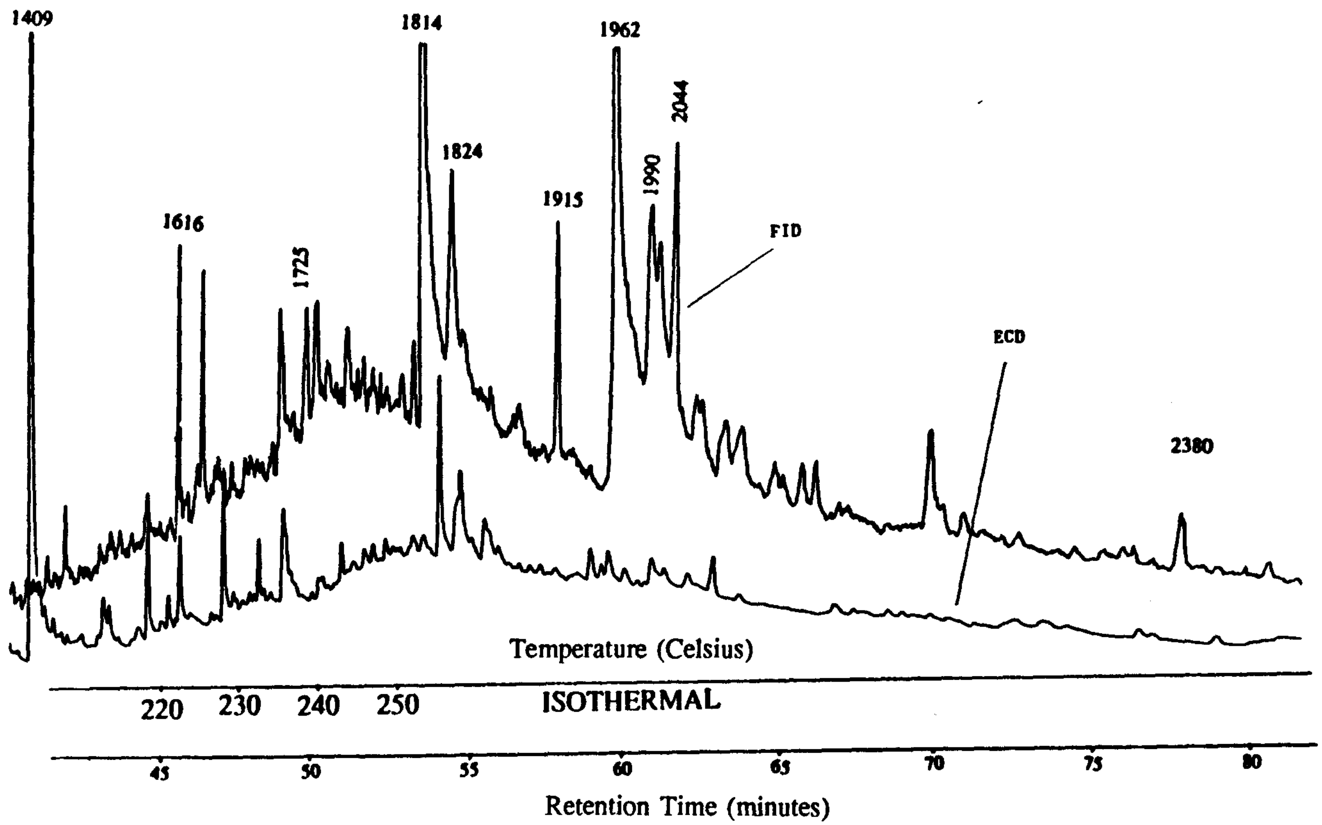


Fig. 12 (Continued)

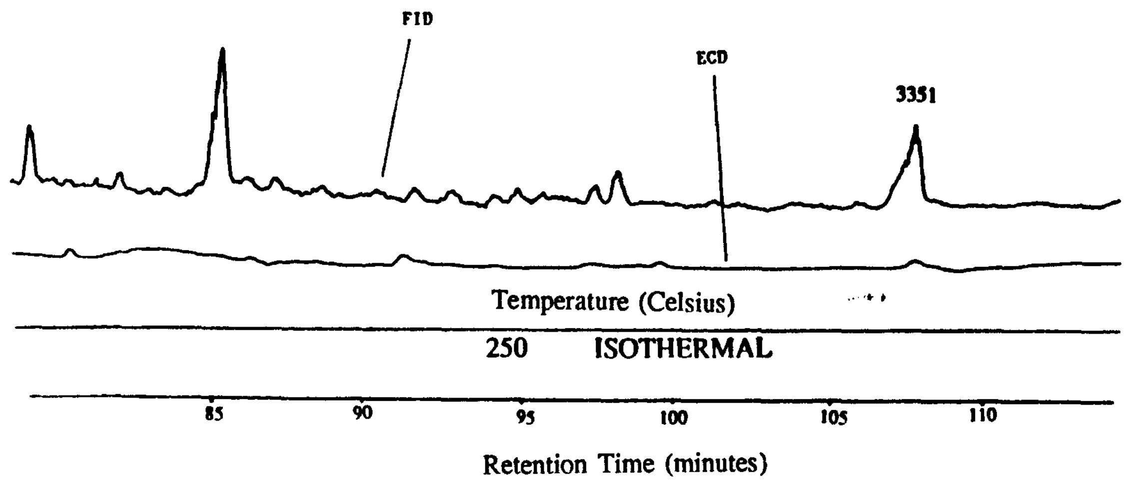


Fig. 12 (Continued)

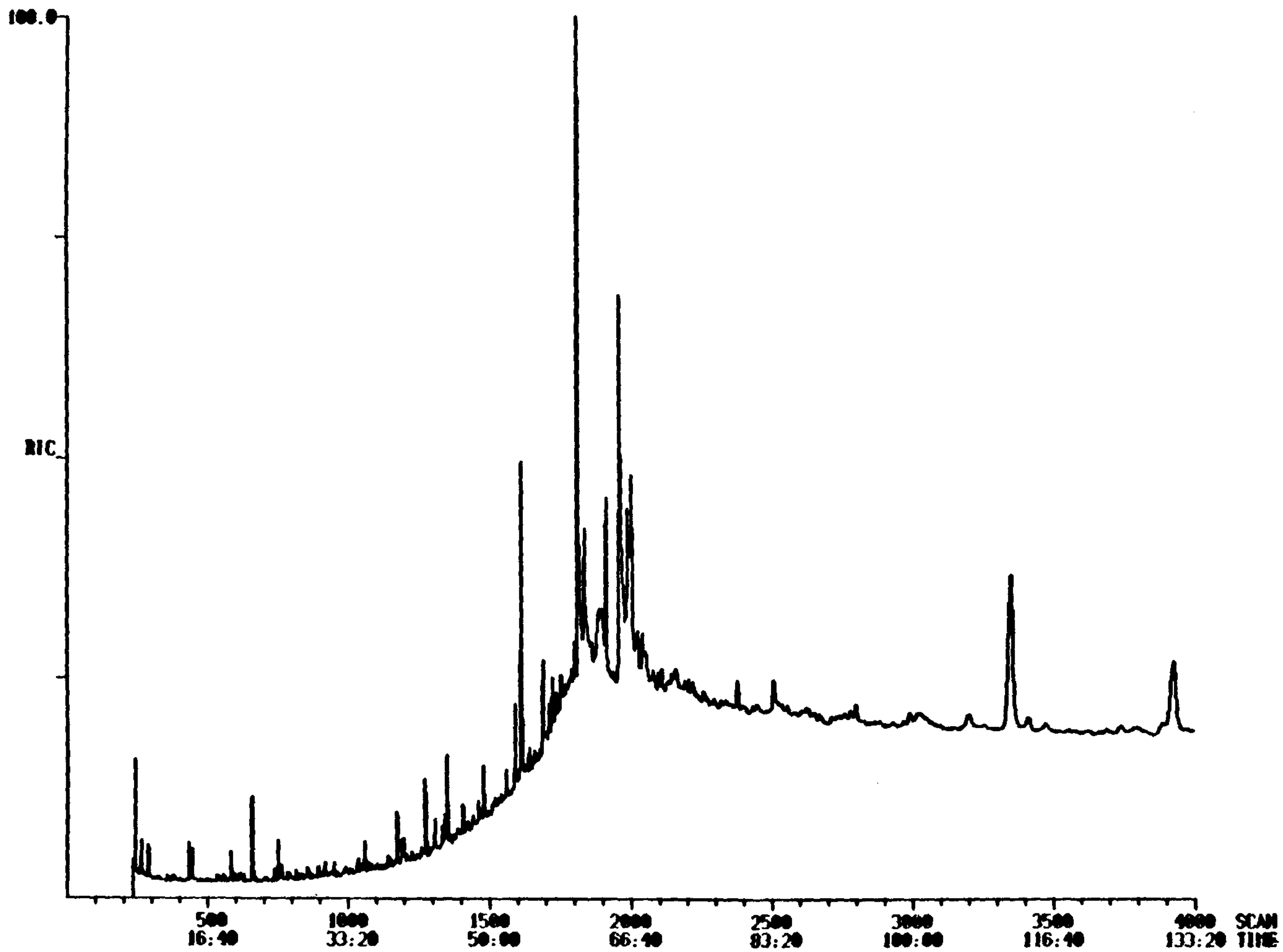


Fig. 13 Reconstructed GC/MS of the Aquaculture Effluent Total Extract

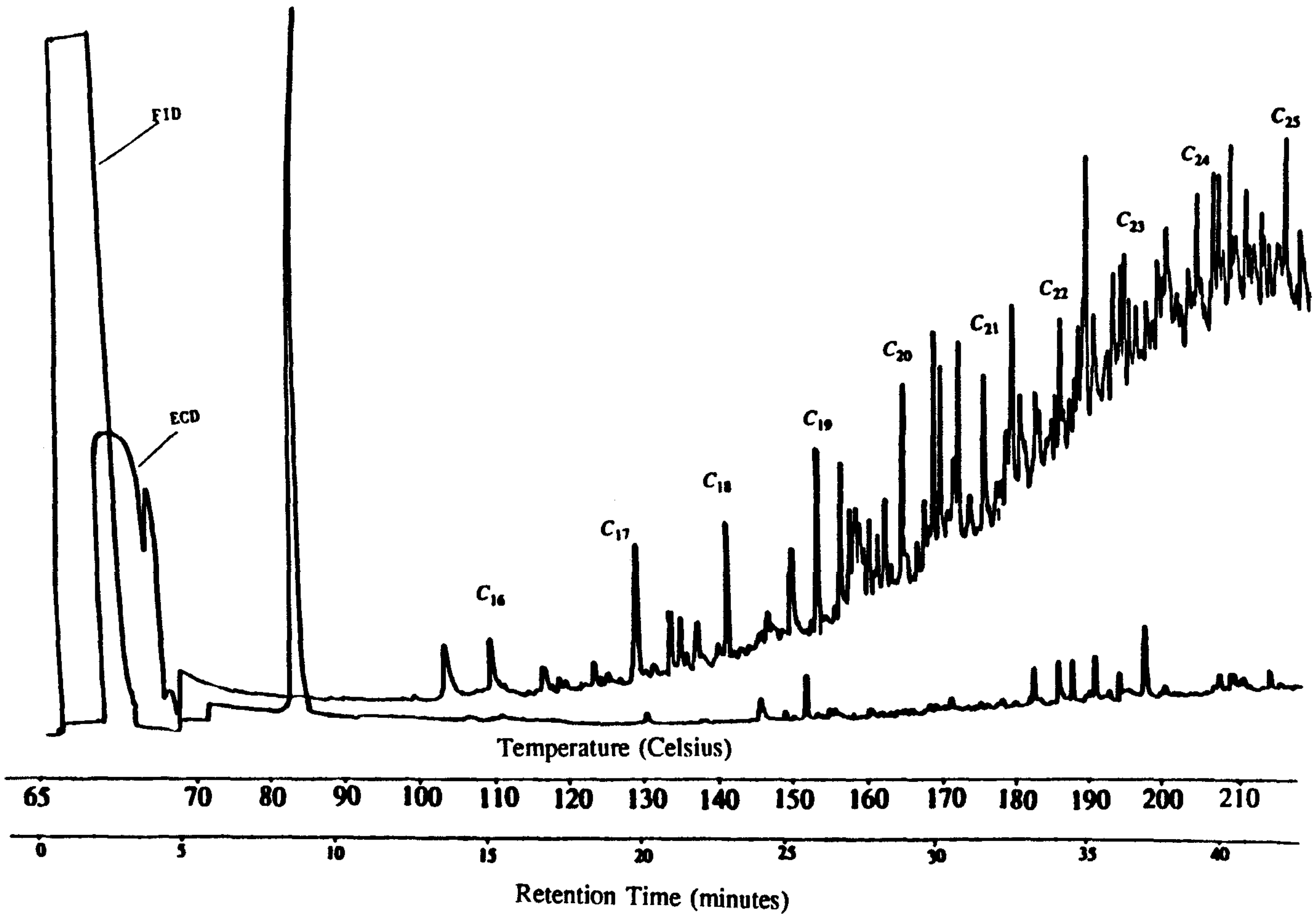


Fig. 14: GC of fraction 1 of the aquaculture effluent extract. GC conditions as specified in analytical procedures. n-alkanes are labeled according to the number of carbons. Axes are labeled for the FID.

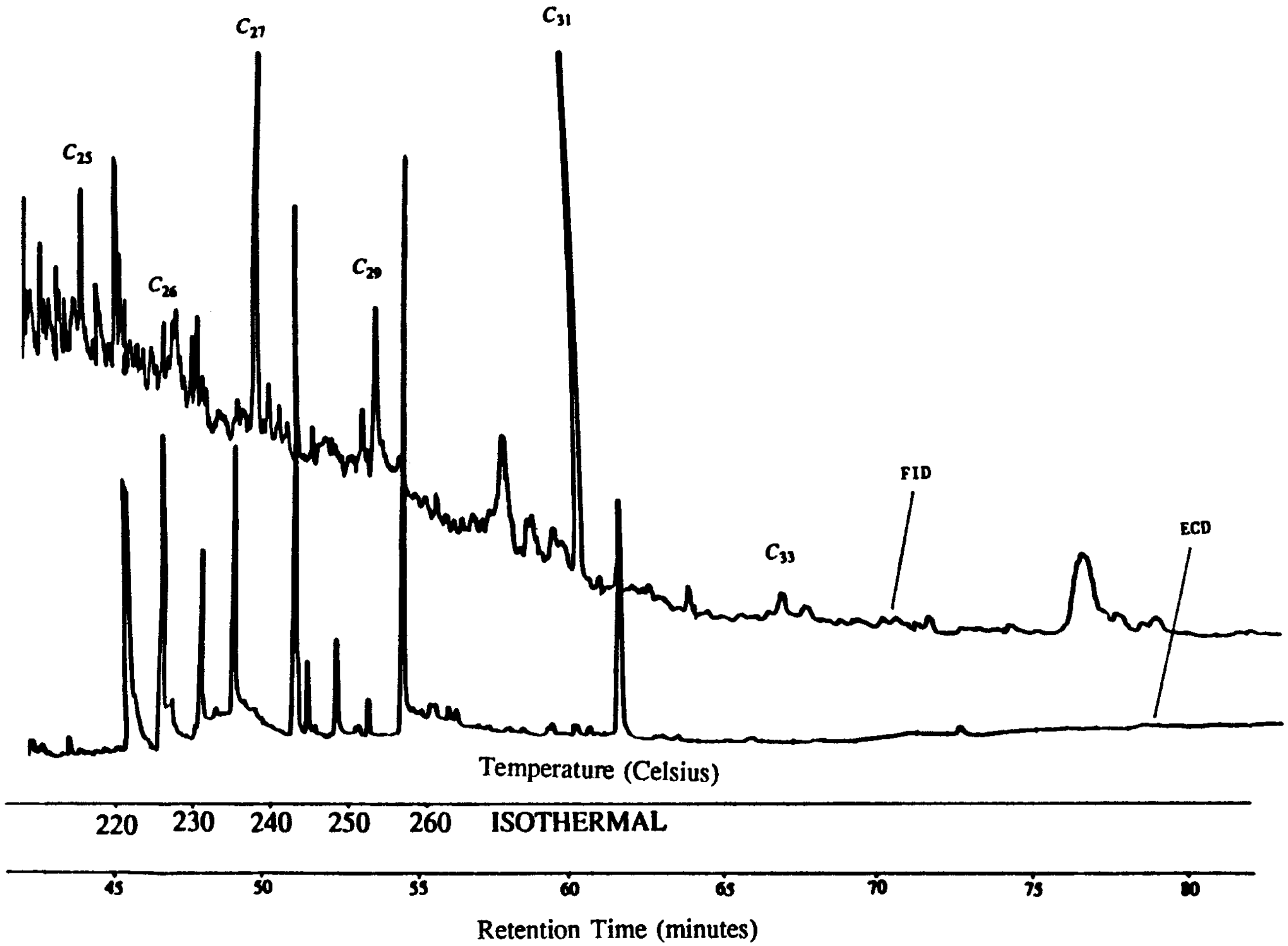


Fig. 14 (Continued)

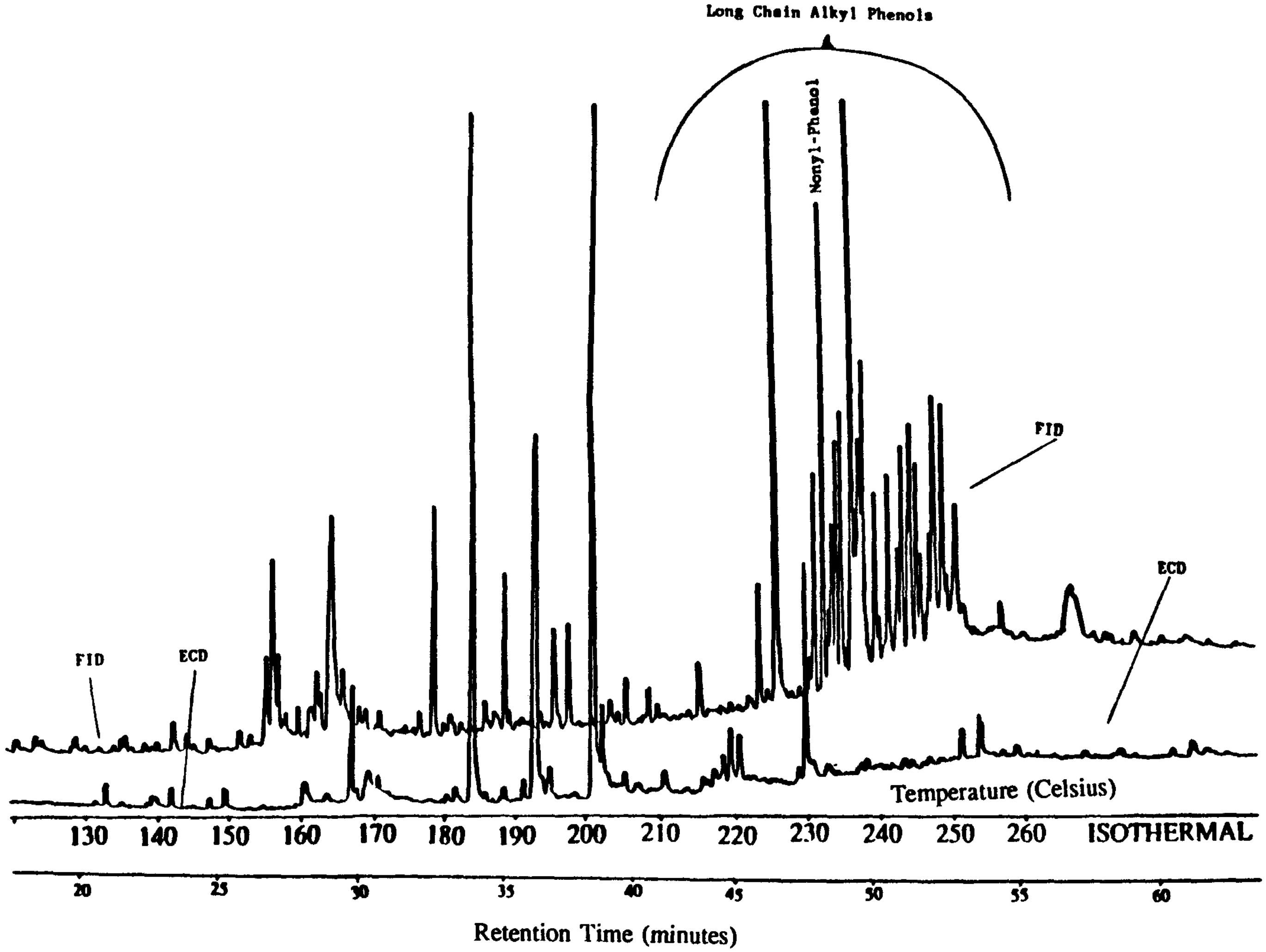


Fig. 15: GC of fraction 2 of the aquaculture effluent extract. GC conditions as specified in analytical procedures. Axes are labeled for the FID. Compound ID in Table 12.

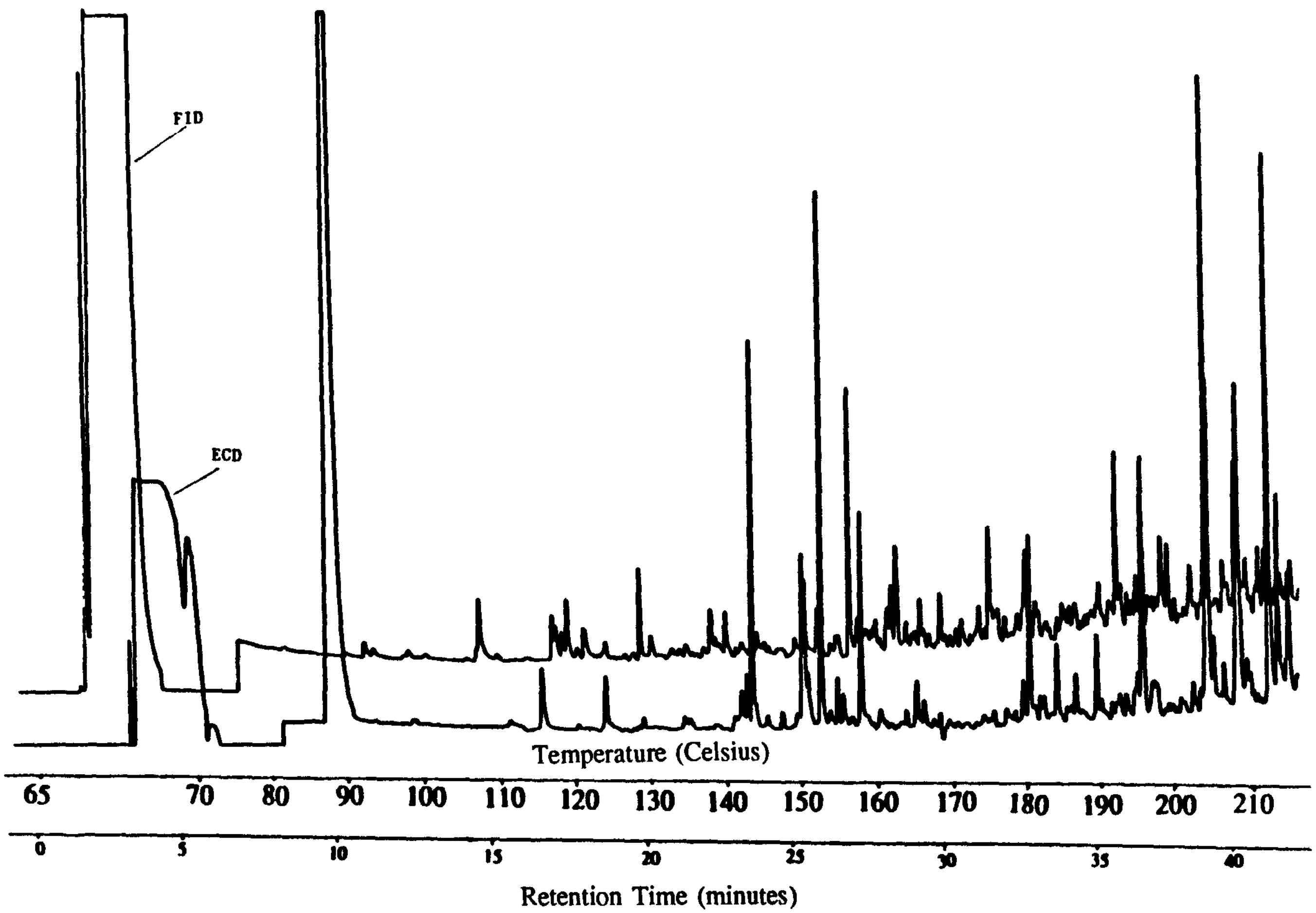


Fig. 16: GC of RO effluent total extract. GC conditions as specified in analytical procedures. Axes are labeled for the FID. Compound ID in Table 12.

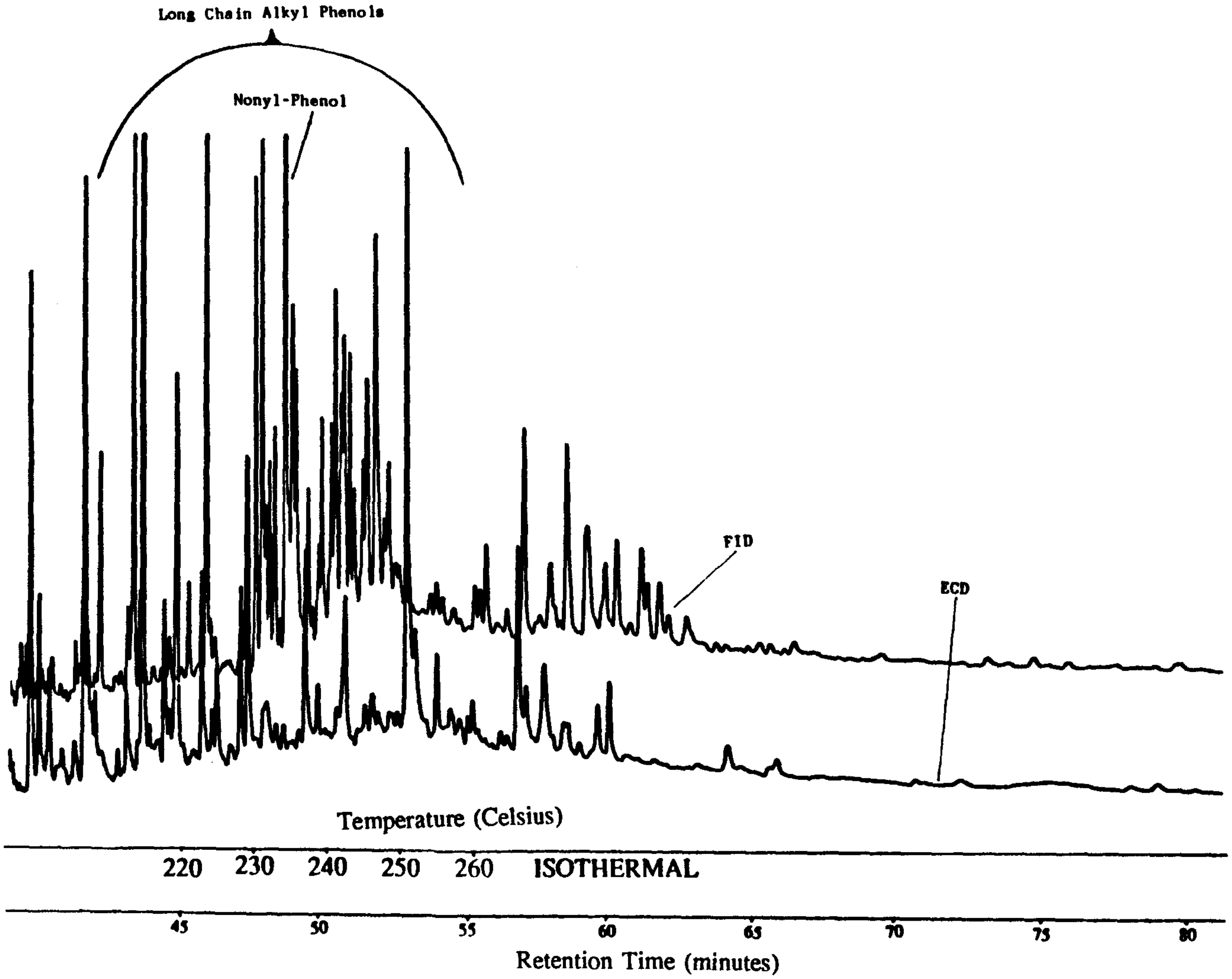


Fig. 16 (Continued)

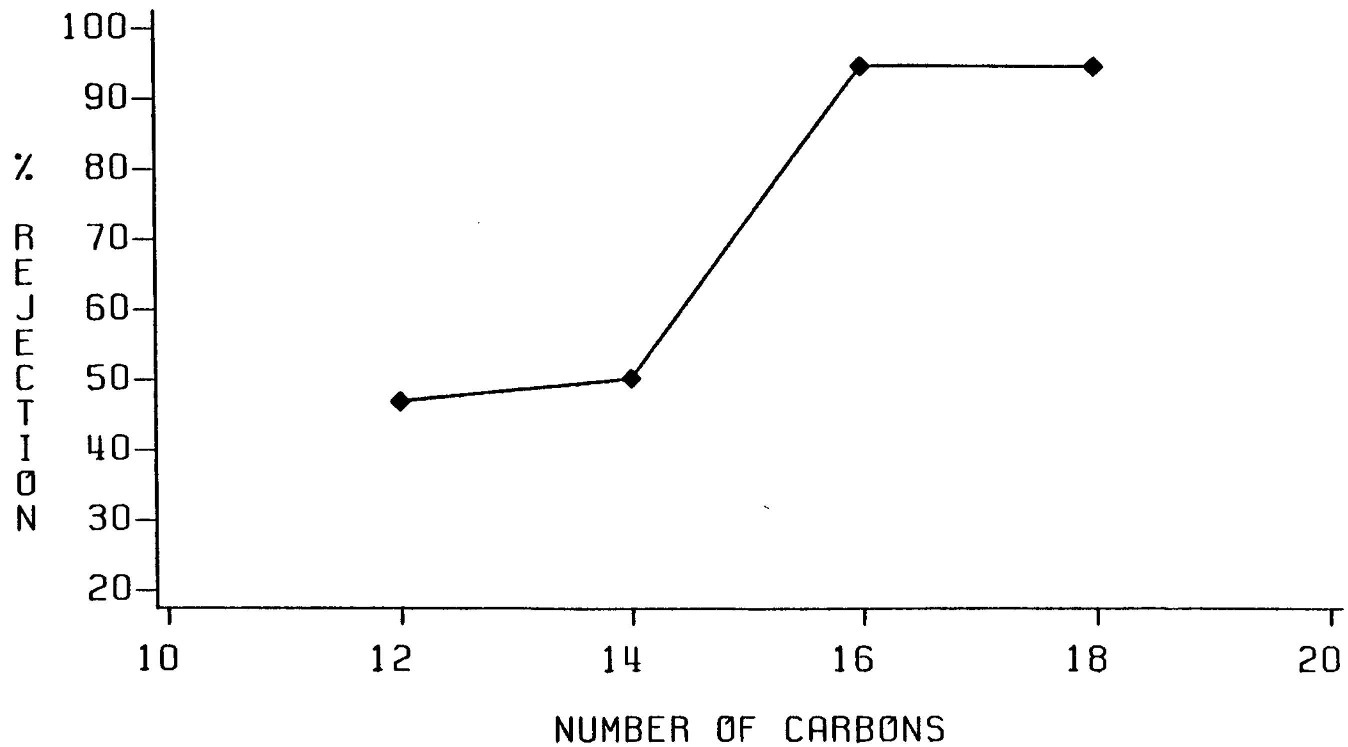


Fig. 17 Rejection of Straight Chain Fatty Acids by the RO Unit

2. IDENTIFICATION OF SOME OF THE NVCO BY GC/MS

The initial samplings at the San Diego treatment plant clearly indicated that chlorination was the problematic treatment step (Tables 9 and 11). An abundance of new halogenated organics are detected by GC and GC/MS.

Some of the compounds are identified by name, others are identified by molecular formula, and several other compounds are only identified by molecular weight or number of halogenated atoms in the molecule. Each sizeable ECD peak produced after disinfection, regardless of its level of identification, is given a reference number. This reference number allows discussion in upcoming chapters on the formation of a particular peak (compound), its precursors, and its treatment. Any other compound which is well identified (regardless of its magnitude) is also given a reference number.

Figure 18 is the gas chromatograph of the extract from the chlorinated product water at the San Diego plant (March 1986). The abundance of halogenated (ECD) peaks is overwhelming. The major ECD peaks, as well as other identified compounds are labeled by reference number in Figure 18. Background compounds (present in the aquaculture effluent) are labeled 'B' and are identified in Table 13. Background peaks which are pthalates are labeled 'P'. The early eluting halogenated compounds are labeled 'A#' and the late eluting chlorinated organics are labeled 'D#'.

It was observed that XAD8 (adsorption resin) adsorbable organics from the aquaculture fields effluent yield a very similar pattern of halogenated organics upon laboratory chlorination (this observation will be discussed in greater detail in upcoming chapters). The chlorinated product water from the

San Diego plant contains halogenated compounds produced during disinfection as well as background halogenated compounds. Since the XAD8 extract does not contain any background halogenated organics (they are not collected by the adsorption/desorption procedure i.e., they are only desorbable by an organic solvent from the XAD8 resin), but contains the majority of chlorination by-products, it provides a simpler chromatographic system for the identification of the organic compounds produced during disinfection.

Figure 19 is the gas chromatograph of laboratory chlorinated XAD8 extract. The similarity of this chlorinated extract to the chlorinated product water from San Diego (Figure 18) is very clear. The major difference is that the large hump eluting at 45-50 minutes in Figure 18 is not present in Figure 19. Only a few of the compounds producing this hump were identified. These compounds were present in large concentrations on occasion (Figure 18) and on other occasions their concentrations were much less.

Since the ECD is much more sensitive than either an FID or an MS detector, thirty times more XAD8 extract was chlorinated than that shown in Figure 19 in order to produce MS detectable compounds. Figure 20 is the GC of this concentrated extract and Figure 21 is the equivalent reconstructed MS chromatogram. Unfortunately, this concentrated extract contains fatty acids from the aquaculture effluent which slightly complicates the chromatograph (labeled B in Figure 20). Some of the ECD peaks in Figure 20 appear very broad due to the high concentrations used. The axes in Figures 18, 19, and 20 are labeled for the ECD. The FID is offset slightly to the left.

A GC/MS analysis was performed for the chlorinated product water from the San Diego (December 1985) plant. Unfortunately, the abundance of compounds in the extract did not allow for good MS identification. Comparison of the MS output from the San Diego product water and the chlorinated extract would usually reveal that the San Diego effluent MS scans contain extraneous fragments from carryover of neighboring compounds. Although fractionation of the San Diego extract and the consequent MS analysis of the fractions would remedy this problem, due to time, equipment limitations, and satisfaction with the XAD8 MS results the fractionation was not performed. The GC/MS scans for the identified compounds are shown in Appendix 2.

Table 14 lists the identified compounds, method of identification, percent confidence in the identification, approximate concentration of the compound in the San Diego effluent (average value from all collected samples), GC retention time and compound reference number for upcoming discussion. A personal communication with R. Christman and D. Norwood indicated that they had not encountered some of these compounds (1986).

The following generalizations can be made about the produced halogenated organics. First, in agreement with Miller (1983), Coleman (1984), Kringstad (1985), Quimby (1980), Snoeyink (1981) and McCreary (1981) chlorinated aromatic compounds were observed. Christman et al. (1979, 1981) only observed aliphatic halogenated compounds in their work with chlorinated humic and fulvic acids.

Second, many of the observed halogenated compounds are unsaturated and contain oxygen atoms. Some unsaturated halogenated compounds are reactive with dechlorinating agents and have consequently escaped detection by several workers in the past. The chapter entitled "Effects of Dechlorinating Agents" details this observation.

Third, many of the compounds contain more than one chlorine atom and consequently produce much more response in the ECD detector (the ECD detector is only sensitive to halogenated compounds) than in the FID detector. Although the FID detector responds to all molecules, it gives the best response to carbon-hydrogen bonds. Since many of the observed halogenated organics are unsaturated (fewer carbon-hydrogen bonds) and are poly-chlorinated, this magnifies the difference between the response of the two detectors.

Fourth, the identified halogenated compounds most closely resemble the structures identified by Coleman, et al. (1984) (Table 4). This is likely due to the fact that Coleman did not add any dechlorinating agents to his samples prior to extraction. Most workers (Christman (1981), Quimby (1980), Miller (1983)) dechlorinate their samples prior to extraction and, as will be discussed in Section 5, sodium sulfite has been found to be reactive with several of the observed compounds. The reaction between the dechlorinating agents and the halogenated compounds precludes their chromatographic identification.

Fifth, the unavailability of a GC/MS on a routine basis precluded more positive identification of the compounds listed in Table 14. It is highly recommended that sample fractionation be performed prior to GC/MS identification in order to minimize carryover. In addition, many of the produced halogenated organics have weak molecular ion intensities which is typical of halogenated aliphatics. Chemical ionization mass spectroscopy would consequently be recommended to assist in more positive identification.

Table 14 Halogenated Compounds Produced during Disinfection

Scan No.	Identification	RT (min.)	Method of ID	% Confidence in ID	ref.	Concentration in chlorinated SD final effluent average (ppb)
255	chloroform	-	1,2,3	>95	E1	ND
279	chloro-bromomethane	-	1,2,3	>95	E2	ND
303	dichloro-propane	-	1,2	90	E3	ND
356	dichloro-cyclohexene	5.52	1,2	60	A1	3.1
383	unknown unsaturated chlorinated compound	6.39	-	-	A2	5.0
-	unknown	6.67	-	-	A3	0.5
429	chloro-iodo methane	7.80	1	>95	A4	0.8
439	2-propanone 1,1 dichloro	8.00	1,2	90	A5	5.7
443	2-propanone 1,1,1 trichloro	8.28	1,2	90	A6	10.0
481	C_3NCl_3	9.17	1	60	A7	0.7
496	1-propene 1,2,3,3 tetrachloro	9.46	1,2	80	A8	<.5
-	unknown	9.85	-	-	A9	<.5
505	unknown	9.91	-	-	A10	0.4
513	$C_4H_6Cl_3N$	10.64	1	60	A11	1.0
541	$C_5H_8Cl_2$	11.17	1	90	A12	2.9
555	MW 152, 2 chlorines $C_4H_2O_2Cl_2$	11.94	1	60	A13	0.3
615	$C_5H_3Cl_3O$	13.25	1	70	A14	4.6
642	cyclopentanol 1,2 methyl	14.24	1,2	90	A15	1.5

672	$C_5H_5Cl_3O$	15.25	1	90	A16	<.5
695	pentachloropropene	15.83	1	90	A17	1.5
702	$C_5Cl_3H_5O$	16.49	1	90	A18	3.3
733	MW 146, 1 chlorine	17.21	1	60	A19	3.1
770	benzaldahyde	17.63	1,2	90	A20	1.2
795	unknown	19.36	-	-	A21	4.2
889	1-hexanone,5 methyl,1-phenyl	22.48	1,2	70	A22	3.1
909	unknown halogenated aliphatic acid	22.64	-	-	A23	<.5
959	unknown	23.43	-	-	A24	<.5
996	unknown halogenated aliphatic. Formed mostly at high pH and low chlorine dose	25.54	-	-	A25	<.5
1297	$C_4H_4Cl_4O$ (may be fragment of larger molecule) molecule	36.23	1	60	D1	ND
1307	$C_4H_2Cl_4O$ (may be fragment of larger molecule)	36.25	1	60	D2	ND
1317	C_4Cl_4O (may be fragment of larger molecule)	36.55	1	80	D3	8.9
1336	2,4, dichloro-6-methyl phenol	37.43	1,2	90	D4	<.5
1368	$C_8Cl_2OH_{14}$	38.60	1	30	D5	1.9
1378	$C_8H_9Cl_2NO_2$	38.87	1	30	D6	7.6
1399	$C_{10}Cl_2H_{12}NO_2$	39.55	1	30	D7	1.0
1427	2,4,6 trichlo-phenol	40.61	1,2,3	>95	D8	2.8
1459	dichloro-propyl	41.61	1	70	D9	0.6

	phenol					
1492	trichloro benzoic acid	42.89	1	60	D10	33.2
1528	MW 232, 3 chlorines	44.12	1	60	D11	0.8
1560	MW 230, 3 chlorines	45.15	1	60	D12	5.1
1589	trichloro-phenol ethoxy	46.03	1	80	D13	5.8
-	unknown	47.59	-	-	D14	<.5

Key:

RT	=	retention time in minutes (Figure 20)
ND	=	not determined
ref	=	reference number for compound for discussion in upcoming chapters
Scan No.	=	MS scan number (Figure 21)
1	=	manual interpretation of MS scan
2	=	computer matched interpretation of MS scan
3	=	GC retention time match with known standard
% confidence in ID	=	personal judgement
concentration	=	based on 10,000 area counts/ng for FID area. Concentration is the average for all samples collected at the San Diego plant. Concentration values should be regarded as ±100%.

This table only lists compounds produced during disinfection. Background compounds are identified in Table 12.

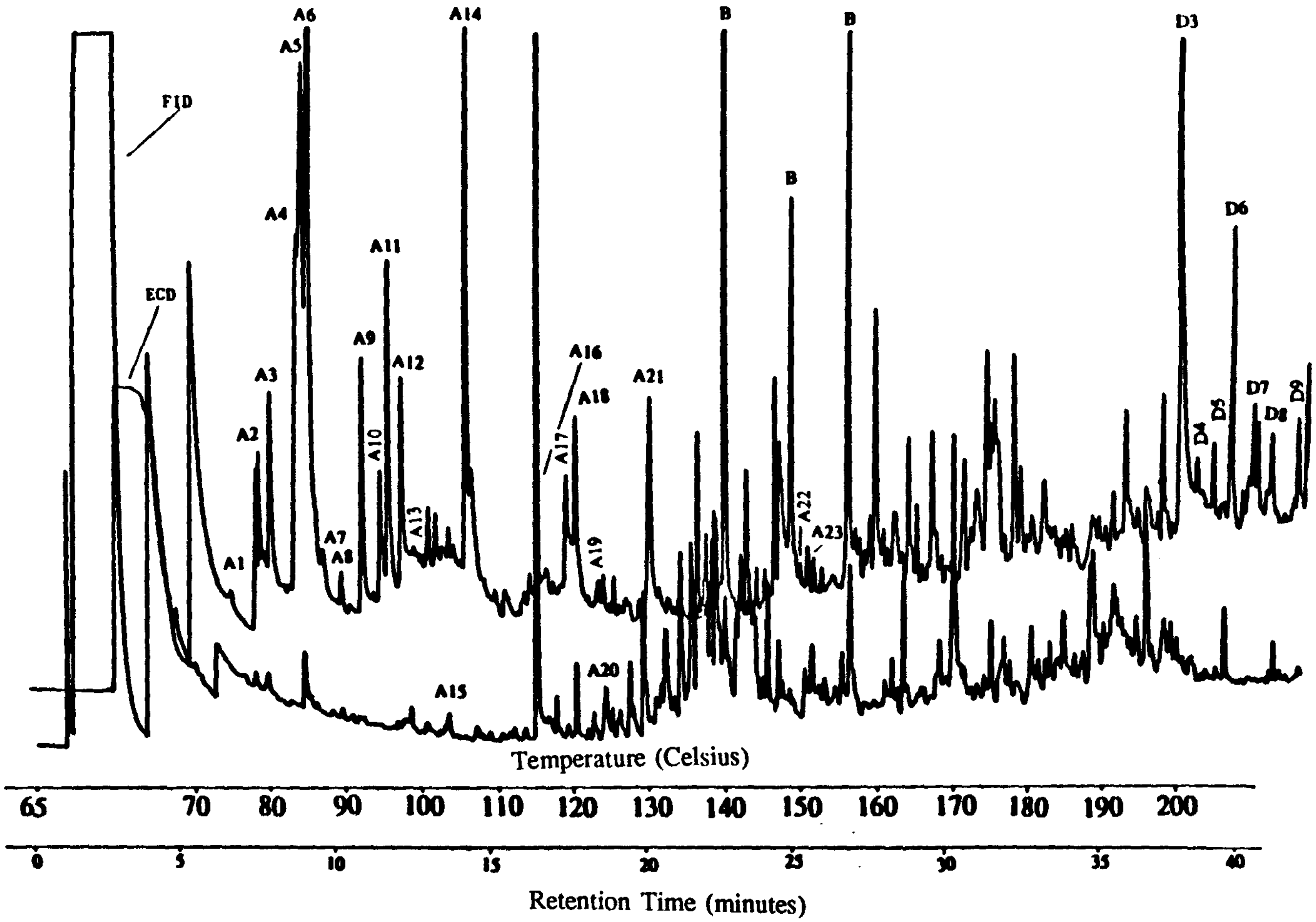


Fig. 18: GC of the San Diego Wastewater Treatment Plant chlorinated final effluent. GC conditions as specified in analytical procedures. Axes are labeled for the ECD. Compound ID in Table 14.

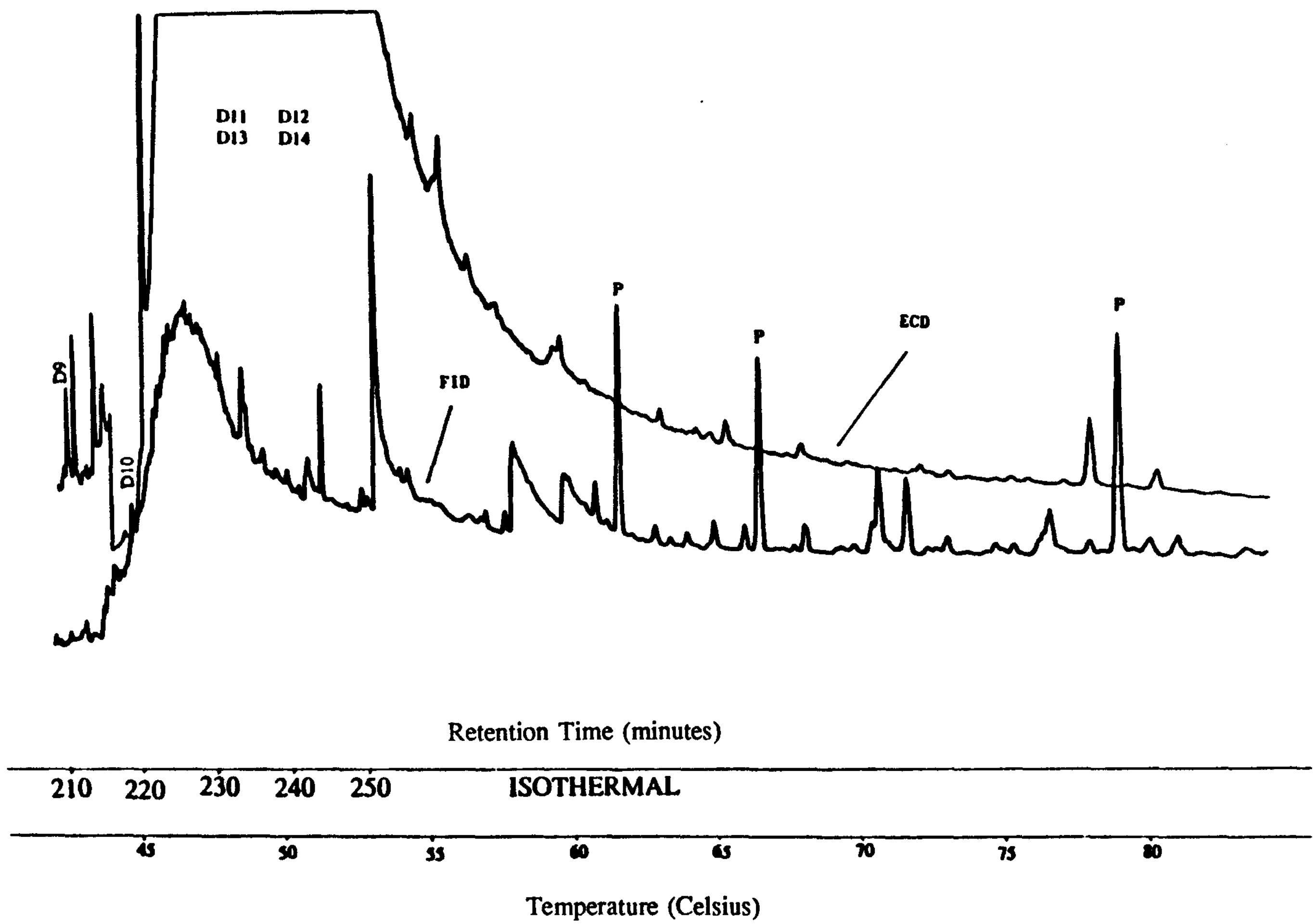


Fig. 18 (Continued)

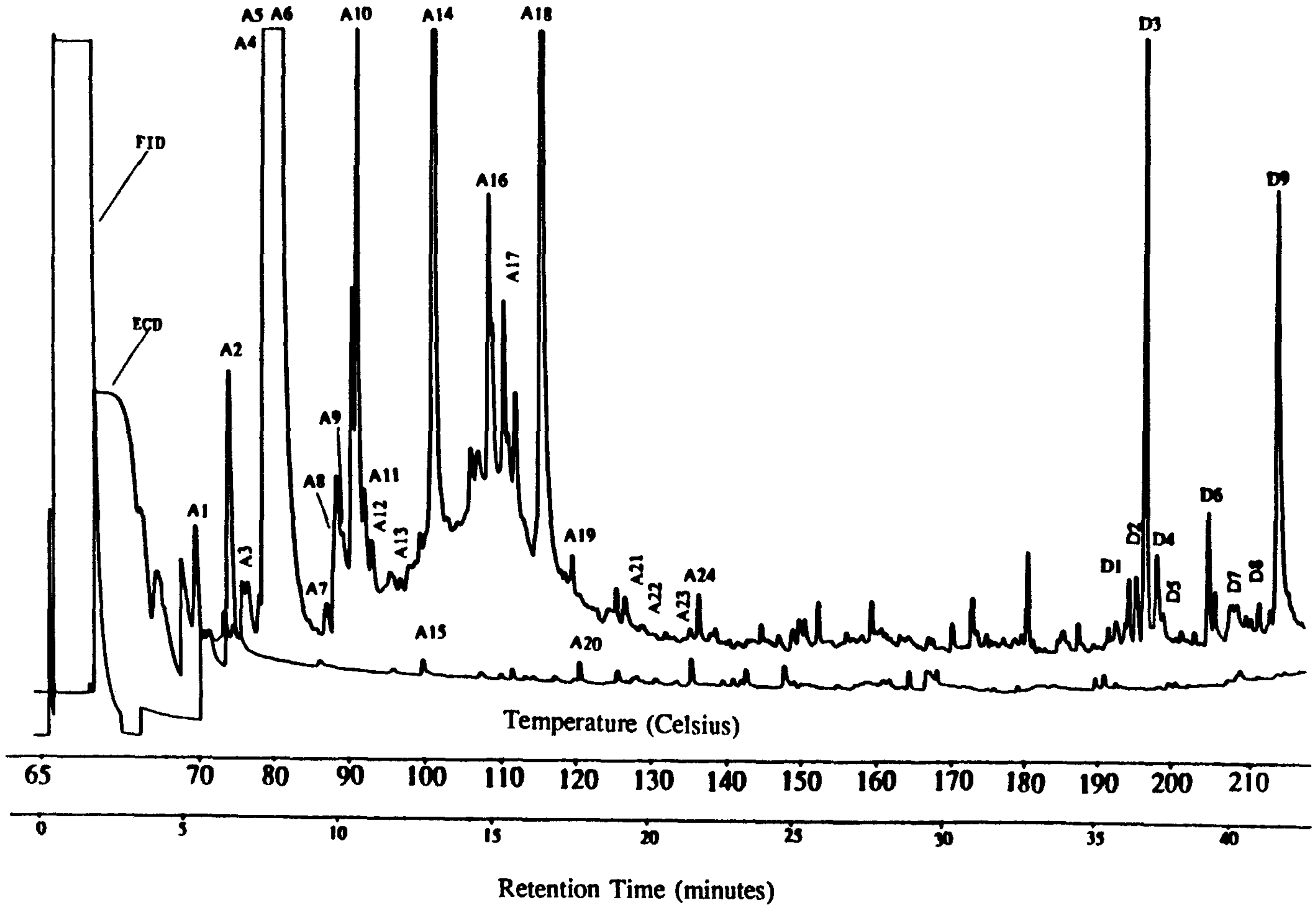


Fig. 19: GC of chlorinated XAD8 aquaculture extract. Chlorination conditions: 1 mg TOC, 10 mg chlorine, pH 7, contact time 2 hours. GC conditions as previously specified. Axes are labeled for the ECD. Compound ID in Table 14.

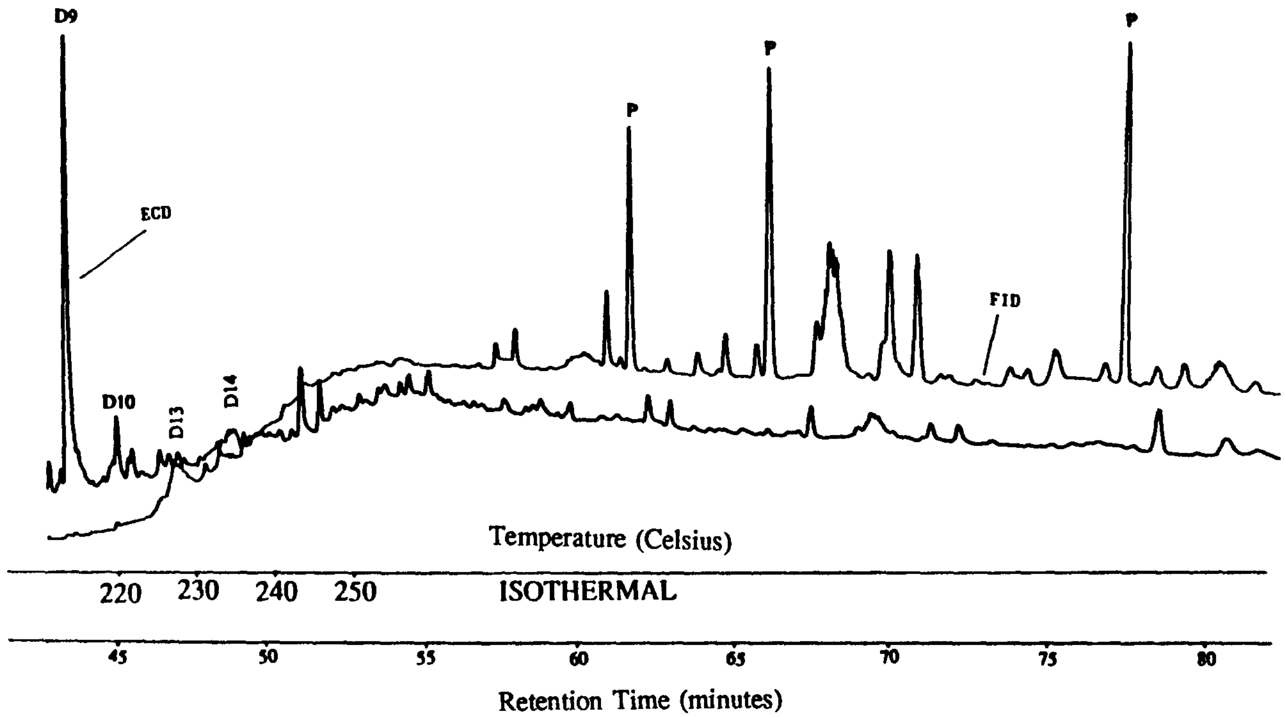


Fig. 19 (Continued)

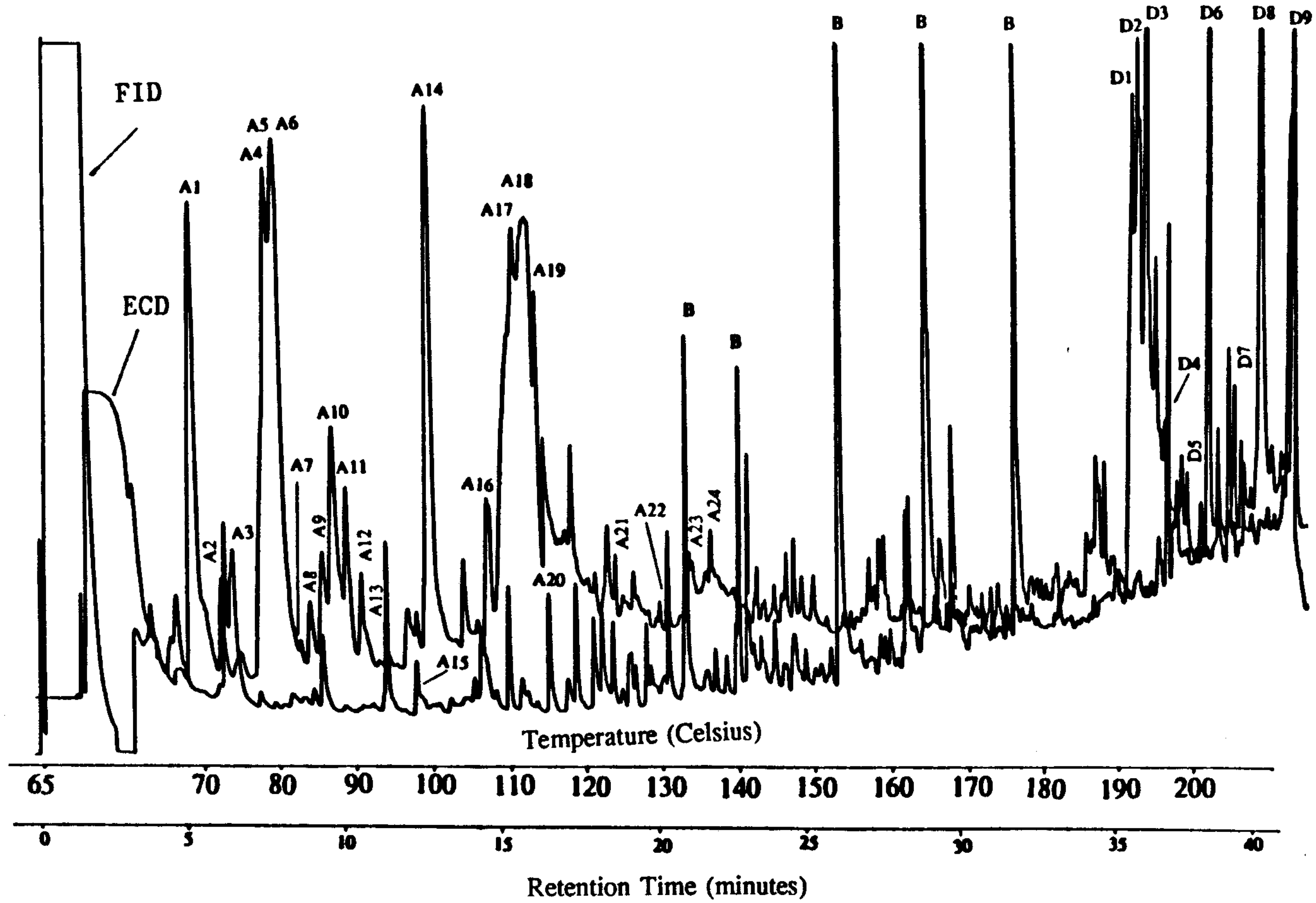


Fig. 20: GC of chlorinated XAD8 aquaculture extract. Chlorination conditions: 30 mg TOC, 30 mg chlorine, pH 7, contact time 2 hours. GC conditions as previously specified. Axes are labeled for the ECD. Compound ID in Table 14.

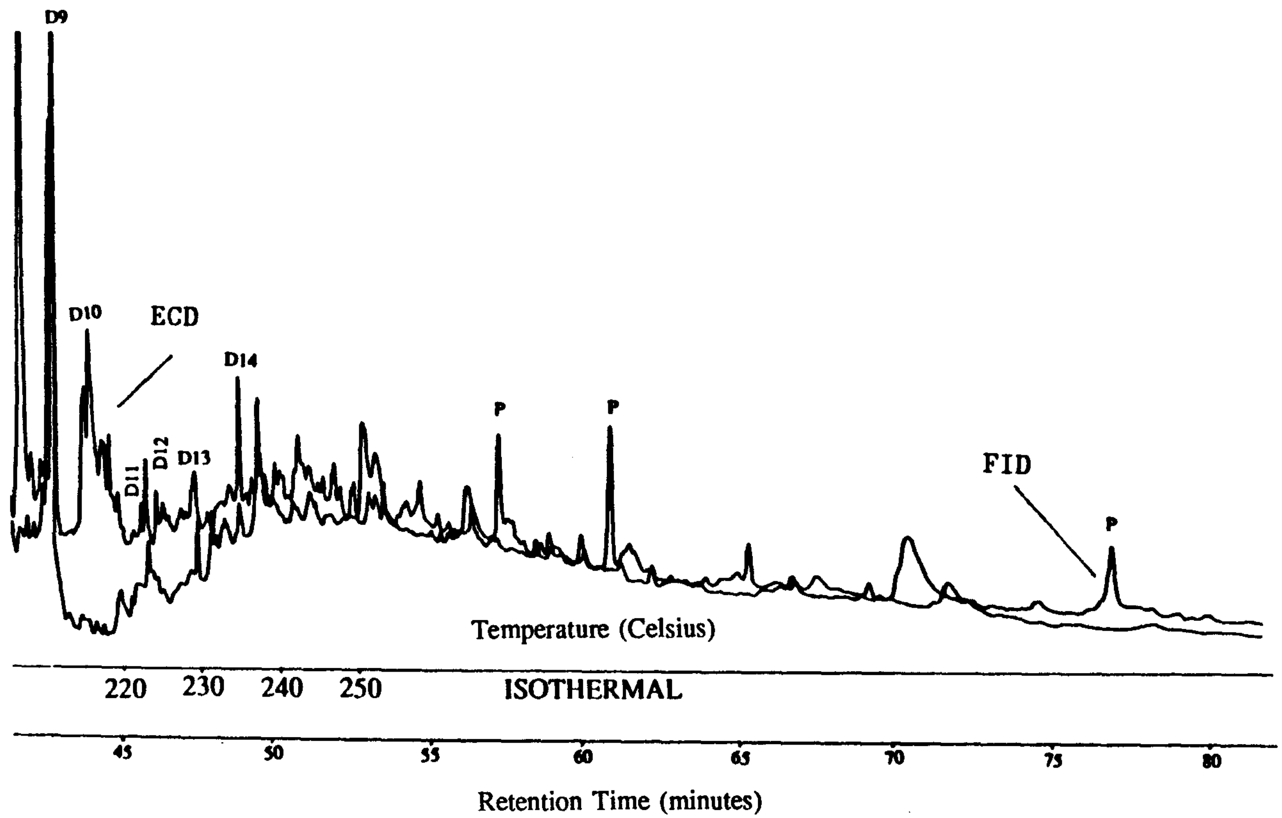


Fig. 20 (Continued)

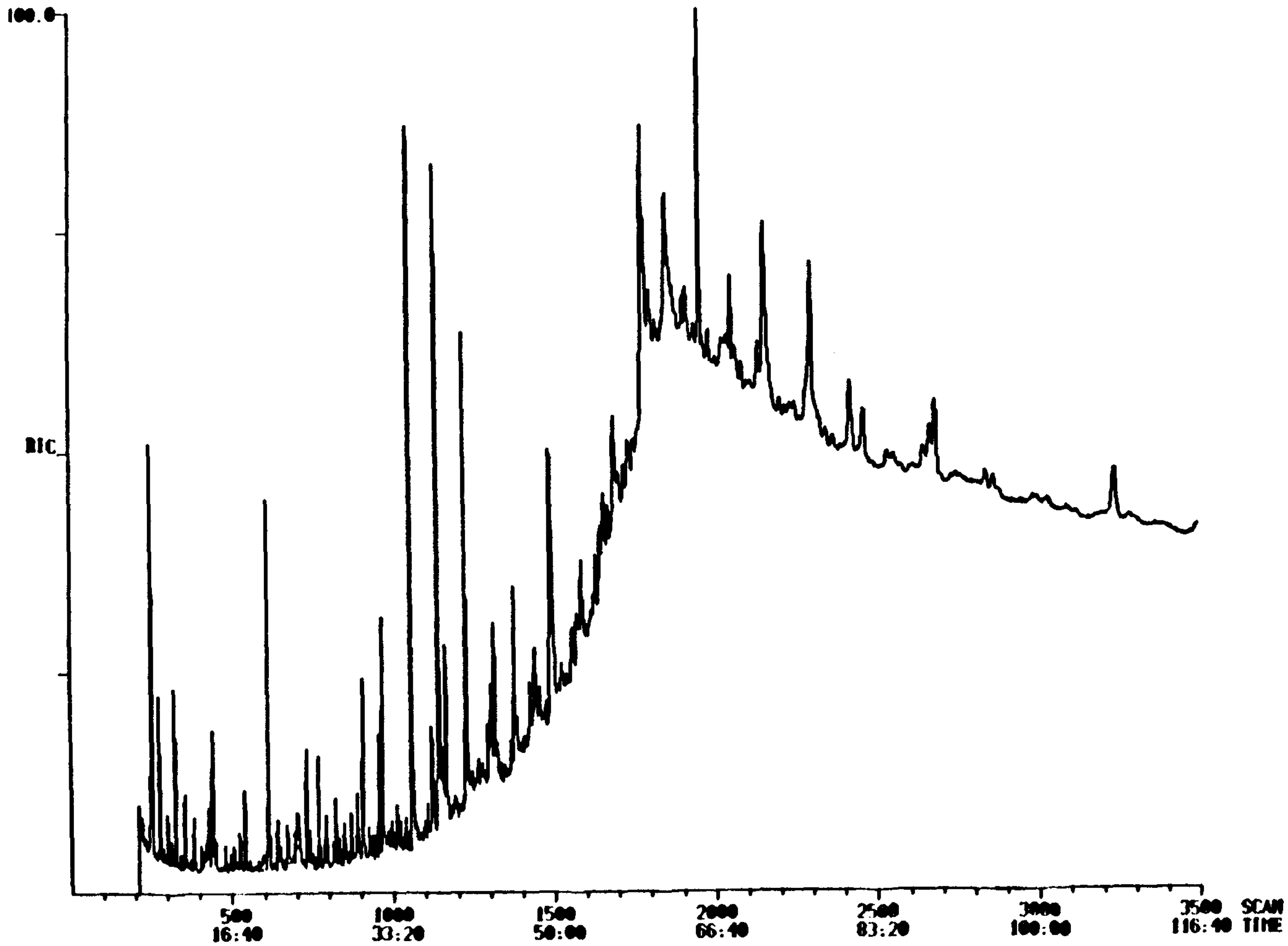


Fig. 21 Reconstructed GC/MS of Chlorinated XAD8 Aquaculture Extract

3. PRECURSORS TO THE OBSERVED NVCO

Several experiments were performed in order to ascertain the nature of the precursors to the observed NVCO. It was assumed that the precursors to the NVCO are present in the aquaculture effluent. This assumption 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 would consequently reduce the required volume of water from which to collect the precursors.

The identification procedure involved laboratory chlorination of various fractions of organic compounds from the aquaculture effluent and comparison of the resultant chromatographs with the chromatographs of the San Diego chlorinated plant effluent. Production of the halogenated organics found in the plant's final effluent, upon laboratory chlorination of a certain fraction, implies that the precursors are present in that particular fraction.

Several different fractionation schemes were used in order 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 18. (chlorinated San Diego effluent). 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 which could likely be present in the aquaculture effluent. The GC outputs from this pure compound chlorination experiment were also compared to Figure 18. The nine performed experiments are listed in Table 15 and will each be discussed separately in this chapter.

Table 15

Experiments to Fractionate the Precursors

Experiment	Description
3.1	Chlorination of XAD8 extract
3.2	Chlorination of CH_2Cl_2 total and silica gel fractions
3.3	Solvent extraction vs. XAD8 adsorption for precursors collection
3.4	Chlorination of organic solvent fractions eluted from XAD8 columns
3.5	Chlorination of humic/fulvic fractions
3.6	Chlorination of 2 pH eluates from XAD8 columns
3.7	Chlorination of ultrafilter separated fractions
3.8	Chlorination of fractions from other treatment plants.
3.9	Chlorination of pure compounds

The experiments described in Table 15 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, as well as suggests the exact nature of the precursors.

3.1 Chlorination of XAD8 Extracts from the Aquaculture Effluent

It was initially conjectured that humic and fulvic acids are the major precursors to the observed halogenated organics. Thurman and Malcolm

(1981) had shown that XAD8 resins are effective in the concentration of these natural acids. Several other workers had shown that chlorinated XAD8 extracts yield an abundance of halogenated compounds (Miller 1983, Quimby 1980). XAD8 resin was consequently chosen to concentrate these precursor compounds from the aquaculture effluent. It should be carefully noted however, that XAD8 resin is fully capable of adsorbing a host of compounds in the water and that humic and fulvic acids are a only small fraction of the different adsorbed organics (Junk 1974, Shinohara 1981).

The carbon adsorption effluent prior to chlorination at the San Diego treatment plant typically has a TOC of 0.5 to 1.0 mg/L. It was consequently decided that the laboratory chlorination be performed with 1.0 mg TOC of XAD8 extract. Figures 18, 19 and 20 have already shown that chlorination of the XAD8 extracts reproduces most of the halogenated compounds seen at the San Diego plant. Figure 22 shows that the produced quantities (total ECD peak areas) in the plant's chlorinated effluent and the laboratory chlorinated extracts are also very similar. This demonstrates that the choice of 1.0 mg XAD8 extract and 2.5 mg chlorine is a good simulation of actual plant conditions.

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

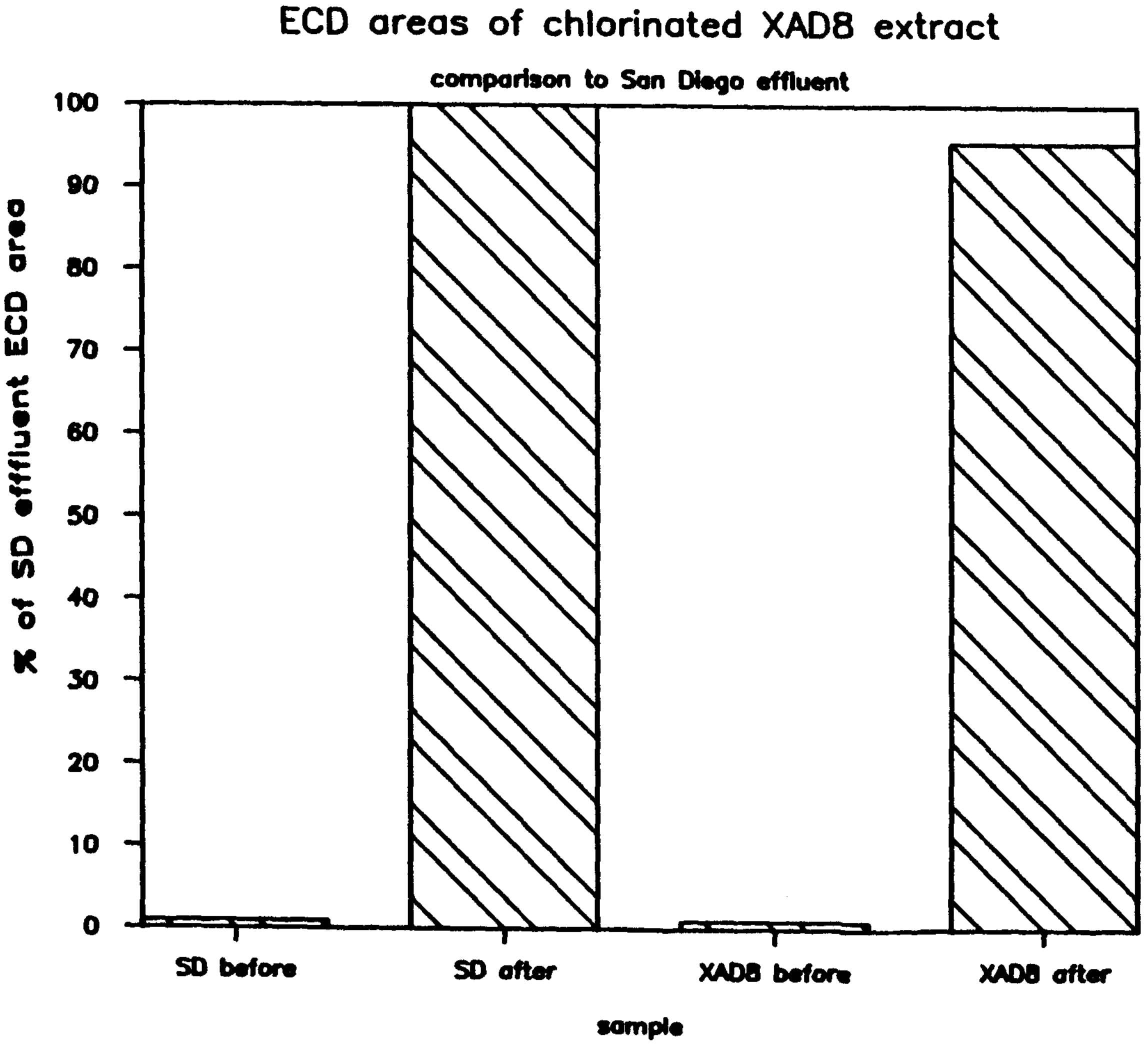


Fig. 22: Comparison of the total chlorination by-product ECD areas of chlorinated XAD8 aquaculture extract and the San Diego Wastewater Treatment Plant final effluent. Before = before chlorination, After = after chlorination.

3.2 Laboratory Chlorination of CH_2Cl_2 Extracts

Total methylene chloride extractable organics from the aquaculture effluent, as well as the silica gel fractionated extract (see analytical procedures for details) were redissolved in distilled Arrowhead brand water and chlorinated as concentrated fifteen milliliter solutions. 1.5 mg (by weight) of aquaculture extract was used and a chlorine dose of 2.5 mg was applied at pH 7 and a two hour contact period. Figure 23 is a schematic of the experimental procedure.

The resultant chromatographs were compared to Figure 18 (chlorinated San Diego effluent). The chlorinated total extract, as well as the chlorinated third fraction (methanol:methylene chloride elutable) gave very similar chlorination patterns to Figure 18. Fraction 1 (hexane eluate) and fraction 2 (benzene eluate) were basically not affected by the addition of chlorine.

Figure 24 shows that 66% of the increased ECD total area brought about from chlorination of the total extract was due to the compounds present in the third fraction. 30% of the increased ECD area in the total extract could not be accounted for in the three collected fractions. It was consequently assumed that compounds which were non-elutable (labeled NEP in Figure 24) from the silica gel column were responsible for the difference.

The results from this experiment point out that the precursors are polar (third fraction and NEP fraction) compounds. This conclusion concurs with the results of Section 3.1. Much more significant, however, is the observation that the precursors are solvent extractable. This implies that they are only moderately polar, since if they were very polar, they would not be solvent

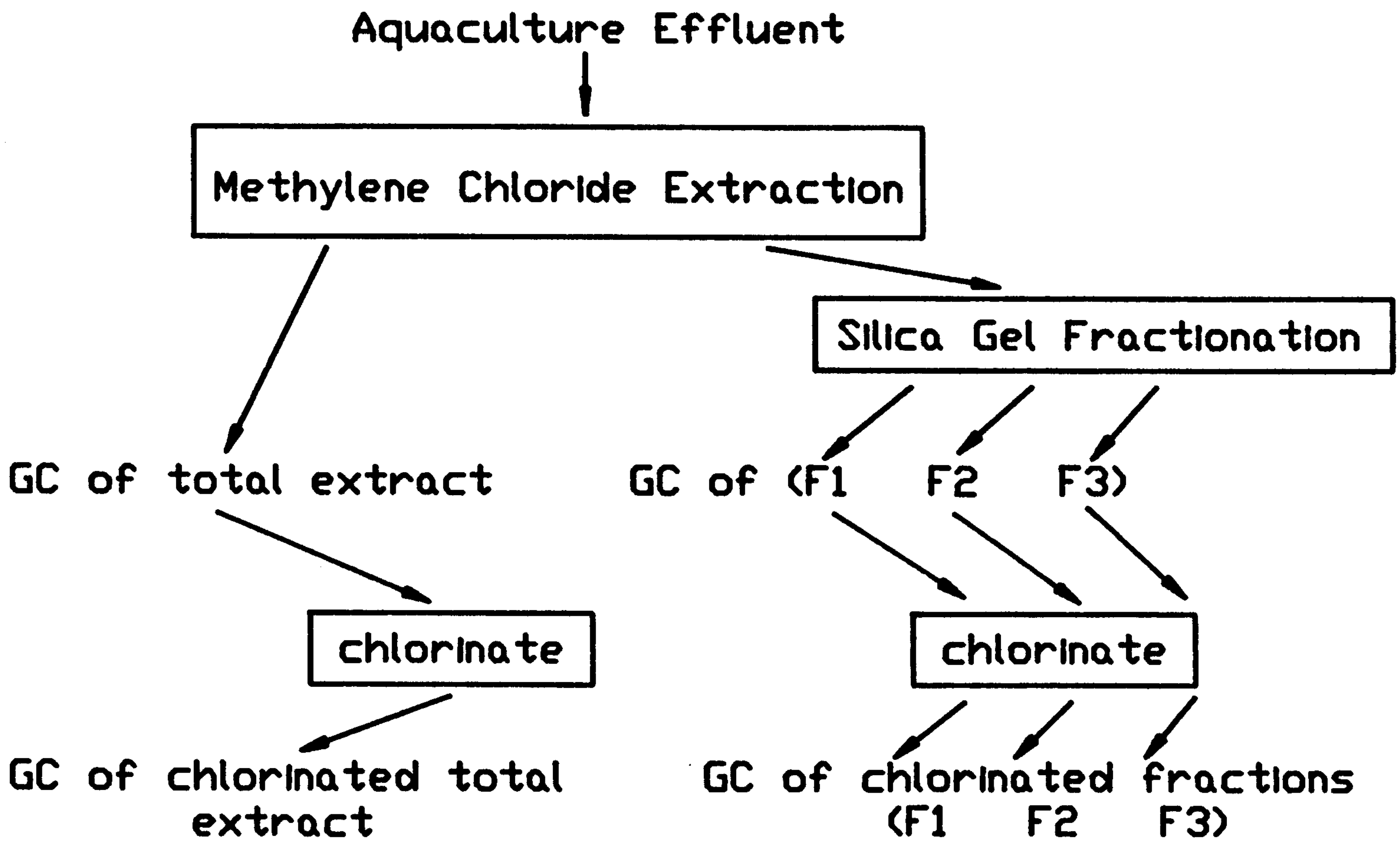


Fig. 23 Fractionation Scheme of the Chlorinated Methylene Chloride Extracts

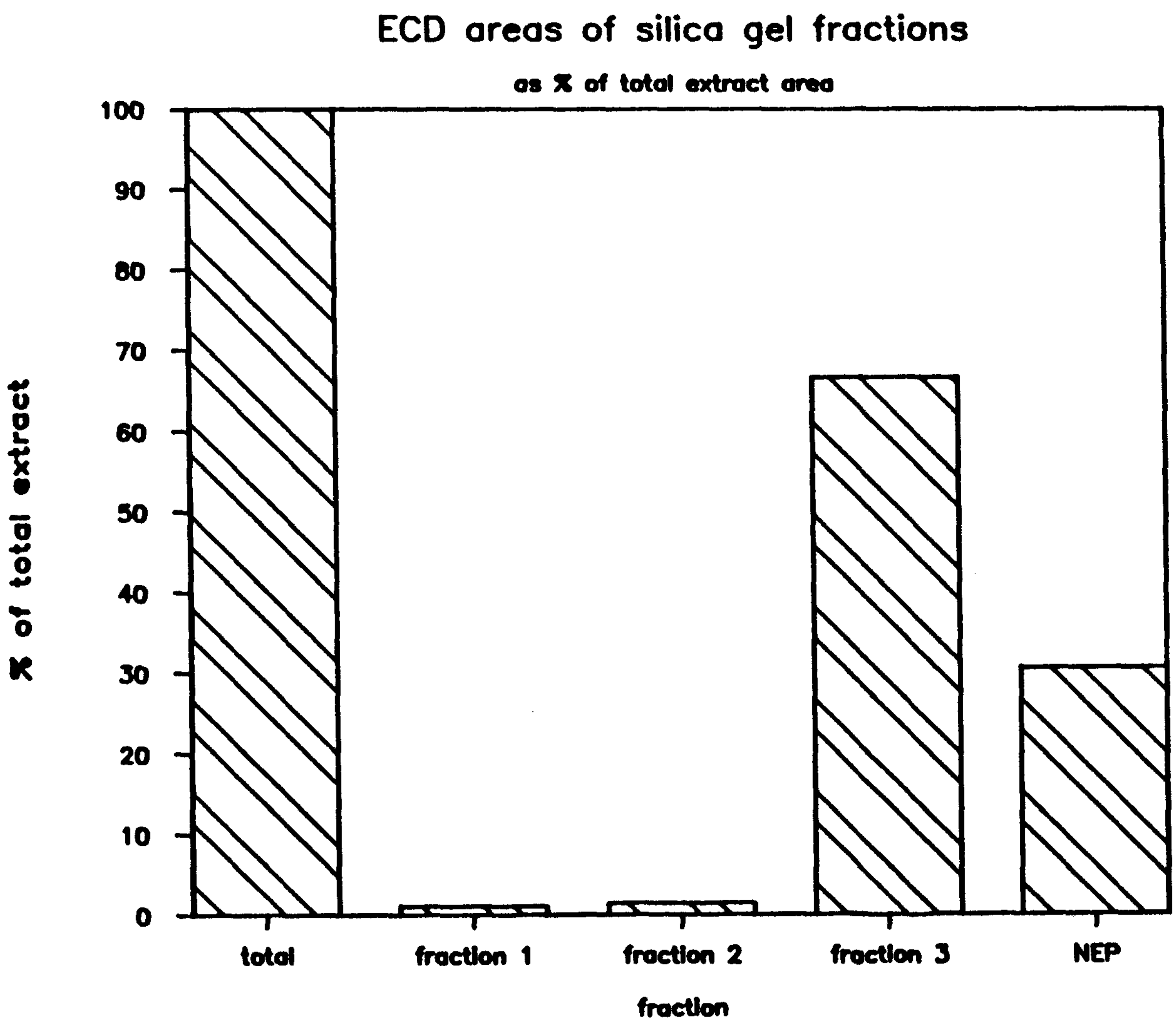


Fig. 24: Total ECD areas of the chlorinated silica gel fractions as a percent of the total extract ECD area. Fraction 1 = hexane eluate, fraction 2 = benzene eluate, fraction 3 = CH_2CL_2: MeOH eluate, NEP = non-elutable polars.

extractable. Although this observation is highly qualitative it is also highly significant. Humic and fulvic acids are generally not considered to be solvent extractable. Indirectly, therefore, this experiment implies that the precursors do not fit the classic definitions of humic and fulvic acids.

3.3 Solvent Extraction vs. XAD8 Adsorption for Precursors Collection

The experiments discussed in Sections 3.1 and 3.2 indicate that the precursors to the observed NVCO can be collected by either XAD8 resin adsorption or by methylene chloride extraction. A simple experiment was designed in order to verify which method is more efficient for the collection of the alleged precursors.

Two one liter samples of reverse osmosis effluent were chlorinated in the laboratory with 10 mg/L NaOCl at pH 7 for two 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. The resultant total ECD areas from each set of samples were then compared.

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

3.4 Chlorination of Organic Solvent Eluted Fractions from XAD8 Columns

In an effort to better understand the solubility properties of the precursors the following experiment was performed. Sixteen liters of aquaculture effluent were adsorbed to a cleaned XAD8 column at pH 2. The adsorbed organics were then 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 .1 N NaOH.

Each fraction was analyzed by GC before and after chlorination with 10 mg/L NaOCl at pH 7 for two hours. As would be expected many of the solvent extractable compounds present in the aquaculture effluent were collected by XAD8 adsorption and appeared in both the ether and methylene chloride fractions. The ether and methylene chloride fractions consequently contained background organics which gave a sizeable ECD response. These compounds are not usually collected in the routinely used XAD8 adsorption procedure because the XAD8 adsorbed organics are normally only collected with .1 N NaOH and these gas chromatographable compounds are not elutable with this alkaline solution.

No effort was made to translate the ECD total areas into concentrations, since the desired results are discernible by comparison of the raw total area values. Table 16 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).

Table 16 Organic Solvent Fractionated XAD8 Extract

Fraction Number	Solvent	Total ECD Area before Chlorine Addition	Total ECD Area after Chlorine Addition	Net Increase in total ECD area due to Chlorine
1	Ether	$3.38 x 10^7$	$3.22 x 10^8$	$285 x 10^6$
2	CH_2Cl_2	$5.73 x 10^7$	$1.53 x 10^8$	$147 x 10^6$
3	Methanol	$2.54 x 10^6$	$7.61 x 10^7$	$73 x 10^6$
4	.1 N NaOH	$5.83 x 10^5$	$2.32 x 10^6$	$2 x 10^6$

The precursors to the observed gas chromatographable NVCO 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 since 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 .1N NaOH (the usual XAD8 desorption protocol) since the background chromatographable compounds are not collected with the sodium hydroxide solution.

3.5 Chlorination of Humic/Fulvic Fractions

The procedure used in this work to collect XAD8 adsorbable organics with .1N NaOH is an abbreviated version of a procedure developed by Thurman and Malcolm (1981) to extract humic and fulvic acids. Thurman and Malcolm further separate the extract into a humic and a fulvic fraction by centrifugation at pH 1. The soluble fraction is fulvic acid and the residue is labeled the humic fraction.

This additional separation step (humic/fulvic split) was performed in order to be able to compare results from this work with the findings of others. The humic and fulvic fractions were analyzed by gas chromatography before and after chlorination with 10 mg NaOCl at pH 7 for two hours. The total ECD response was compared with the unfractionated sample (no humic/fulvic split).

Figure 25 illustrates that the fraction labeled fulvic acids is fifteen times more productive than the humic fraction. 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 can be attributed to experimental error.

The results of this experiment conclusively demonstrate that humic acid is not the major precursor to the observed NVCO. The precursors are present in the fraction which Malcolm and Thurman, as well as numerous other workers have labeled fulvic acids. It should be stressed that hundreds of compounds can be collected in this fraction. Operationally, this fraction contains acidic compounds which 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 (Sections 3.2, 3.3, and 3.4) and classically, fulvic acids are only water (low and high pH) soluble.

3.6 Chlorination of Two pH Eluates from XAD8 Columns

In a 1979 publication, McCarthy et al. demonstrated that two distinct fractions may be eluted from XAD resins if one varies the pH of the eluant. A similar experiment was attempted in an effort to asses the acidity of the precursors.

Aquaculture effluent was adsorbed onto an XAD8 column at pH 2. The first fraction was eluted at pH 6 and a second fraction was collected at pH 13. Each fraction was subsequently chlorinated at pH 7 with 10 mg chlorine for two hours.

Within experimental error, there appeared to be no quantitative or qualitative differences between the two fractions. It appears that the precursors are partially eluted at pH 6 and that their increased solubility at pH 13 allows for more complete desorption. No definitive conclusions may be reached from this experiment.

3.7 Chlorination of Ultrafiltration Fractions

The XAD8 adsorbed organics from the aquaculture effluent were (40 ml from 2000 ml of concentrated extract collected from 360 liters; TOC of 1 mg/10 ml of concentrated extract) separated into five molecular weight ranges by ultrafiltration (see analytical procedures section for more details). Ten milliliters (one 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

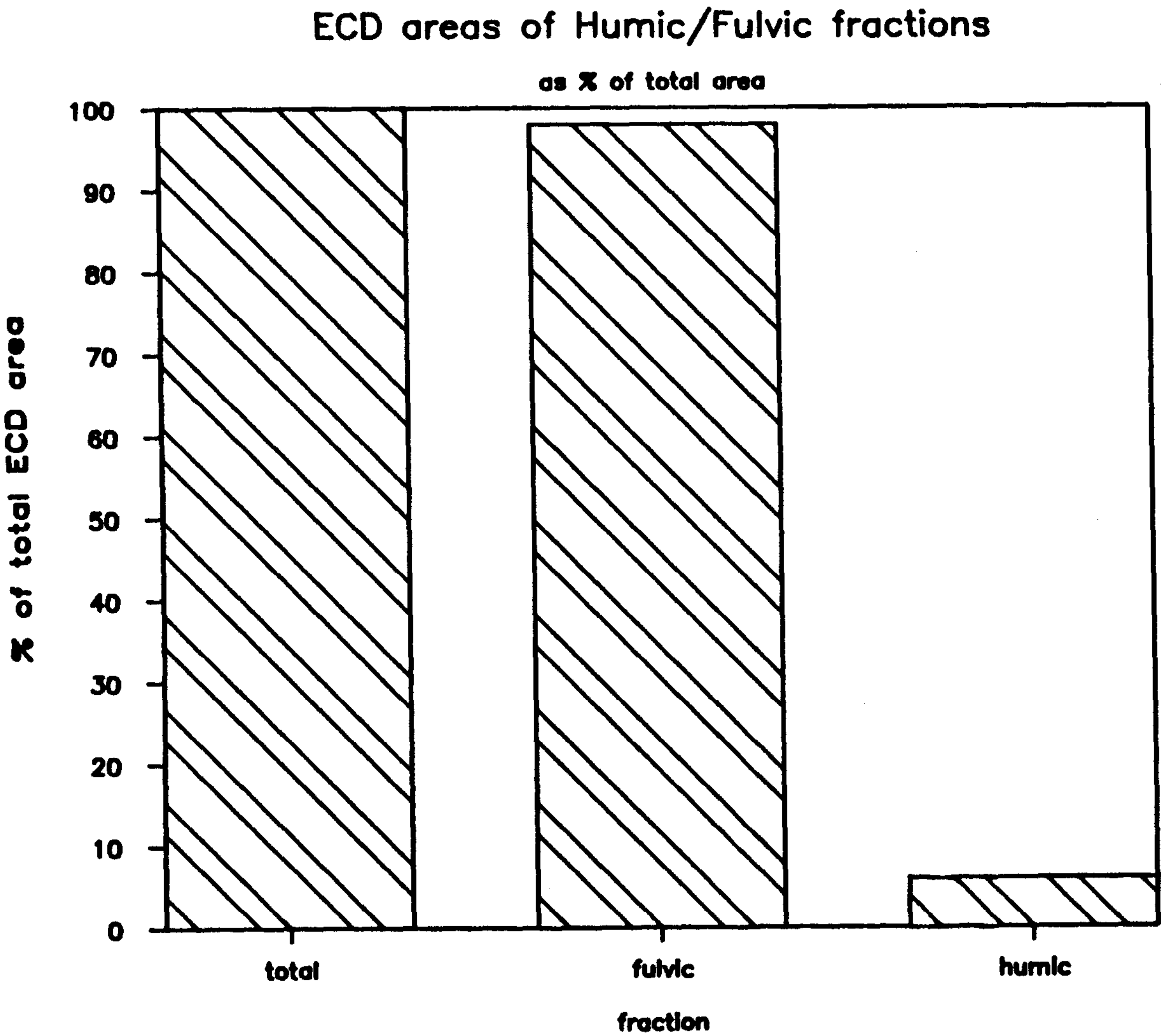


Fig. 25: Total ECD areas of chlorinated humic/fulvic fractions as a percent of the total extract ECD area.

consequently chlorinated with a dose of 10 mg chlorine at pH 7 for two hours before extraction. 30 ml of the less than 1,000 MW fraction was chlorinated under the same conditions. Thirty milliliters was 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.

Table 17 summarizes the experimental results. Figure 26 is a bar graph showing the total ECD area attributable to chlorination from each fraction. The unchlorinated fractions gave virtually no ECD peaks. It is quite clear that the NVCO precursors are predominantly present in the less than 1,000 MW fraction. No effort was made to translate total ECD areas into concentration because only a relative comparison between the fractions is desired. The sum of the total ECD areas for the five fractions is slightly greater than the area of the unfractionated extract (103%), but lies within experimental error.

3.8 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 of the two chosen plants used activated sludge secondary treatment (Whittier Narrows Wastewater Treatment Plant in Whittier, California), while the other plant, located in Florida, used water hyacinth fields for secondary treatment.

Table 17 Untrafilter Fractionated XAD8 Extract

Fraction	Total ECD Area No. 1 (x 10^{-7})	Total ECD Area No. 2 (x 10^{-7})	Average Total ECD Area x 10^{-7})
> 100K	0.28	0.22	0.25
100-30 K	0.26	0.14	0.20
30-10 K	0.18	0.21	0.20
10-1 K	0.18	0.16	0.17
< 1 K	3.71	4.59	4.15
Total Extract	4.53	5.19	4.86

Key:

> = greater than
< = less than
K = thousand daltons

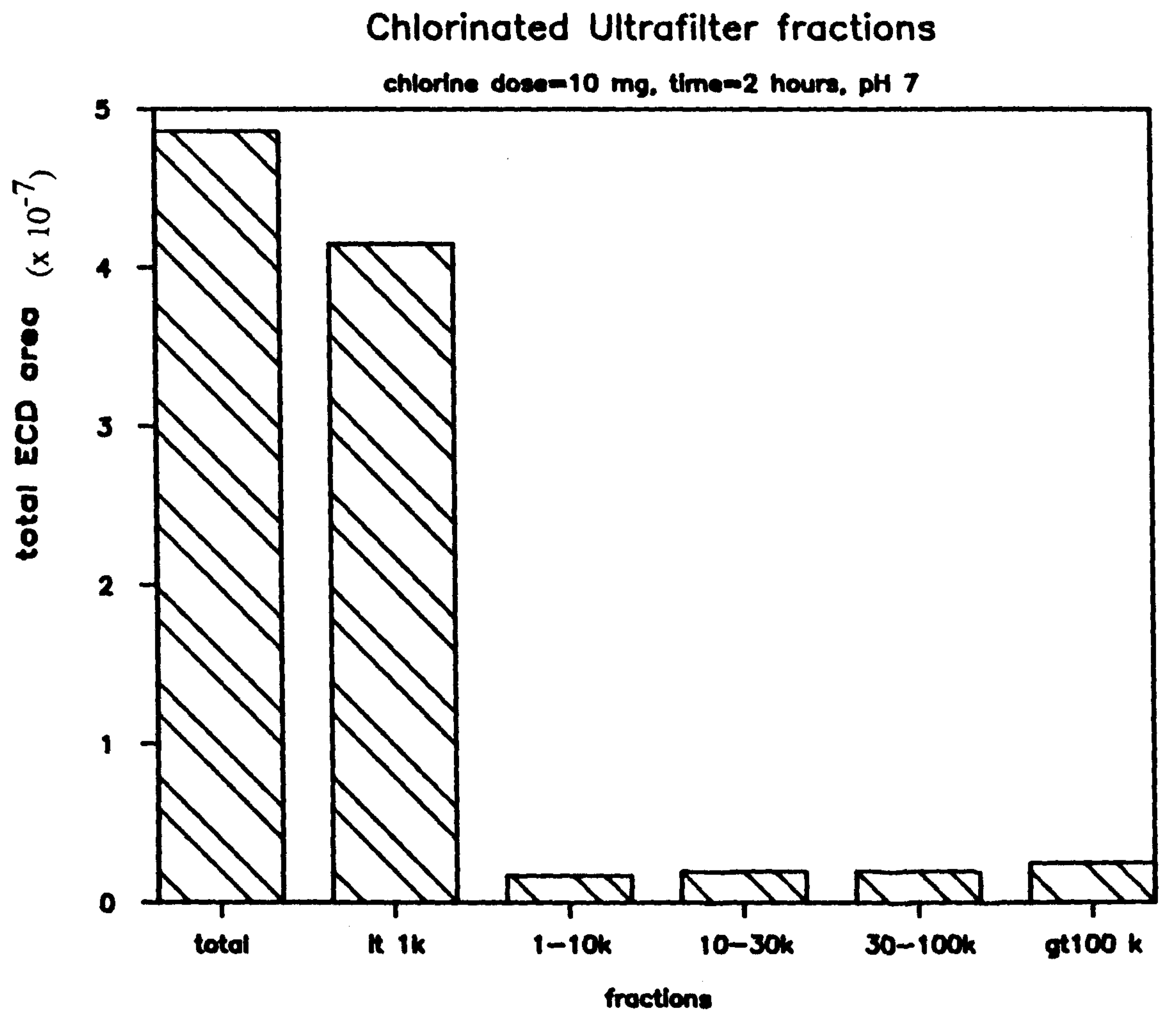


Fig. 26: Total ECD areas of chlorinated UF fractions from the San Diego Wastewater Treatment Plant XAD8 extract. lt = less than, gt = greater than, K = 1000 daltons.

Twenty liters of secondary effluent from each plant was adsorbed onto XAD8 columns at pH 2. The .1 N NaOH eluted extract was next fractionated into 5 molecular weight fractions as previously described. The TOC analyzer was not operational during the time that the experiments were performed. The laboratory chlorinations were consequently done using an unknown quantity of extract. An equivalent amount of extract (based on volume adsorbed and volume of eluate) as that used for the San Diego samples was used in the chlorination experiments to minimize the variability. Since no direct comparisons are made between the NVCO formation potential (NVCOFP) of the extracts from the various plants, the quantity of extract used for each plant is irrelevant. The comparisons made between the various plants are qualitative and merely compare the gas chromatographs. Comparisons of the NVCOFP of each molecular weight fraction for a given plant are also valid since the chlorination conditions are constant for a given treatment plant.

Figure 27 is the GC output for the chlorinated Whittier Narrows XAD8 extract. Figure 28 is the similar output from the water hyacinth treatment plant. A comparison of Figure 19 (chlorinated San Diego plant XAD8 extract) to the Whittier Narrows and the Florida water hyacinth treatment plant extracts immediately shows that the halogenated organics observed in San Diego are also common to the latter two wastewater treatment plants. The axes in Figures 27 and 28 are labeled for the ECD. The FID is slightly offset to the left.

Figures 29 and 30 contrast the total ECD areas attributable to chlorination for the five molecular weight fractions from each treatment plant. Once again the less than 1,000 molecular weight fraction accounts for nearly 85% of the NVCOFP of the total unfractionated extract. The sum of the total areas for the five fractions is not 100% of the ECD area for the unfractionated extract , but lies within reasonable experimental error.

In summary, the two wastewater treatment plants show very similar NVCO profiles upon laboratory chlorination to the San Diego plant. This points out that the NVCO precursors are not unique to the San Diego plant nor to water hyacinth based secondary treatment.

3.9 Chlorination of Pure Compounds

Twenty four pure compounds which 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. Since 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 NVCO formation potential of the chosen classes of compounds.

Although only one mg TOC had been used in the chlorination of the XAD8 extract, it was decided to use larger amounts (usually 5 mg TOC) of the pure compounds in order to increase the detection limits. All chlorinations were done at pH 7 for two hours using approximately 2:1 chlorine:TOC ratios.

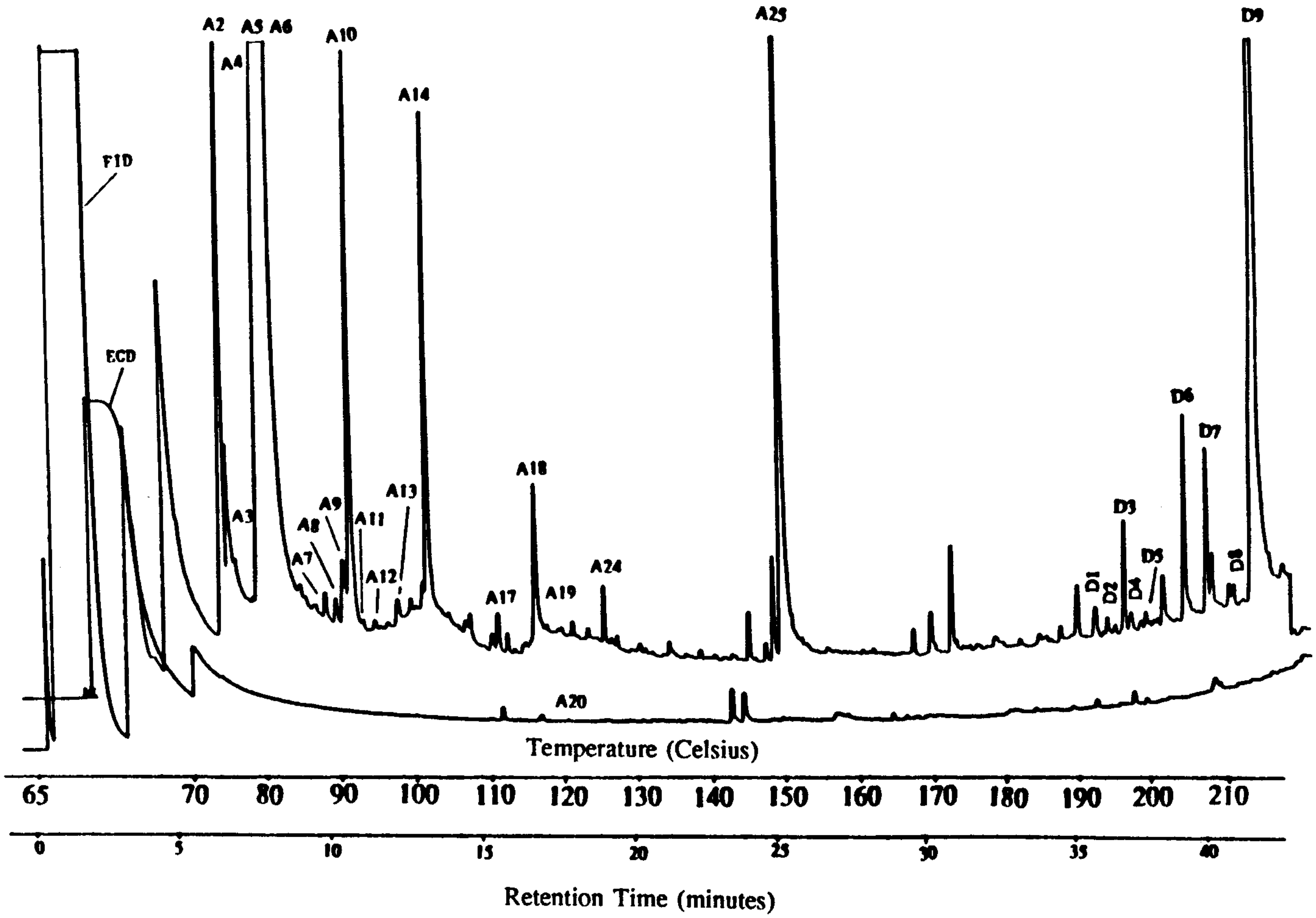


Fig. 27: GC of chlorinated XAD8 extract from Whittier Narrows Wastewater Treatment Plant. GC conditions as previously specified. Axes are labeled for the ECD.

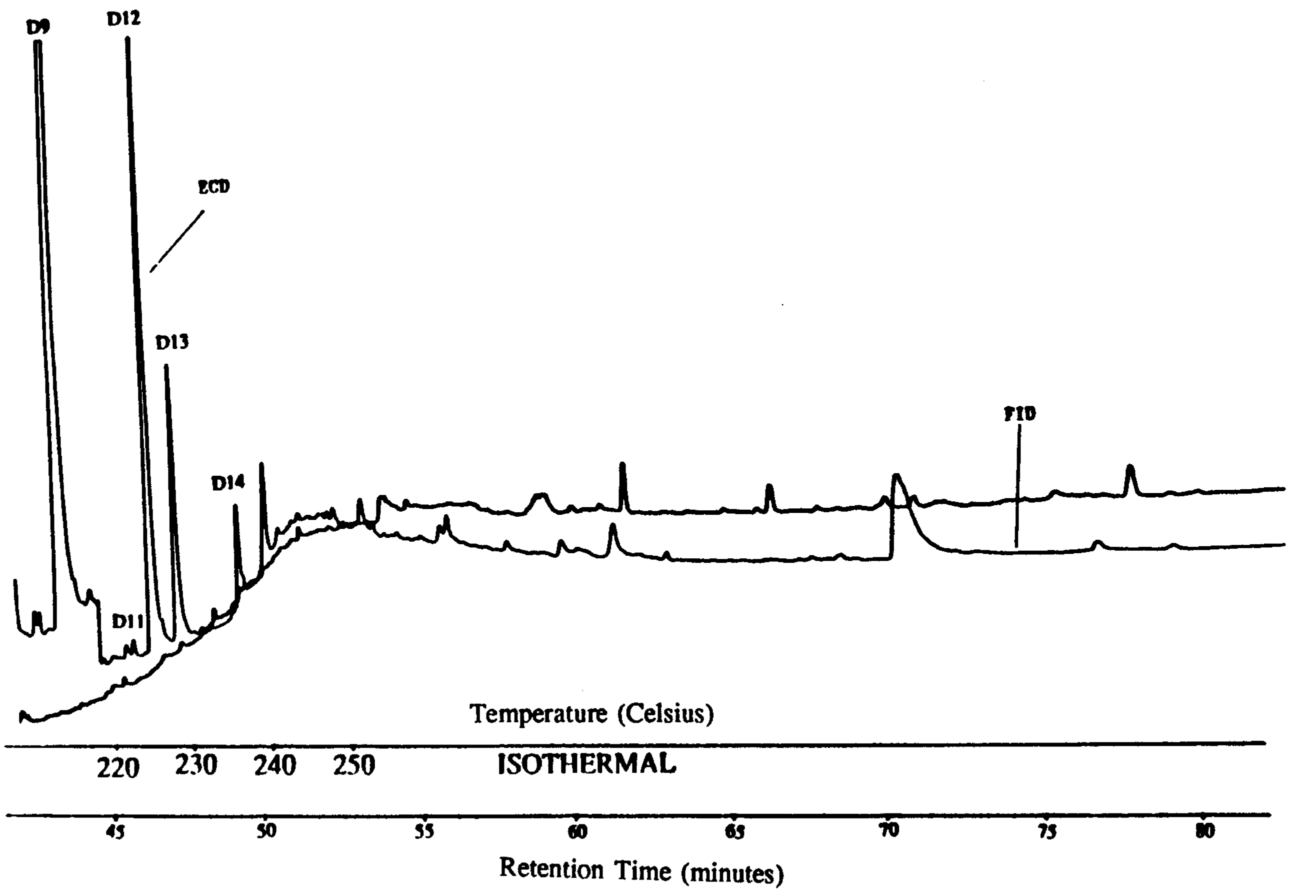


Fig. 27 (Continued)

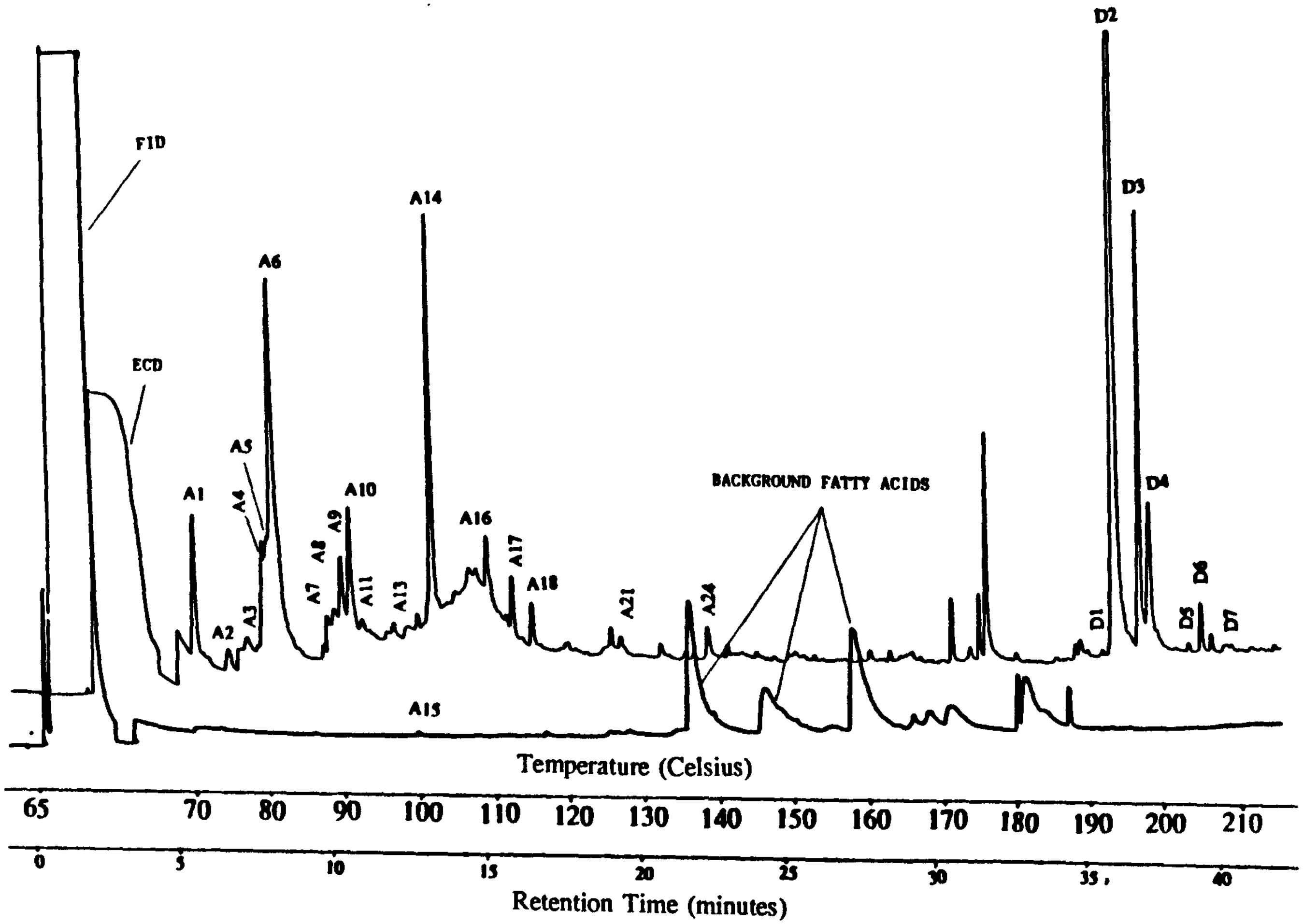


Fig. 28: GC of chlorinated XAD8 extract from the Water Hyacinth Wastewater Treatment Plant. GC conditions as previously specified. Axes are labeled for the ECD. Compound ID in Table 14.

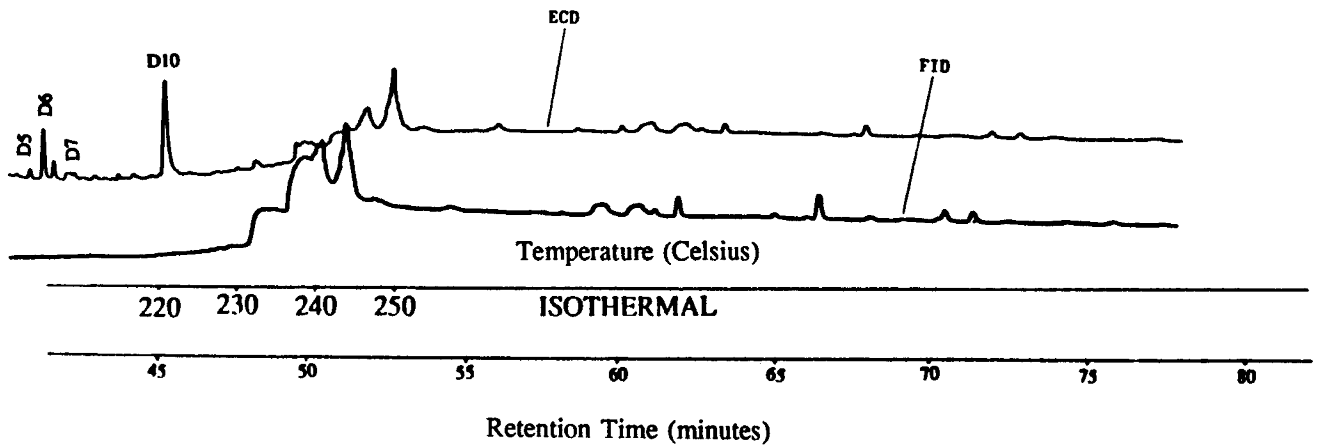


Fig. 28 (Continued)

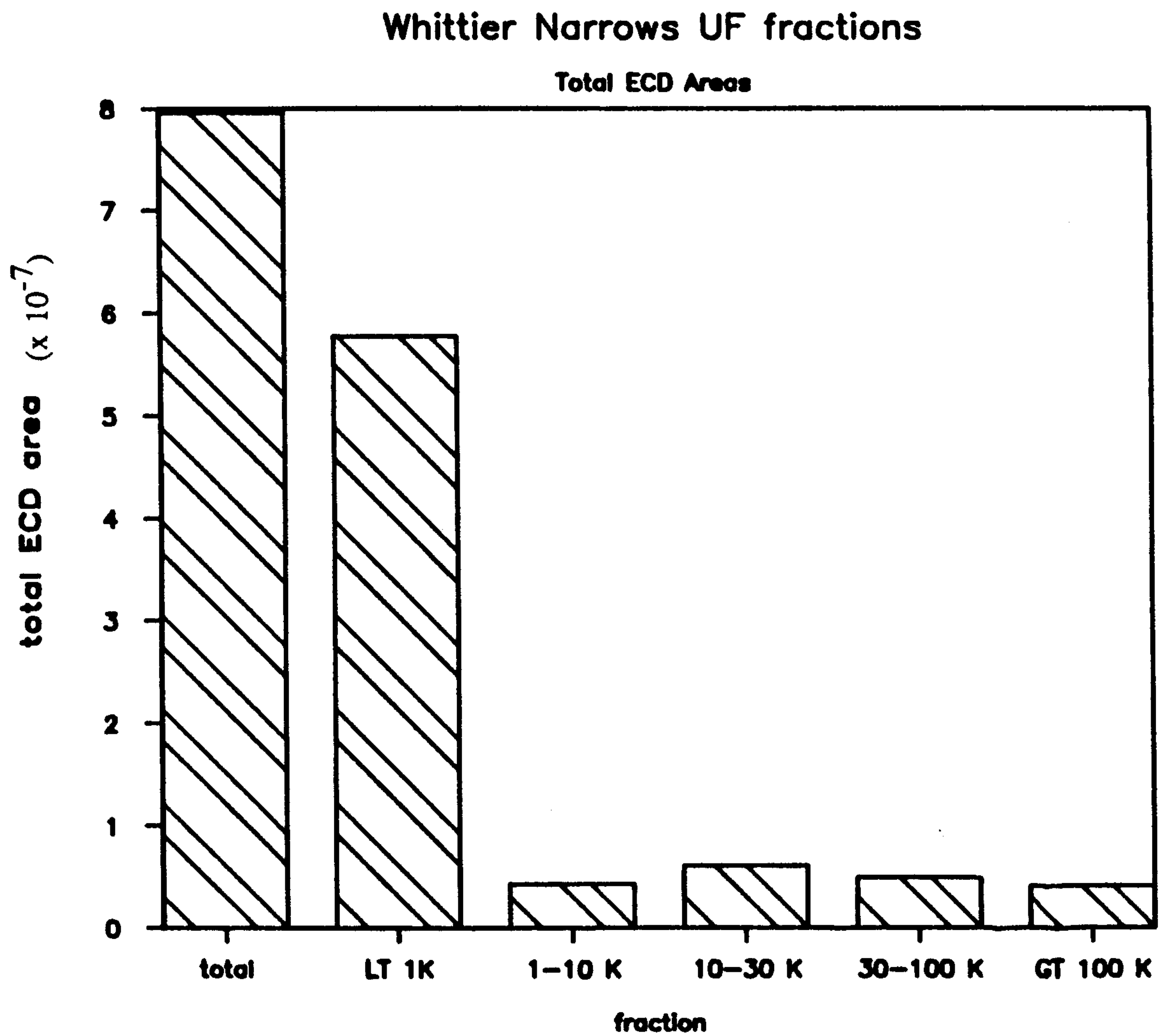


Fig. 29: Total ECD areas of chlorinated UF fractions from the Whittier Narrows Wastewater Treatment Plant. LT = less than, GT = greater than, K = 1000 daltons.

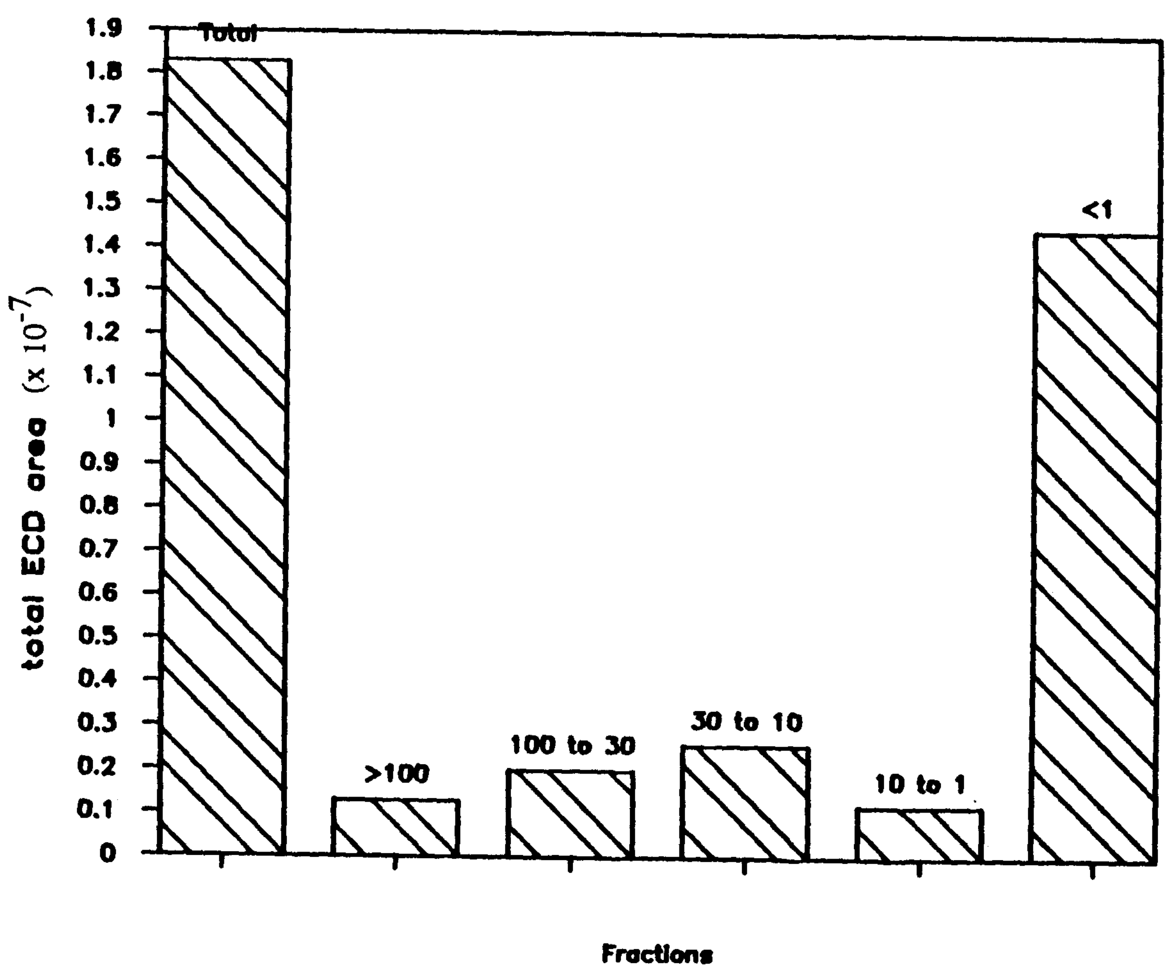


Fig. 30: Total ECD areas of chlorinated UF fractions from the Water Hyacinth Wastewater Treatment Plant. Ranges for 1000 daltons.

All TOC values were calculated theoretically using gravimetric data. In some cases, five mg TOC was not available so a lesser amount was used. Several chlorine doses were used if the chlorination with the 2:1 Cl:TOC ratio was highly productive.

Table 18 lists the compounds which were chlorinated, the class and amount of the compound which was chlorinated, as well as the applied chlorine dose. The reference numbers (see Table 14 for reference numbers) for the NVCO which were produced during chlorination are also included.

Examination of Table 18 points out that carbohydrates, lipids and fatty acids are not likely to be precursors to the observed NVCO. 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. Humic acid purchased form Aldrich Chemical Company was also chlorinated in the laboratory (data not presented in Table 18). The chlorination of 5 mg of humic acid with 10 mg of free chlorine was productive of compounds A1 and D1. The 5 mg (in 15 ml of water) solution, however, was black in color and showed no color resemblance to the aquaculture XAD8 extract (pale yellow color). A 40 mg (by weight) solution of humic acid, chlorinated with 80 mg of chlorine produces several other compounds but again is black in color. In brief, it requires 40 milligrams of this humic acid to form a total ECD response produced by the chlorination of one mg of aquaculture XAD8 extract.

Figure 31 is the GC of chlorinated Morin, a plant flavonol. Flavones and flavonols are the most widely distributed of all the yellow plant pigments, although the deeper yellow colors of plants are normally due to carotenoids. Figure 31 shows resemblance to the chromatographs of the chlorinated aquaculture XAD8 extracts (Figure 19). The axis labeled in Figure 31 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 molecular weight is less than 1000 (typically 220-400). 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 aquaculture extract. In summary, this list of properties closely matches the properties of the precursors in the San Diego XAD8 extract discussed in Sections 3.1-3.8.

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.

The data presented thus far in conjunction with the knowledge that reverse osmosis treatment is much more effective in the treatment of large molecules (humic and fulvic acids) strongly suggests that the precursors bear some structural similarity to these plant pigments. Reinhard (1984) had also stated that in tertiary treated waters, the small MW fractions (less than 1000) are the most important reactants with aqueous chlorine.

Figure 32 shows the molecular structure of flavone and kaempferol. Chlorination of the center puran ring could potentially lead to the formation of compounds D1, D2, D3, and D4. The unsaturated 'A' reference number compounds could result from breakage of either of the unsaturated rings. The chlorophenols could be formed by chlorine addition to either aromatic ring.

In conclusion, the precursors to the observed NVCO are not unequivocally defined. The presented data however, should point out that small, partially organic solvent soluble, non-humic molecules are important chlorination precursors. Plant pigments provide excellent laboratory model chlorination compounds and may quite possibly be the major NVCO precursors.

Table 18 Chlorinated Pure Compounds

Compound Name	mg used (TOC)	mg Chlorine Added	Reference No. of NVCO Produced in Trace[3] Amounts	Reference No of NVCO Produced in Large Amounts	Other Halogenated Compounds Produced[1,2]
			Carbohydrates		
Cellulose	10.2	20.4	NP	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

Table 18 Chlorinated Pure Compounds (Continued)

			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

Key:

1 = Low indicates that the ECD area of the compounds is less than three times the background ECD noise blank level

2 = High indicates compounds are greater than three times background levels

3 = 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

NP = not productive

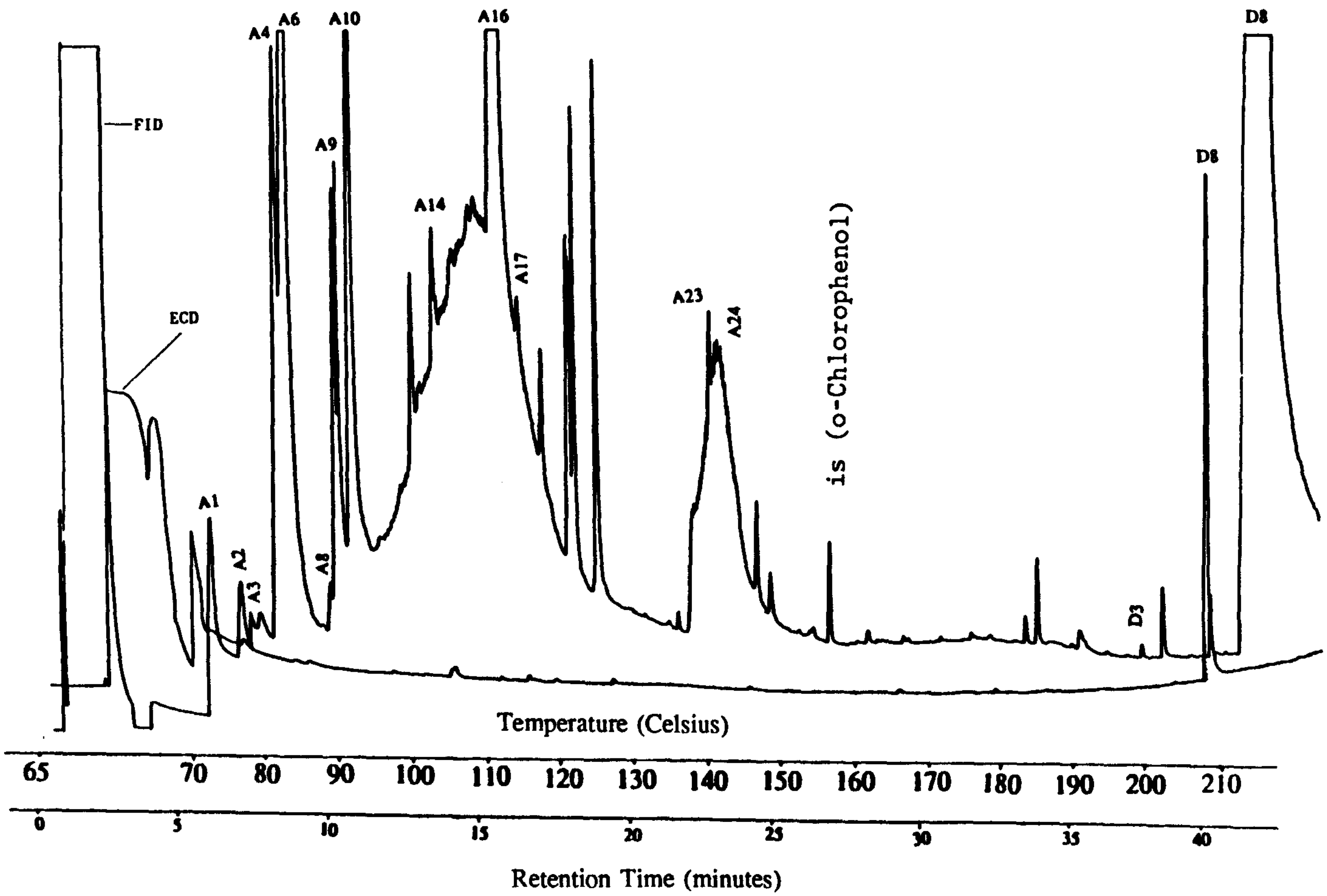


Fig. 31: GC of the breakdown products of chlorinated morin. GC conditions as previously specified. Axes labeled for the ECD. Compound ID in Table 14.

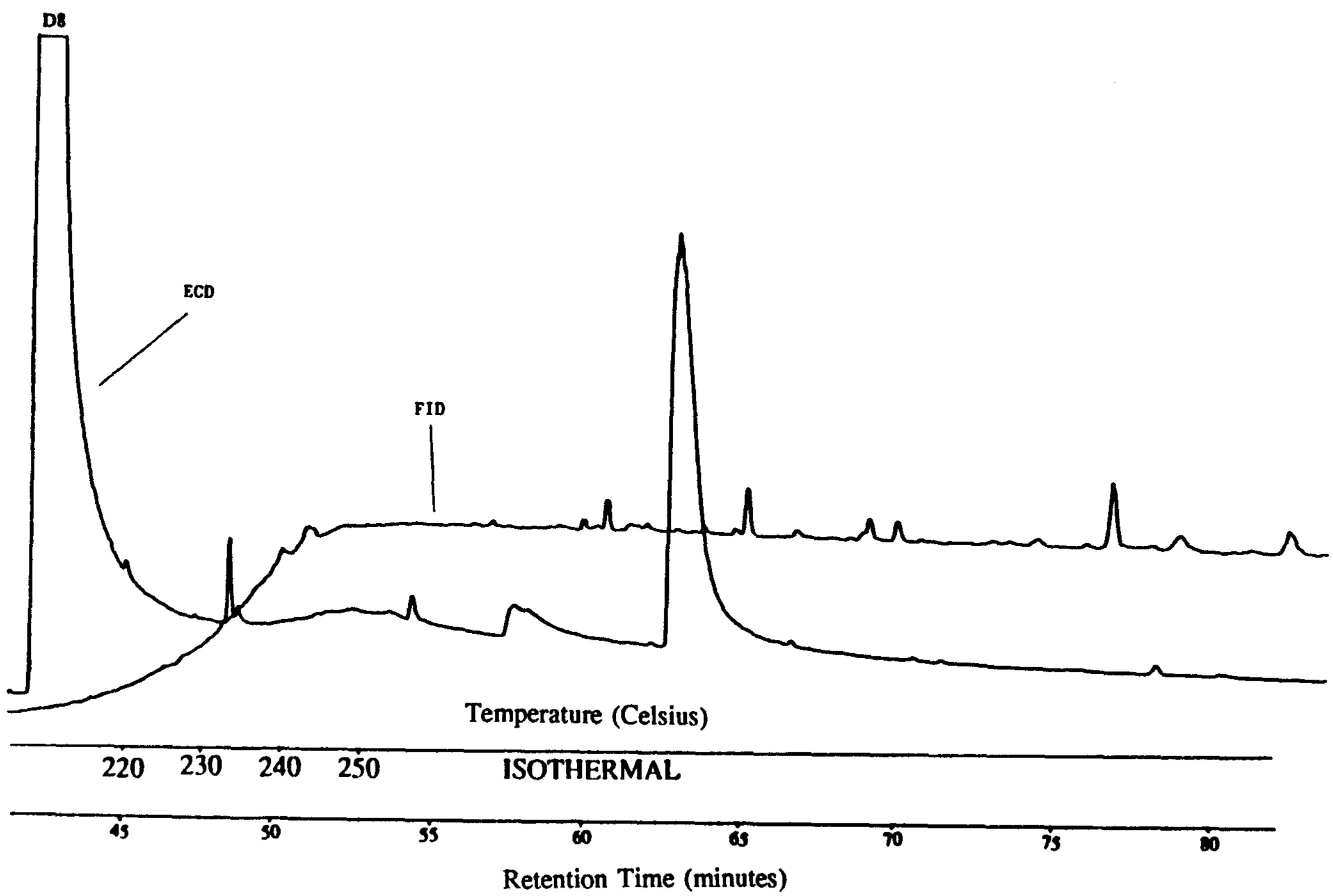
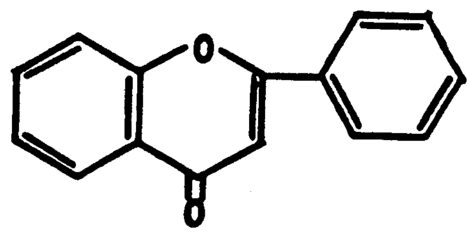
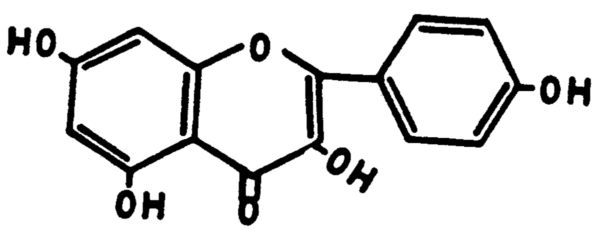


Fig. 31 (Continued)



FLAVONE



KAEMPHEROL

Fig. 32 Molecular Structure of Flavone and Kaempherol

4. EFFECT OF CHLORINATION PARAMETERS ON THE PRODUCTION OF NVCO

Several chlorination parameters were varied in order to assess their effects on the formation of the observed gas chromatographable NVCO. The effects of pH, chlorine dose, contact time and bromide ion concentration were investigated. pH 7, a chlorine dose of 2.5 mg, a two hour contact period, 1.0 mg TOC and 0.0 mg of bromide ion were chosen as the base conditions. One parameter was varied while the others were maintained constant.

This experiment was performed on three different occasions. The carbon adsorption effluent, as well as XAD8 extract from the aquaculture effluent were chlorinated in 8/85. The XAD8 extract was again chlorinated under these varying conditions in 5/86. All three experiments showed the exact same trends. Unfortunately, the chromatographs from 8/85 contain four large contaminant peaks which, although can easily be subtracted, make the chromatographs more difficult to visualize. The quantitative results after subtraction of the contaminant peaks are very similar to the 5/86 experiment. The GC integrator reports from some of these experiments are included in Appendix 3. Only the data from the 5/86 experiment will be presented in this section however.

4.1 Effect of Chlorine Dose

The chlorine dose added to the XAD8 extract has a noticeable effect on the relative quantities of produced halogenated organics, as well as the total produced gas chromatographable NVCO. Figure 33 shows the GC profiles for three of the applied chlorine doses (pH 7, 2 hour contact time, 0 mg bromide ion). High chlorine doses bring about the breakdown of larger halogenated molecules and one observes a shift in the chromatogram to lighter compounds (smaller retention times).

The GC's shown in Figure 33,as well as others to be shown in Figures 35, 37, 39, 42, 43, and 46 only show the initial portions of the output. This was done in order to present more than one chromatograph on the same page. The latter part of the chromatographs (not shown) only contain a few compounds.

In addition, only a few of the peaks are labeled in these small chromatographs due to size limitations. The figures may be compared to the larger GC's (Figures 18, 19, and 20) as well as Table 14 for complete peak referencing.

The first moment of the chromatogram was evaluated according to Equation 9.

$$First\ moment = \sum (RT)_i\ x\ (ECD\ area)_i\ /\ (total\ ECD\ area) \tag{9}$$

where

$(RT)_i$	=	retention time of compound i
$(ECD\ area)_i$	=	ECD area of compound i

The first moment is the centroid of the chromatograph. A low centroid indicates a predominance of smaller compounds, whereas a large first moment reflects the presence of larger compounds. The first moment of the chromatogram, as well as the total ECD area are plotted in Figure 34. Higher chlorine doses lead to lower chromatograph centroids, but surprisingly do not lead to higher total NVCO areas. The highest production was observed with the addition of only one milligram of chlorine. The formation of each individual peak (compound) at the varying chlorine doses may be monitored from the data provided in Appendix 3. Dilutions for the GC outputs are the same and the areas are directly comparable. The retention times from one run to the next usually match within a 0.04 minute window.

As has been previously mentioned in the literature review section, many workers have noted that THM formation increases with increasing chlorine doses. It has consequently been routinely recommended that chlorine doses be kept low in order to minimize THM formation. Higher amounts of THM's were undoubtedly formed by the higher chlorine doses used in this experiment and yet an unknown amount of non-gas chromatographable TOX was formed. Since neither THM's nor total TOX were monitored in this work, it is not possible to state which chlorine dose leads to the formation of the least halogenated organics.

This experiment demonstrates that an abundance of halogenated organics are formed during chlorination, whose relative amounts can be controlled by the applied chlorine dose. This observation immediately suggests that a chlorine dose should be applied which would lead to the formation of minimum toxic products (possibly a choice between toxic and very toxic). Since the relative size and volatility of the chlorination products can also be controlled by the applied chlorine dose, other decision variables must be addressed. The ultimate decision about chlorine doses may favor the production of components which may be removed from the water with an additional treatment step. If treatment by activated carbon is possible, it may be wiser to use low chlorine doses since heavier components are more easily removed by carbon adsorption. On the other hand, if aeration is to be used as a final polishing step, high chlorine doses could be used to maximize the production of lighter compounds which would be amenable to air stripping.

The above mentioned ideas highlight the need for an investigation which would simultaneously address the questions of toxicity of the various fractions and the dependence of toxicity on chlorination parameters. The work of Coleman (1984) was a step in this direction. Such an investigation would be lengthy, tedious and expensive, but would certainly be worthwhile.

In summary, advocating the use of low chlorine dosages in order to minimize THM formation is an incomplete recommendation. Chlorine dose appears to be a parameter which can be utilized to minimize harmful chlorination by-products and can be tailored to subsequent treatment steps.

4.2 Effect of Contact Time

Contact time, like chlorine dose, affects the relative amounts of the produced NVCO. Figure 35 shows the GC outputs of three of the tested contact times (pH 7, 2.5 mg chlorine, 0.0 mg bromide). Figure 36 is a plot of the total ECD areas and the first moments of the chromatographs vs. contact time.

Increased contact time leads to the formation of smaller components (lower first moment) and a slight reduction in the total ECD area. Increased

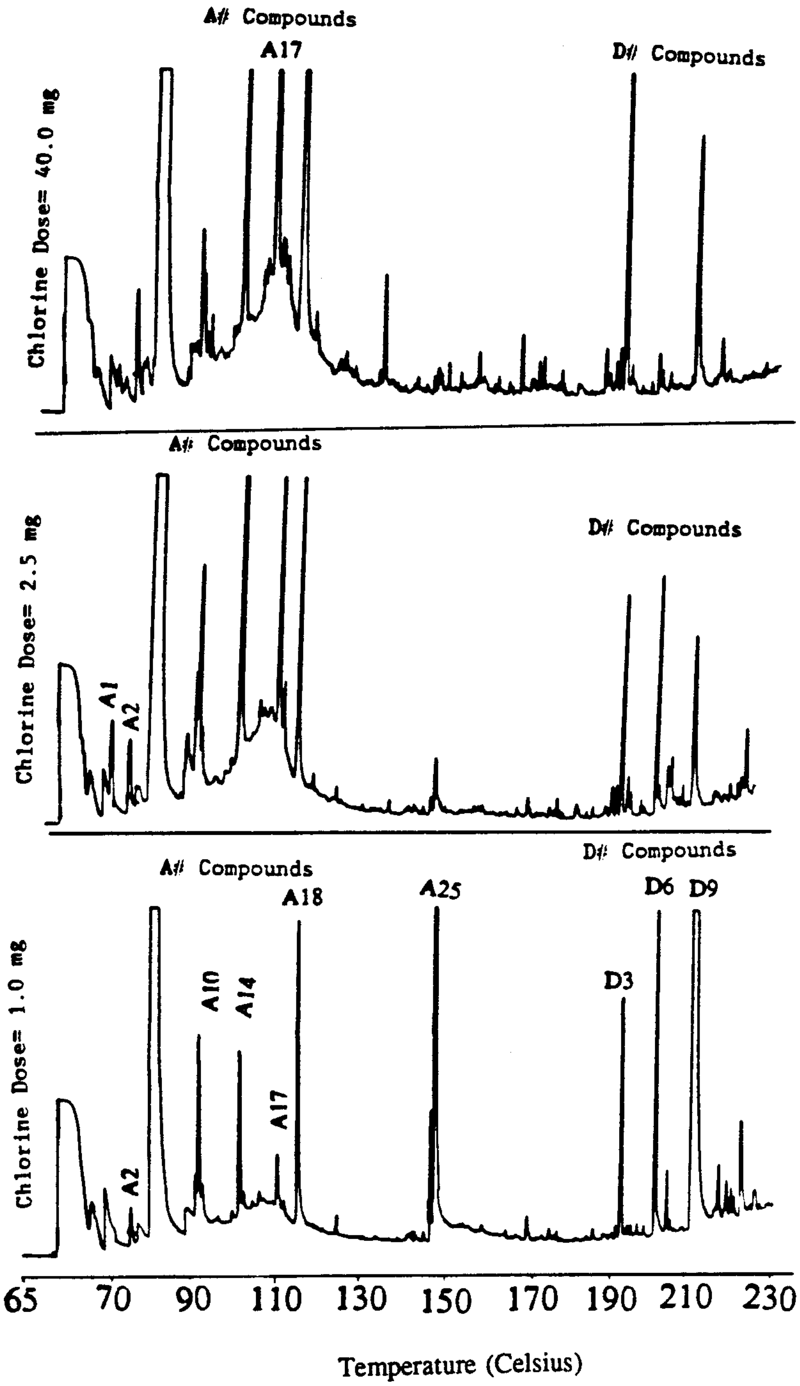


Fig. 33: GC's (ECD) of chlorinated aquaculture XAD8 extract at various chlorine doses. pH 7, contact time = 2 hours, TOC = 1 mg. GC conditions as previously described. Compare to Figure 19 and Table 14 for compound ID.

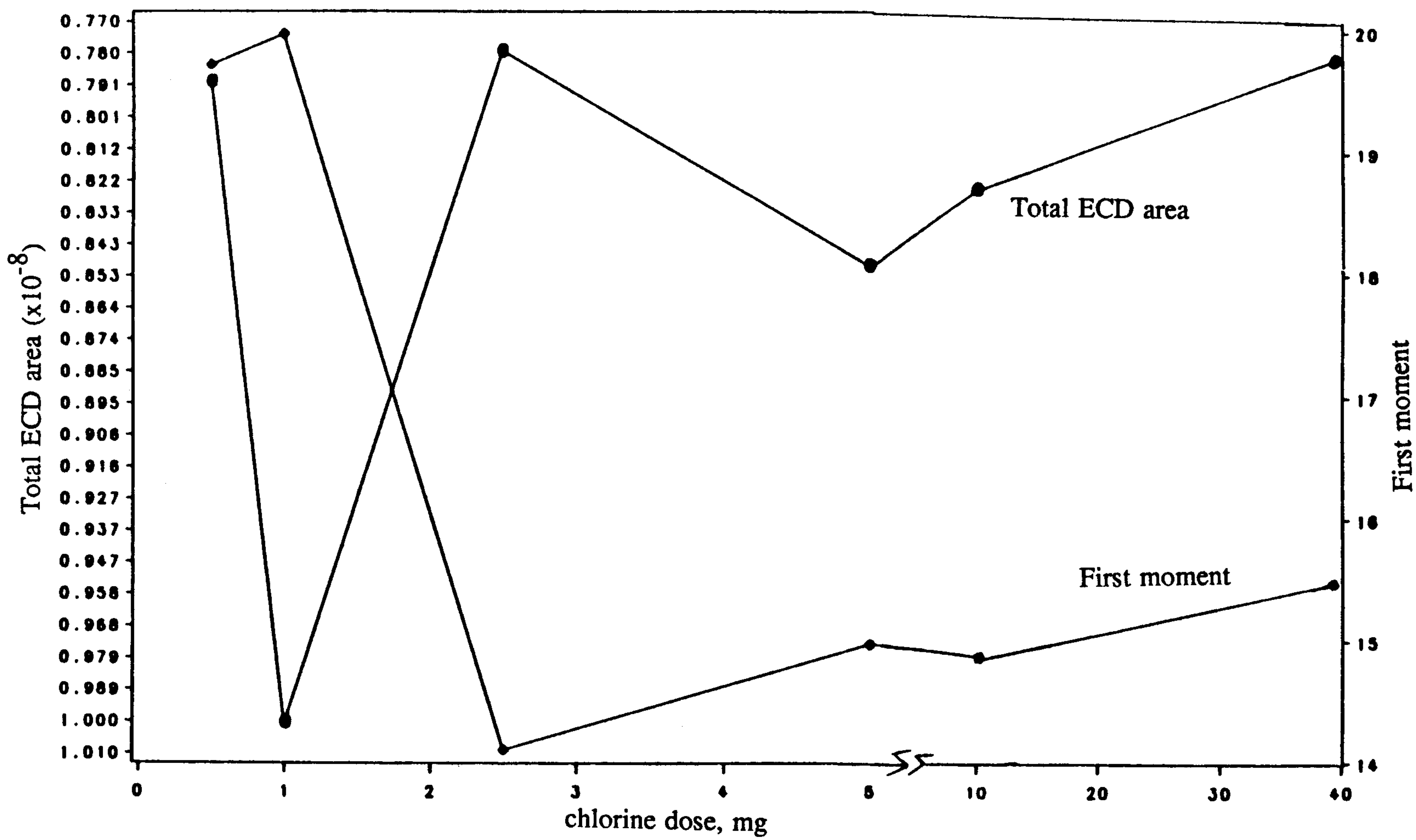


Fig. 34: Effect of chlorine dose on the breakdown products of chlorinated XAD8 extract.

contact time allows for further reaction of the free chlorine with the available TOC and the consequent breakdown of the larger molecules.

It is plausible to utilize the effects of contact time to minimize the more toxic components of TOX as well as to allow chlorination to proceed to the point which is most amenable to a further treatment step. These ideas were discussed in Section 4.1.

4.3 Effect of pH

The chlorination of the XAD8 extract was performed at several pH values. pH is an extremely important parameter in determining both the total produced NVCO and the relative amounts of the various compounds. Figure 37 shows the GC's for pH 3, 7, and 11 while Figure 38 shows the quantitative analysis of the chromatograms. Low (3) and high (11) pH result in the production of the heavier components, while the near neutral pH values (5,7,9) show similar profiles. Overall, high pH is the most NVCO productive.

The production of the heavy NVCO, 'D' reference number compounds is most likely an addition step to an unsaturated bond which may proceed by either base or acid catalysis.

4.4 Effect of Bromide

The aquaculture XAD8 extract was chlorinated with varying amounts of bromide ion in solution. The chlorinations were done at pH 7, using 10 mg of chlorine for two hours. The extract solution was spiked with 1, 5, 10, or 20 mg of potassium bromide before chlorination.

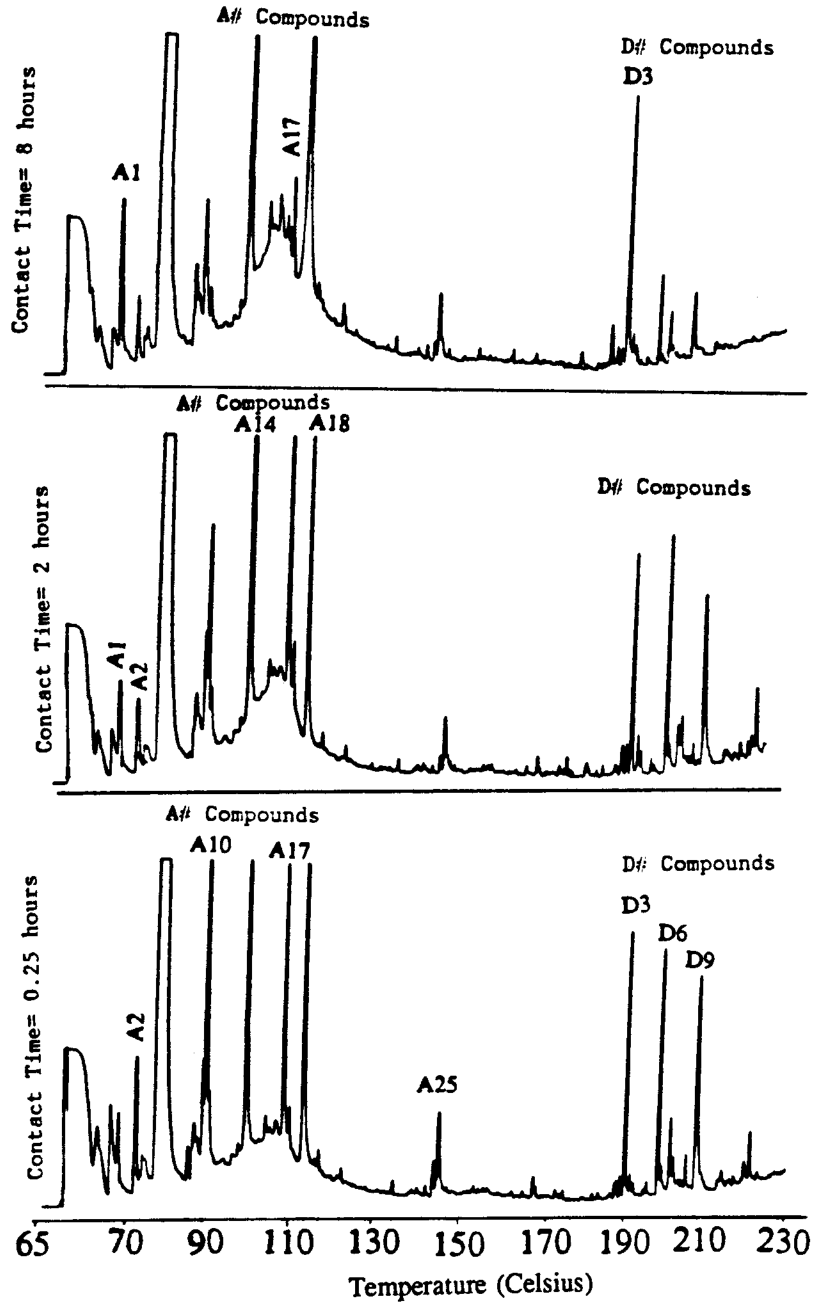


Fig. 35: GC's (ECD) of chlorinated aquaculture XAD8 extract at various contact times. pH 7, chlorine dose = 2.5 mg, TOC = 1 mg. GC conditions as previously specified. Compare to Figure 19 and Table 14 for compound ID.

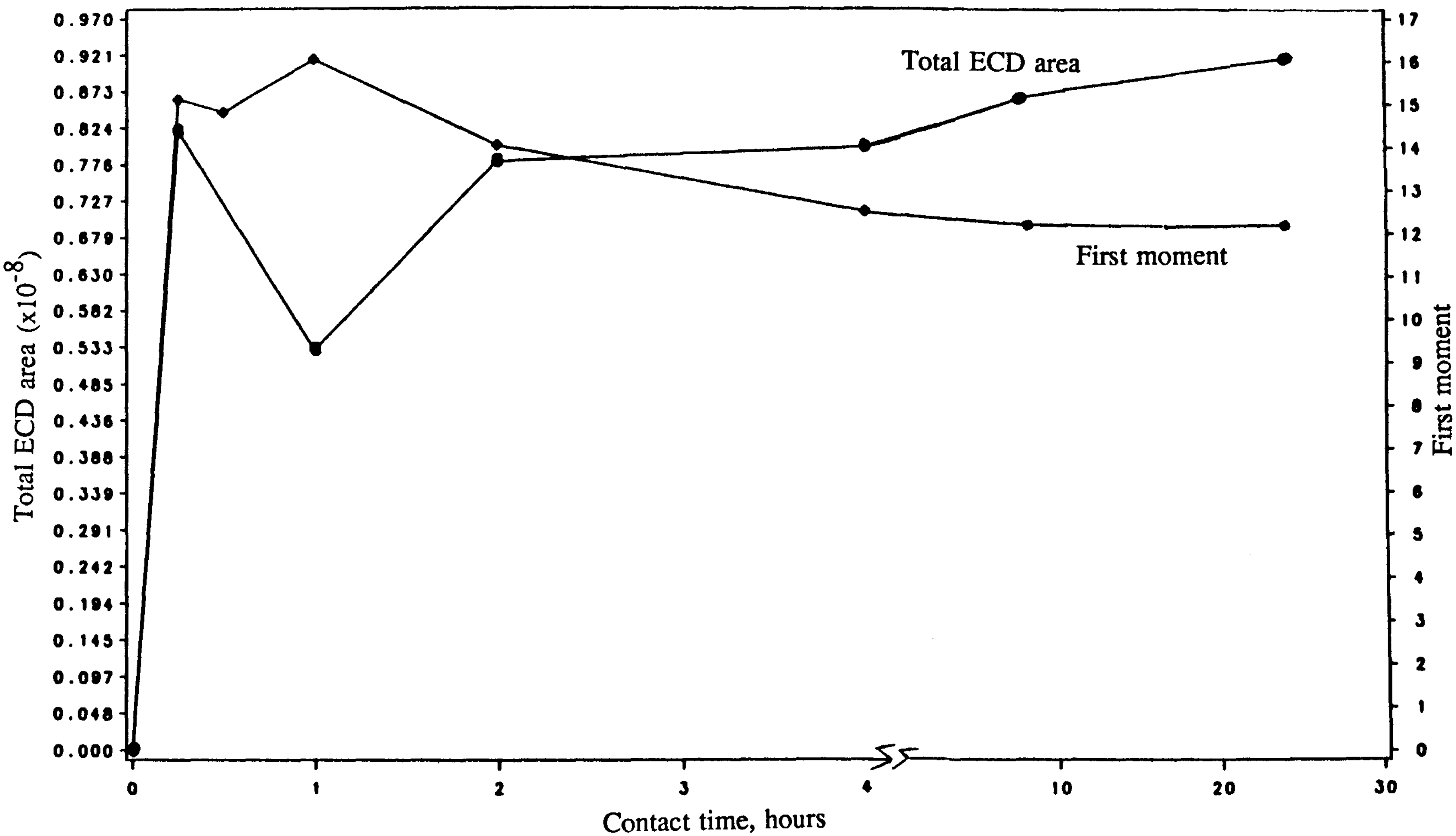


Fig. 36: Effect of contact time on the breakdown products of chlorinated XAD8 extract.

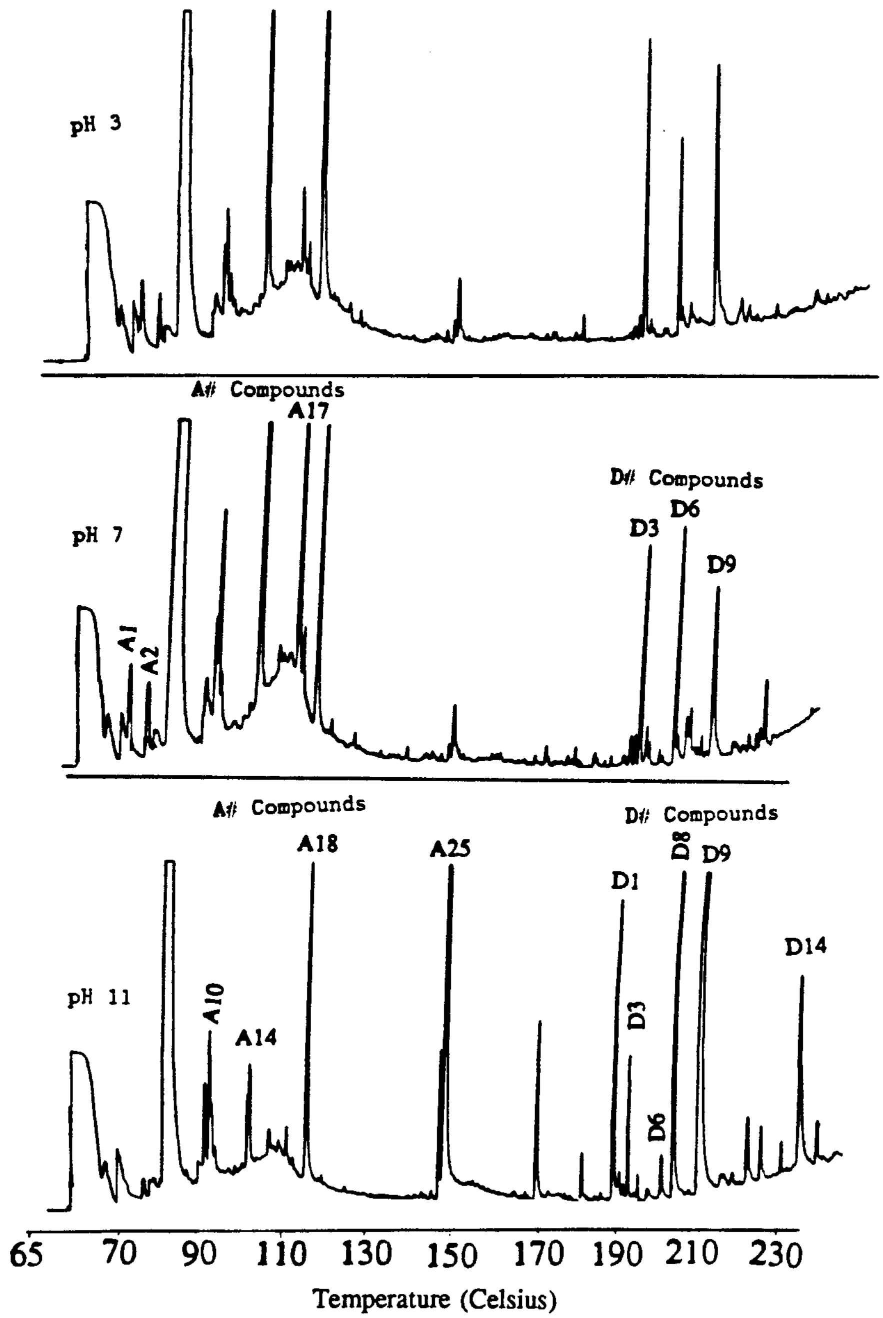


Fig. 37: GC's (ECD) of chlorinated aquaculture XAD8 extract at various pH values. Chlorine dose = 2.5 mg, TOC = 1 mg, contact time = 2 hours. GC conditions as previously specified. Compare to Figure 19 and Table 14 for compound ID.

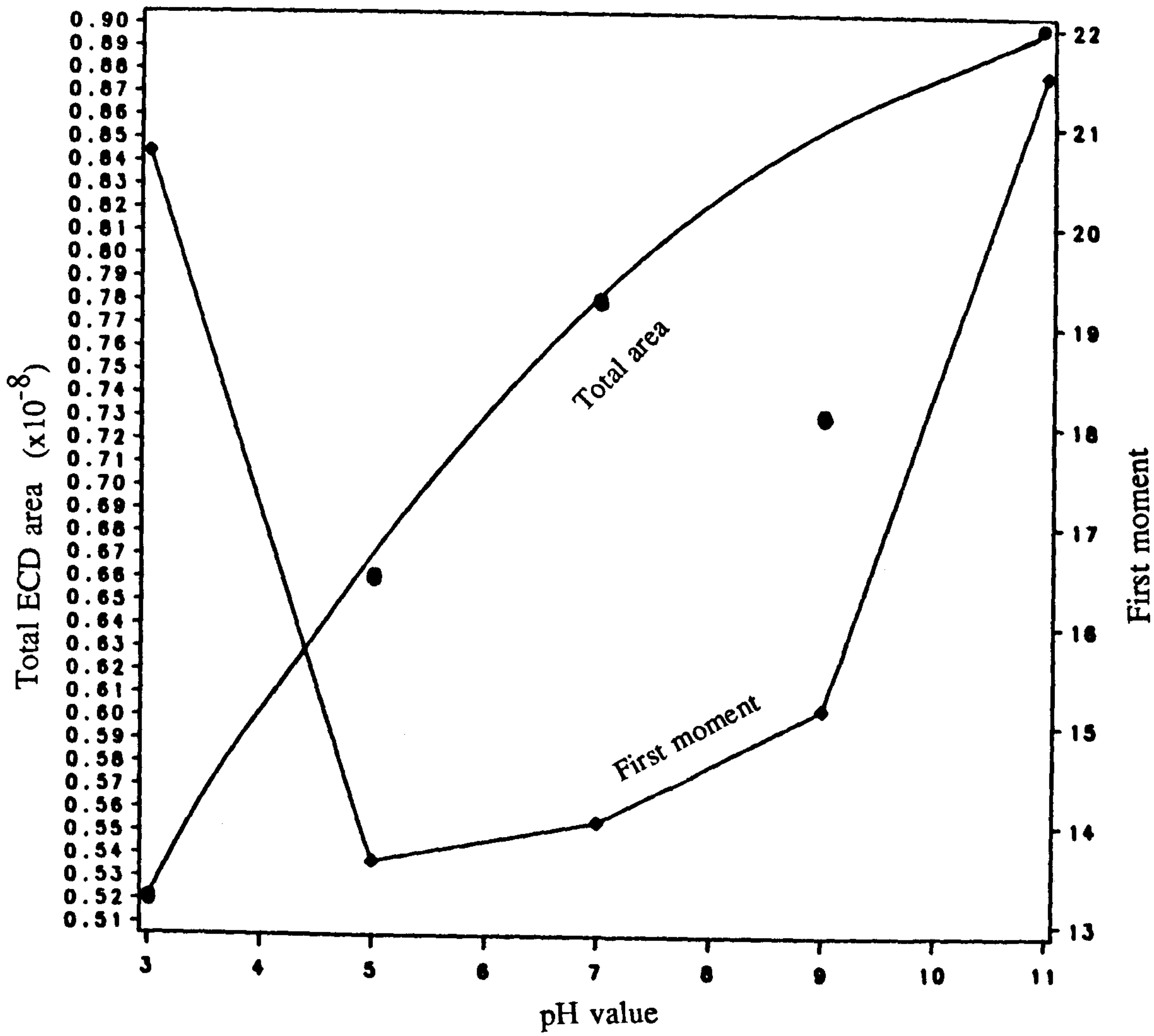


Fig. 38: Effect of pH on the breakdown products of chlorinated XAD8 extract.

The bromide ion has a significant effect on the produced halogenated organics. Figure 39 compares the chromatographs of zero and ten milligram bromide ion addition. Figure 40 shows that the total ECD area nearly triples after the addition of one mg bromide, but does not increase with further addition of bromide ion. Some of the chlorinated compounds show a decrease with the addition of bromide ion, at the expense of the formation of new brominated compounds (Figure 39).

4.5 Summary of the Effects of the Chlorination Variables

The gas chromatographable NVCO which were monitoried in these experiments are only a subset of the total organic halogens (TOX) produced during the disinfection of water. The concern for chlorination by-products centers around the health effects of these by-products. These experiments demonstrate that while certain compounds can be reduced by varying the chlorination conditions, the concentrations of other compounds are often increased at their expense. The choice of chlorination conditions should depend on minimizing the most harmful by-products.

Chlorination at low pH, long contact time, high chlorine dose (10 mg/L), and zero mg/L bromide concentration minimizes the formation of this subset of TOX. A recommendation of these chlorination conditions would be inappropriate until the relative toxicity of the various components of TOX is examined.

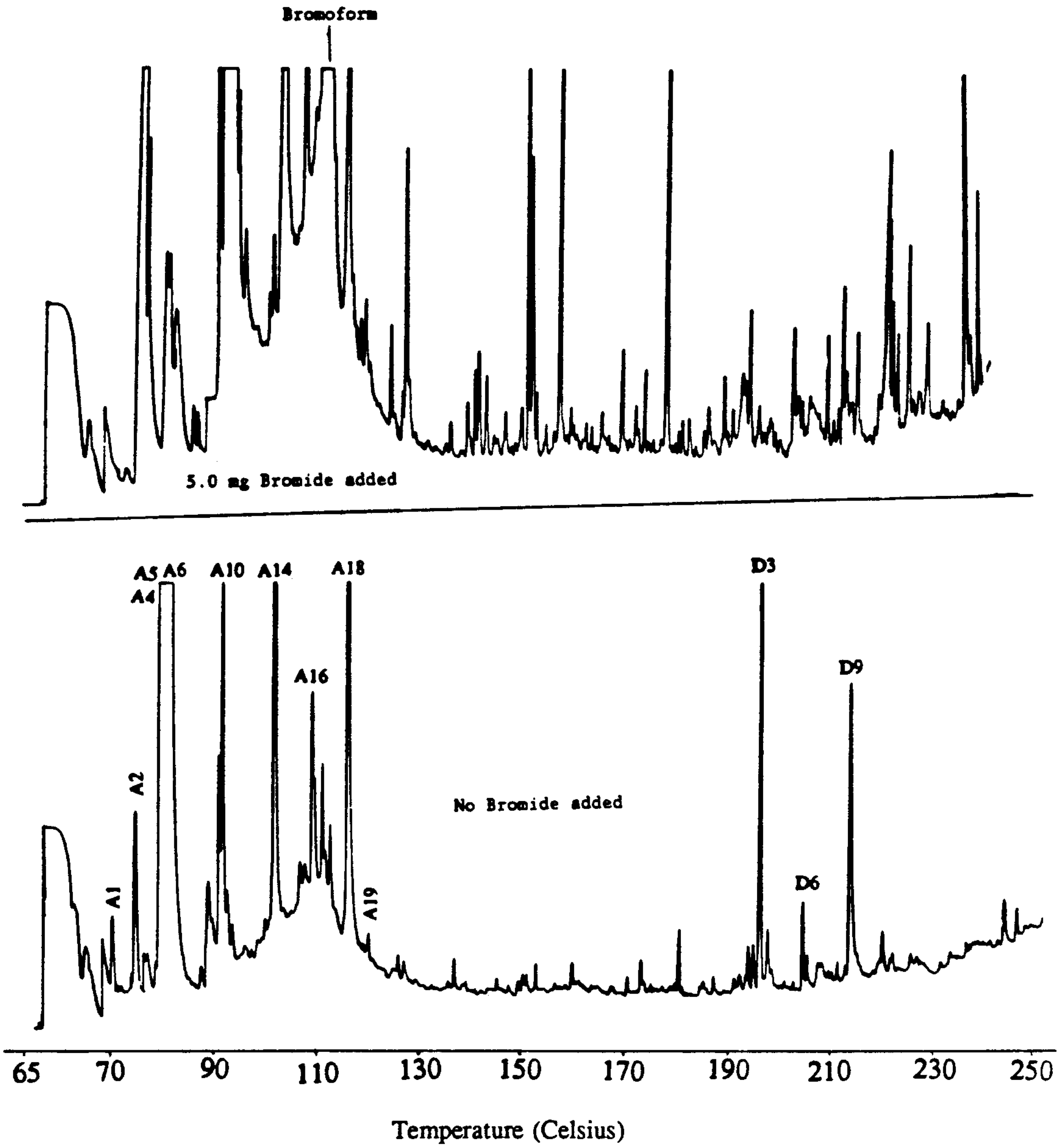


Fig. 39: GC's (ECD) of chlorinated aquaculture XAD8 extract in the presence of bromide. Top 5 mg bromide added, bottom no bromide addition. Chlorine dose = 10 mg, contact time = 2 hours, TOC = 1 mg, pH 7. GC conditions as previously described.

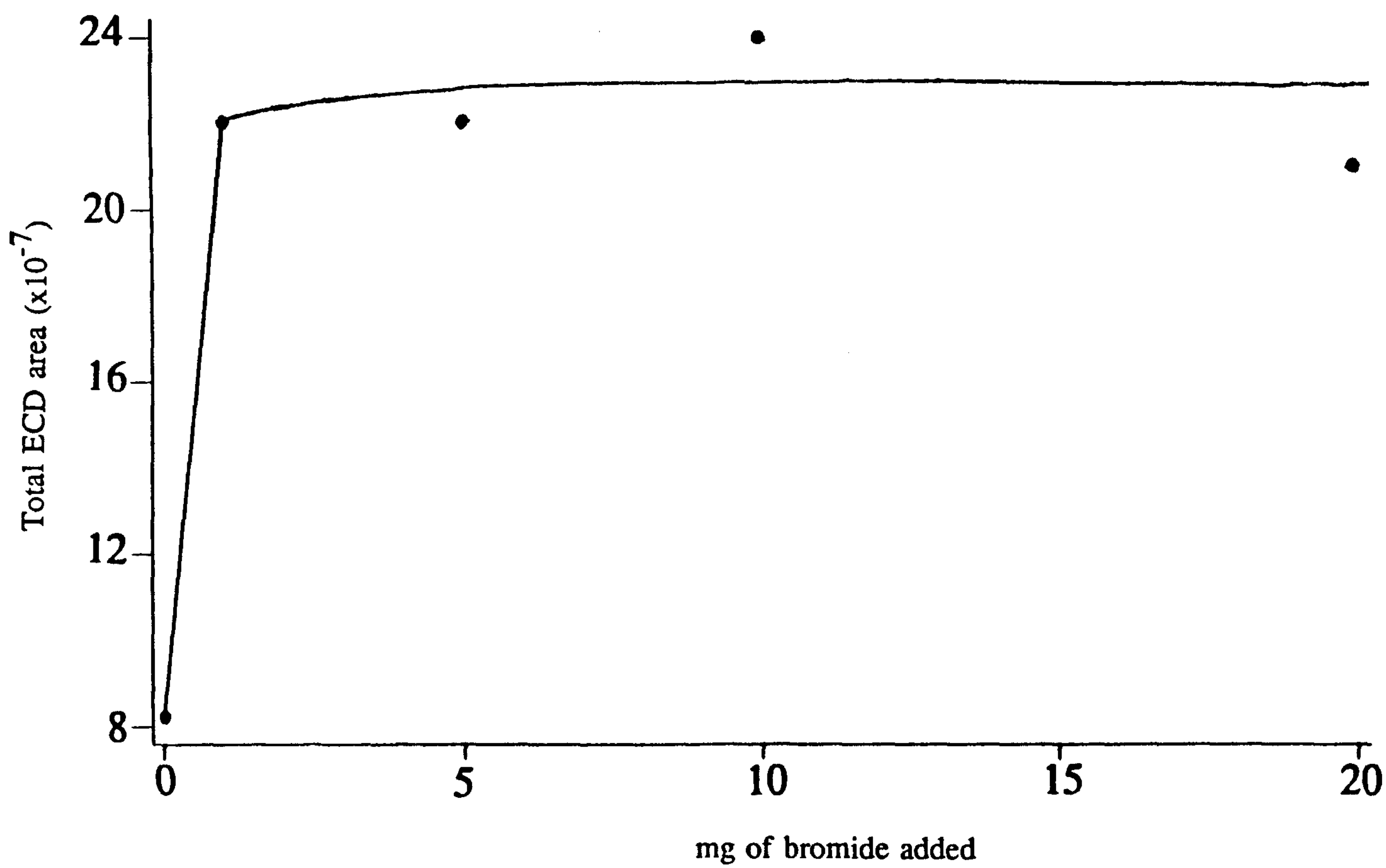


Fig. 40: Effect of bromide on the breakdown products of chlorinated XAD8 extract. Chlorine dose = 10 mg, contact time = 2 hours, pH 7, 1 mg TOC.

5. EFFECTS OF DECHLORINATING AGENTS

It has been commonplace to add a dechlorinating agent such as sodium sulfite to quench the residual chlorine before analyzing the organic compounds in a chlorinated water sample. This is usually done in order to arrest the further reaction of chlorine with the carbon sources in the water. Since dechlorinating agents are not reactive with THM's, this protocol gained wide acceptance with researchers who studied the kinetics of THM formation.

The recent interest in the analysis of other halogenated chlorination by-products proceeded by mimicking the residual chlorine quenching step from the THM analytical protocols. The question regarding the effects of dechlorinating agents on these non-volatile halogenated organics has not been addressed. It has been assumed that dechlorinating agents are not reactive with all of the chlorinated organic by-products.

It was observed that the addition of sodium sulfite or sodium thiosulfate to the chlorinated water samples (from the San Diego Wastewater Treatment Plant) before extraction had a significant effect on the quantity and makeup of the methylene chloride extract.

This observation was first made in an experiment designed to reproduce the halogenated organics observed in the San Diego Wastewater plant in the laboratory. The residual chlorine in the chlorinated San Diego effluent was not regularly quenched before extraction. The carbon adsorption effluent (from San Diego) was chlorinated in the laboratory under a variety of conditions (contact time, pH, and chlorine dose) in order to determine which set of conditions most closely reproduces the chlorination by-products seen in San

Diego. The residual chlorine was quenched with sodium sulfite before extraction for the laboratory chlorinated samples. There consistently appeared to be a difference between the laboratory chlorinated samples and the San Diego chlorinated effluent. After several iterations of parameter modifications, it was finally realized that sodium sulfite addition is the reason for the difference between the chromatographed extracts.

Three experiments were designed to assess the effects of sodium sulfite on the produced halogenated organics. First, sodium sulfite was added to several categories of aqueous solutions of pure halogenated compounds. Second, sodium sulfite was added to the chlorinated San Diego final effluent. Lastly, sodium sulfite was added to laboratory chlorinated XAD8 aquaculture extracts before methylene chloride extraction. Some of the XAD8 solutions were spiked with bromide ion before chlorination. Each of these experiments will be discussed separately.

5.1 Addition of Sodium Sulfite to Pure Halogenated Compounds

Eight classes of halogenated organics were treated with sodium sulfite before extraction from a prepared aqueous solution. Control samples were extracted under identical conditions minus the sodium sulfite addition step (see analytical procedures section for more details). All samples were analyzed in triplicate. Table 19 lists the classes of compounds used, the compound name and the average percent decrease in the integrator area of the compound caused by the addition of sodium sulfite. The decrease in the area of the compound implies that the compound reacted with the sulfite ion and consequently the area of the original compound (reactant) decreases.

The two unsaturated aliphatics (3-chloro-1-butene, and 3-bromopropene) as well as chloro-benzene were the only three compounds which were reactive with sodium sulfite. Although the tested list of compounds is not exhaustive, it is still very informative.

It was predictable that chloro-phenols, and halogenated saturated aliphatics would not be reactive with the sulfite ion since they have been successfully analyzed in the past by numerous workers. The presence of oxygen (aldehydes, phenols, and alcohols) or nitrogen atoms does not lead to reactivity with the sulfite ion. The three reactive molecules are unsaturated. Other unsaturated compounds, however, were unreactive (dichlorobenzenes) which means that the presence of a carbon double bond may be necessary, but is not sufficient to render the compounds reactive with sulfite.

It is hypothesized that the sulfite ion displaces the halogen atom, forming a sulfonic acid (or possibly a di-sulfonic acid). Sulfonic acids are not methylene chloride extractable (too polar) and consequently do not appear in the gas chromatograms after sulfite addition. It is postulated that the reaction is a substitution and not an addition reaction because, brominated compounds are more reactive with sulfite than chlorinated compounds. This is seen with 3-bromopropene and with the brominated compounds produced by the reaction with the XAD8 extracts (Section 5.3). Bromide is a better leaving group than chlorine and is consequently more likely to undergo substitution reactions (Gutsche and Pasto 1975). A leaving group is the moeity in a molecule which is displaced during a reaction. The alkyl bromide ion is a fifty times better leaving group than the alkyl chloride ion. Figure 41 is a schematic of the postulated reaction between 3-bromopropene and sodium sulfite.

The fast reaction of the the sulfite ion with unsaturated carbonyl compounds has been reported as early as 1966 (Schroeter 1966). These reactions were reported for applications in the food processing and pharmaceutical industries. The reactions reported in this work are very similar to Schroeter's reports.

5.2 Addition of Sodium Sulfite to the Chlorinated Effluent

Two liters of chlorinated final effluent were extracted without addition of sodium sulfite (Figure 18). Excess (five fold) sodium sulfite was added to a duplicate sample before extraction. The gas chromatograms of the two extracts are shown in Figure 43. The ECD area for peaks eluting before twenty minutes (most of the 'A' reference number peaks) drops by 75% after sulfite addition (from 1.9×10^7 to 4.8×10^6) whereas the area drop for peaks eluting after twenty minutes is only 37% (from 1.1×10^8 to 6.9×10^7). The early eluting peaks which are most affected by sodium sulfite are mostly unsaturated halogenated compounds.

The chromatographs shown in Figures 42 and 43 were chosen so as to illustrate the fact that the early eluting peaks ('A') are the ones most affected by sodium sulfite. On several occasions, probably due to differing chlorination conditions at the treatment plant, most of the compounds in the chlorinated effluent extract were 'A' peaks. Under these latter conditions, sodium sulfite has a more pronounced effect on the total gas chromatographable NVCO. This observation may be of practical utility. If the sulfonated compounds are less of a health hazard than their halogenated counterparts, it may be advantageous to chlorinate under conditions which produce compounds

Table 19 Addition of Sodium Sulfite to Pure Compounds

Compound Name	Compound Class	% Drop Caused by Sulfite
o-chlorophenol	phenol	0
2,4,5-trichloro-phenol	phenol	0
2,4,6-trichloro-phenol	phenol	0
chloro-cyclohexane	cyclic aliphatic	0
bromo-cyclohexane	cyclic aliphatic	0
trichloroethane	straight aliphatic	0
chloroform	straight aliphatic	0
chloro-ethanol	alcohol	0
chloro-pyridine	nitrogen containing	0
bromo-analine	nitrogen containing	0
2,4-dichlorobenzaldehyde	aldehyde	0
2,4-dichlorobenzene	aromatic	0
1,3-dichlorobenzene	aromatic	0
1,4-bromochlorobenzene	aromatic	0
chloro-benzene	aromatic	31
3-chloro-1-butene	unsaturted aliphatic	26
3-bromo-propene	unsaturated aliphatic	95

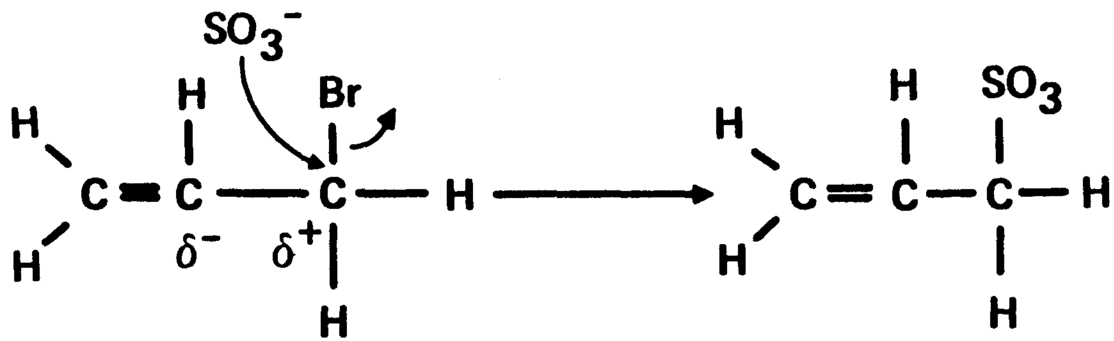


Fig. 41 Reaction of Sodium Sulfite with 3-Bromopropene

that are reactive with the sulfite ion.

5.3 Addition of Sodium Sulfite to Chlorinated XAD8 Extract

Aquaculture effluent XAD8 extracts were chlorinated and sodium sulfite was added (five fold excess) before methylene chloride extraction. Once again, one observes a large drop in the total ECD area (68%, 10 mg chlorine at pH 7, 4 hours) and an even greater drop for the early eluting peaks (77% for peaks eluting before 20 minutes, 'A' peaks). Table 20 summarizes some of the data.

An XAD8 extract sample spiked with five milligrams of bromide ion was treated with sodium sulfite before extraction. Although the percentage decrease is less than that observed without addition of bromide, the magnitude of the drop was more than twice that without bromide addition (Table 20). This may indicate that brominated compounds are more reactive with the sulfite ion. As was indicated in Section 5.1, the bromide ion is a better leaving group than the chloride ion and may be more likely to undergo this substitution reaction.

5.4 Summary of the Effects of Sodium Sulfite

Sodium sulfite is reactive with many of the observed halogenated organics seen in the San Diego chlorinated final effluent. Sodium sulfite should only be added in the laboratory before extraction if the compounds of interest are not reactive with the dechlorinating agent (THM's). This observation is critical for proper and accurate quantitation of the chlorination by-products. In addition, this observation may have practical significance if the

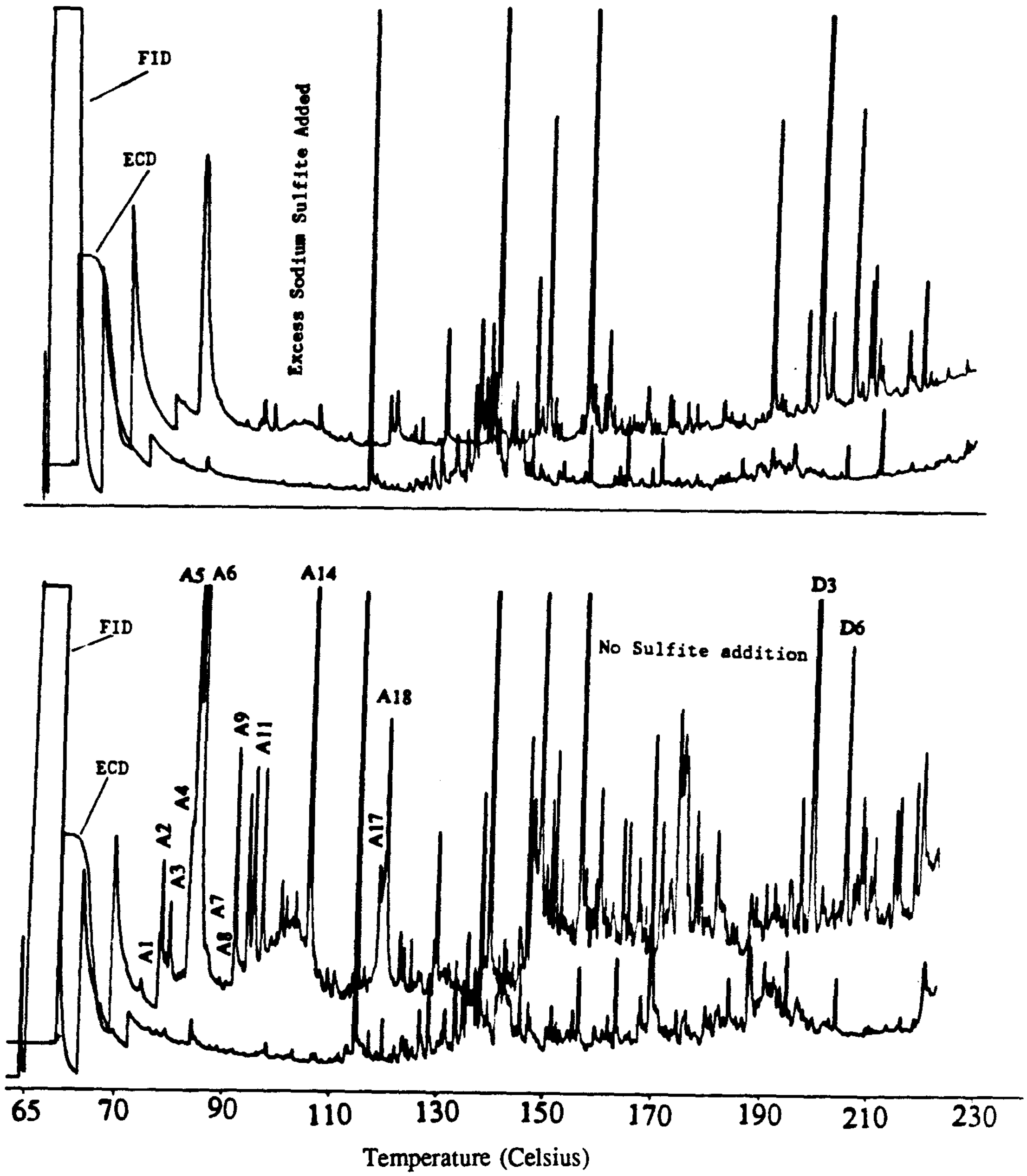


Fig. 42: GC's showing the effect of sodium sulfite on the chlorinated San Diego Wastewater Treatment Plant effluent. Top: excess sulfite added; bottom: no sulfite addition. Compare to Figure 19 and Table 14 for compound ID. GC conditions as previously specified. Axes labeled for ECD.

sulfonated compounds are found to be less hazardous than their halogenated counterparts.

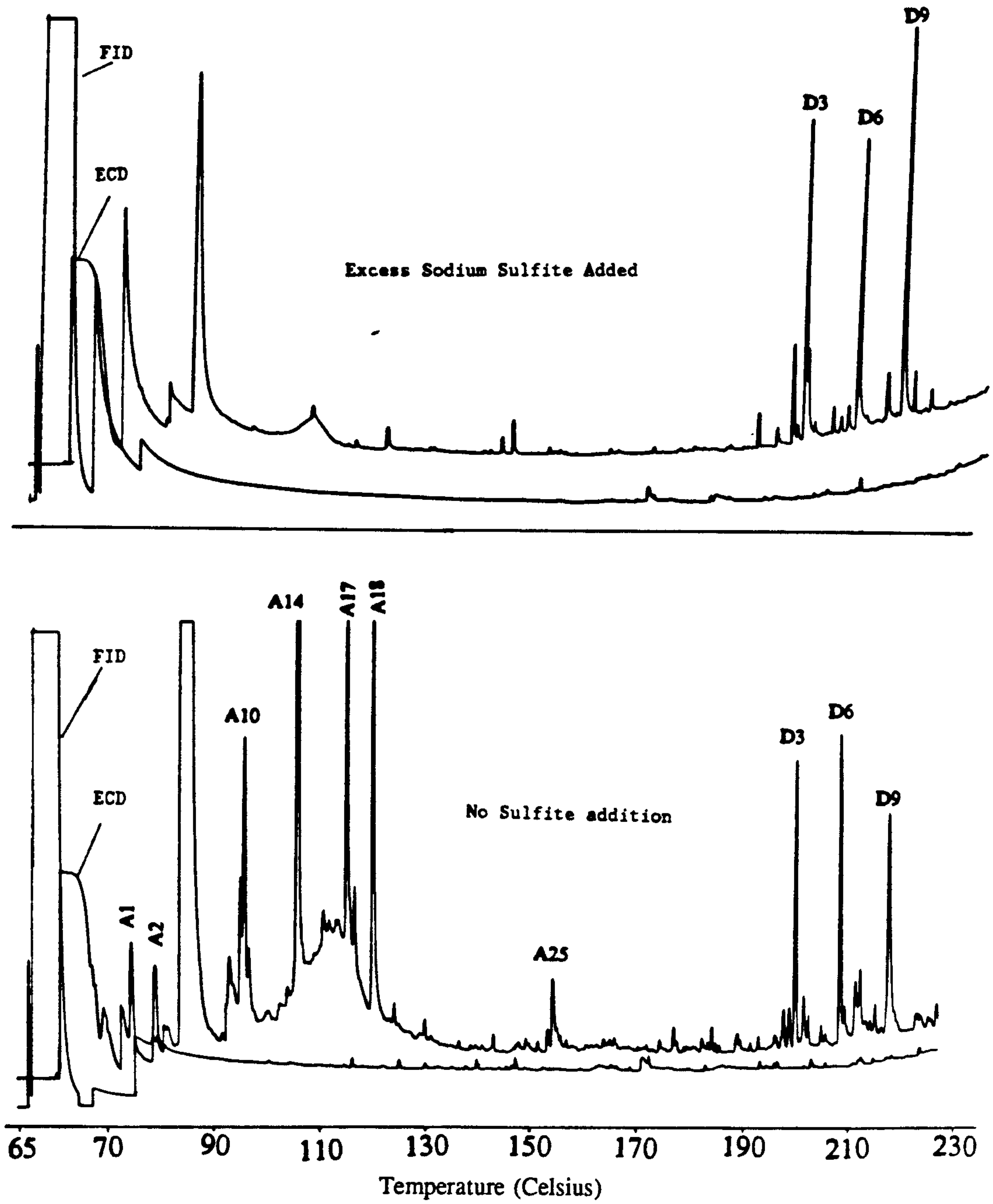


Fig. 43: GC's showing the effect of sodium sulfite on the chlorinated aquaculture XAD8 extract. Top: excess sulfite added; bottom: no sulfite addition. Compare to Figure 19 and Table 14 for compound ID. GC conditions as previously specified. Axes labeled for ECD.

Table 20 Effects of Sodium Sulfite on Chlorinated XAD8 Extract

Conditions	Total ECD Area		Area Before 20 minutes		Area After 20 minutes	
(all for 4 h Cl and 10 mg C_{12})	minus sulfite	plus sulfite	minus sulfite	plus sulfite	minus sulfite	plus sulfite
	x 10^7	x 10^7	x 10^7	x 10^7	x 10^7	x 10^7
pH 3	6.0	1.7	4.5	1.1	1.5	0.6
pH 7	6.5	2.1	5.6	1.3	1.0	0.9
pH 11	6.9	1.8	4.1	0.9	2.7	0.9
5 mg Br, ph 7	22.0	12.0	18.0	9.2	4.0	3.4

6. TREATMENT OF THE OBSERVED HALOGENATED ORGANICS

Several treatment schemes were screened for their ability to minimize the formation of the observed halogenated organics. First, the application of powdered activated carbon (results would be comparable for granular activated carbon) before and after chlorination was evaluated. Second, disinfection with chloramines instead of free chlorine was tested. Third, aeration of chlorinated water samples in order to minimize the formation of the observed NVCO was attempted. Fourth, ozonation before and after chlorination was evaluated. Last, partial dechlorination and a two stage chlorination scheme which would involve chlorination, dechlorination and a subsequent chlorination were evaluated for treatment of the NVCO. Each of these treatment schemes will be described and discussed separately.

6.1 Treatment with Powdered Activated Carbon

One liter volumes of activated carbon effluent from the San Diego Wastewater Treatment plant (pre-chlorination water) was chlorinated in the laboratory with ten milligrams of chlorine at pH 7 for two hours. The water samples were treated with varying doses of powdered activated carbon (PAC) either before or after chlorination. The PAC used was Westvaco Nuchar SA-15 which had been rinsed three times with distilled methylene chloride before baking at 105^{o}C for 24 hours. The weighed amount of PAC was added to the water sample in a one liter flask and was stirred for one hour. The filtered water sample was consequently extracted and analyzed by GC as previously described. Six of the eight samples were analyzed in duplicate.

Carbon treatment before chlorination investigates the ability of activated carbon to adsorb the NVCO precursors. Carbon treatment after chlorination addresses the ability of activated carbon to adsorb the formed halogenated organics.

1000 and 4000 mg doses of PAC were added before chlorination and 4000, 1000, 250, and 100 mg doses were added after chlorination. An untreated sample (San Diego carbon adsorption effluent) was also analyzed as well as a laboratory chlorinated sample which was untreated with PAC.

Figure 44 illustrates that PAC, added after chlorination, is very effective in reducing the total observed NVCO to the same level as before chlorination. The total NVCO ECD areas plotted in Figure 44 were evaluated as the area after chlorination minus the ECD area of the untreated carbon adsorption effluent (blank sample from San Diego).

Carbon treatment before chlorination does not seem to be effective in removing the NVCO precursors. This is the situation at the San Diego waste-water treatment plant, since the water is treated with activated carbon before chlorination, but still produces high halogenated organics concentrations.

6.2 Chloramines

Disinfection using chloramines has been successfully used by several workers to minimize THM and TOX formation and has been discussed in previous sections. An experiment was performed to quantify the utility of chloramines in reducing the observed halogenated organics.

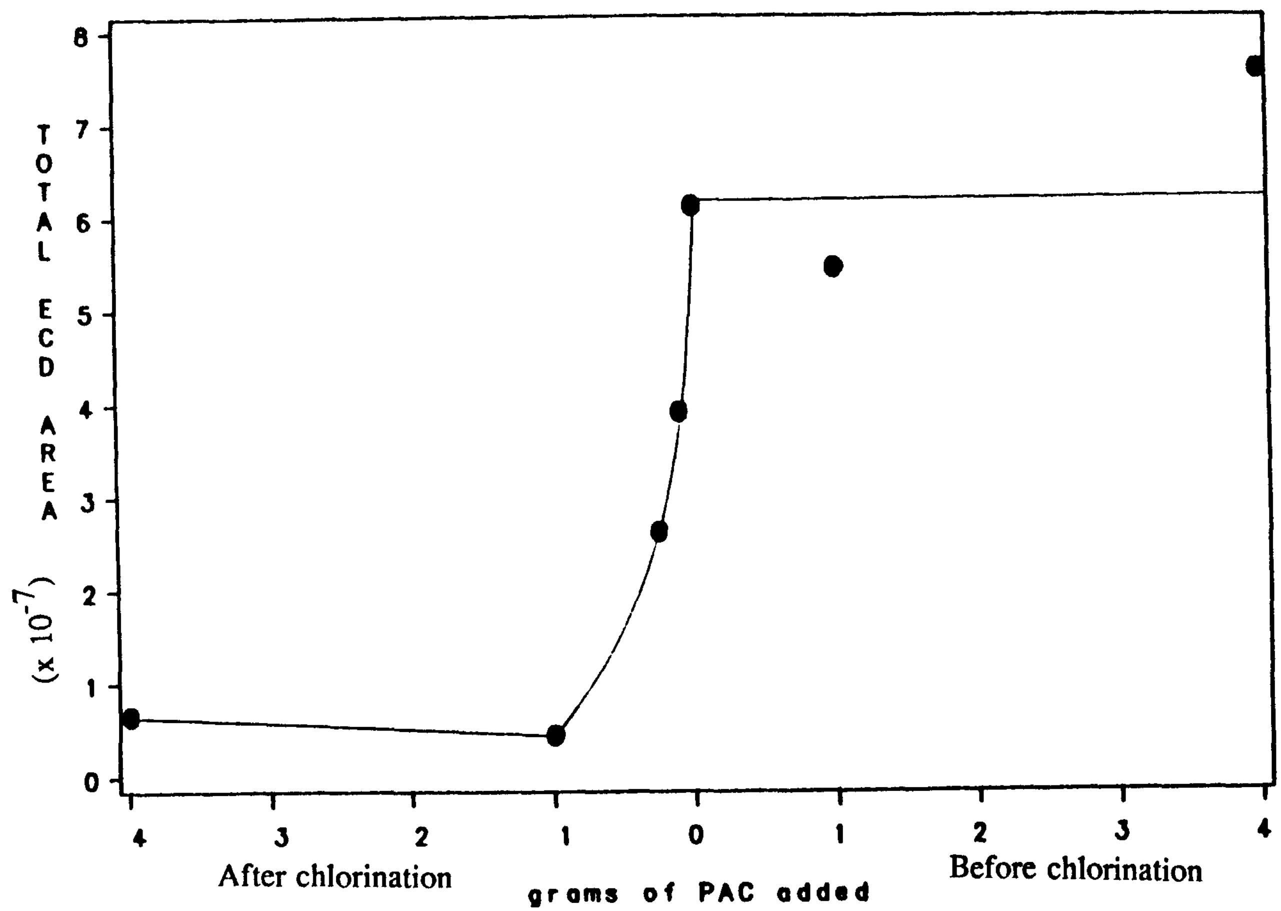


Fig. 44: Treatment of NVCO by PAC. Chlorine dose = 10 mg/L, pH 7, contact time = 2 hours represented by 0 point. Left is PAC treatment after chlorination. Right is PAC treatment before chlorination.

XAD8 extractable organics from the aquaculture fields were chlorinated with ten milligrams of chlorine for two hours at pH 3, 7 and 11. Ammonia (NH_4Cl) was added using a 70 mg/ml N–NH_4 stock solution. Three doses of ammonia were added before chlorine addition at each pH. The ammonia doses used were 14, 35 and 70 milligrams and each lies at a different point along the breakpoint curve. At high pH the dominant chlorine species is monochloramine and at low pH the dominant species is dichloramine. Six of the twelve samples were run in duplicate and the given values in Figure 45 are the calculated averages. The Supelcowax column (GC) was in poor condition at the time of the analysis and consequently a Carbowax 20M column was used in its place. The injector temperature was 215^{o}C, and the detector maintained a 250^{o}C temperature (since an effluent splitter was used, the detector temperature could exceed the column limit). The GC oven was programmed from 65 to 205^{o}C at four degrees per minute after an initial four minute hold. Peak areas from this experiment are therefore not comparable with other previously described work, but in themselves allow for comparisons between disinfection with free and combined chlorine.

Figure 45 shows the total ECD area vs. the chlorine:NH_4^+ ratio for the chlorinated 1 mg TOC. Figure 45 also shows the location of each point along the breakpoint curve. The use of combined residuals reduces the observed NVCO levels by 32-62%. The chromatograms of the free and combined residuals extracts are very similar with a few exceptions. Basically, chloramines result in lower levels of most compounds and produce low amounts of a few new (unidentified) peaks.

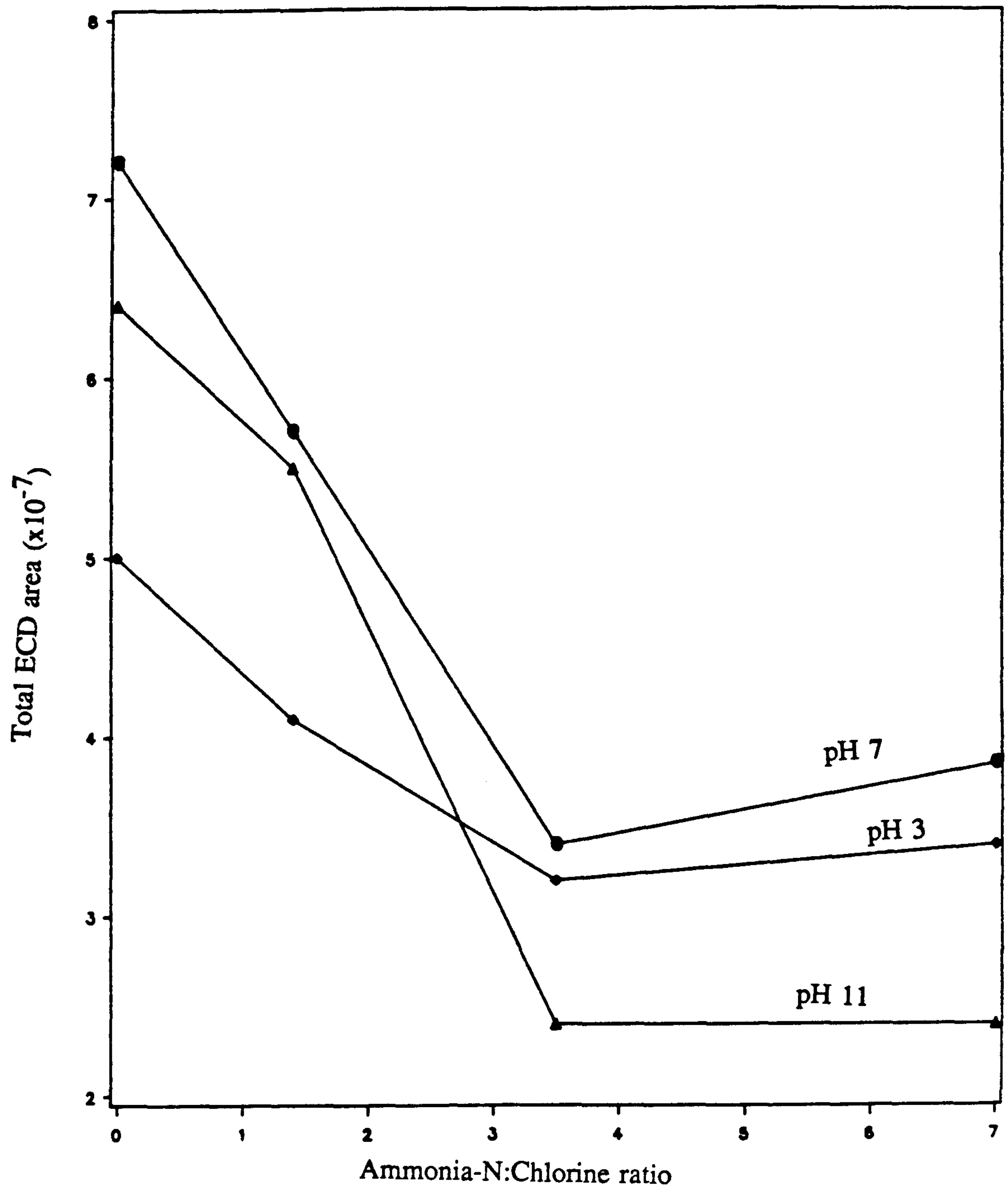


Fig. 45: Reduction of NVCO levels by the use of chloramines. Chlorine dose = 10 mg, TOC = 1 mg, contact time = 2 hours.

6.3 Aeration

Chlorinated water samples were aerated with high purity air in order to determine whether aeration is a viable treatment scheme for the observed halogenated organics. Eight hundred milliliters of distilled water was spiked with one milligram TOC of aquaculture XAD8 extract. The samples, each placed in a one liter beaker were chlorinated for two hours with 2.0, 10.0, and 50.0 milligram doses of chlorine at pH 7. The oxygen transfer coefficient K_LA was also measured (K_LA = 0.43) and the data are provided in Appendix 4. The samples were aerated for three hours using a stone bubble diffuser with the diffuser placed in the center of the beaker, one inch from the bottom. Samples were also chlorinated for the total 5 hours without aeration as well as for two hours without aeration. The Carbowax 20M column was used in this experiment using the GC conditions described in Section 6.2.

The experiment was designed to show that heavy chlorine doses (50 milligrams) could be used to produce lighter compounds which could then be removed by aeration. The results of the experiment were disappointing in that aeration was not effective in removing even the lightest compounds ('A' reference numbers). The results were also difficult to interpret because aeration stripped the residual chlorine so the aerated samples were neither comparable to the two hour chlorinated samples nor the five hour chlorinated samples (without aeration). For example, the total ECD area for two hours of chlorination was 6.4 x 10^7 (2 milligrams dose) and 2.71 x 10^7 after five hours. With aeration the total area was 3.68 x 10^7. It is reasoned that aeration stripped the available chlorine at a point somewhere between two and five hours and consequently arrested further reaction (0 residual chlorine was measured after aeration). Table 21 shows the total ECD areas for the nine tested conditions. Six of the nine points were run in duplicate.

Although the data is difficult to interpret, it is still evident that aeration is not effective in reducing the levels of the observed compounds. Aeration as a treatment method was consequently not pursued after this initial experiment.

Table 21 Treatment of NVCO by Aeration

Chlorine Dose	Total ECD Area 2 hours C_{12}	Total ECD Area 5 hours C_{12}	Total ECD Area Aerated
Milligrams	$x\ 10^7$	$x\ 10^7$	$x\ 10^7$
2.0	6.4	2.7	3.7
10.0	5.6	4.5	3.7
50.0	3.5	4.0	3.4

6.4 Ozonation

Ozonation was screened for its ability to reduce the levels of the observed halogenated organics. In one experiment, the aquaculture XAD8 extract was ozonated before chlorination in order to render the precursors unreactive to subsequent chlorination. In a latter experiment, ozone was used to destroy the formed halogenated organics after chlorination. Neither experiment showed ozone to be a promising method to reduce the observed chlorination by-products. Ozonated samples without chlorination showed very little methylene chloride extractable organics.

One milligram of XAD8 aquaculture extract was diluted to twenty five milliliters. The sample was chlorinated at pH 7 for two hours with ten milligrams of chlorine. Ozone was applied by passing oxygen gas through a UV sterilizer. The formed ozone was bubbled into the XAD8 extract solution using a six inch pipet. The ozone residual was measured at 0.75 - 1.0 mg/L (orthotolidine method, *Standard Methods* 1985) and this residual was maintained throughout the ozonation period. The flask containing the XAD8 extract was stirred during the ozonation and was capped with parafilm in order to minimize evaporative losses. The samples were ozonated for one, two and four hours before chlorination. In the experiment designed to evaluate ozonation after chlorination the samples were ozonated for two hours. In both experiments, nitrogen gas was applied to the samples (in place of ozone) so as to insure that the observed differences are due to the reactive ozone species and not simply due to aeration. The final sample which was analyzed was ozonated for four hours without chlorination. All samples were analyzed in duplicate.

Ozonation after chlorination showed no significant improvement. One observes a 42% drop in total ECD area with ozone treatment and 43% drop with nitrogen treatment, implying that the decrease is attributable to evaporative losses. The gas chromatographs of the untreated and ozonated samples also look qualitatively identical.

The samples which were ozonated prior to chlorination showed different chromatographic patterns form the un-ozonated samples. Figure 46 compares the GC's for the un-ozonated sample and a sample which was ozonated for four hours prior to chlorination. One observes a sharp drop in the heavy, 'D', compounds and an increase in the unresolved 'hump' associated with the lighter 'A' compounds. The total ECD area drops by 37% for the four hour ozonated sample. Ozone has a powerful bleaching effect on the XAD8 extracts (color changes from yellow to milky-clear) and one observes identical chromatographs for the one, two and four hour pre-ozonated samples. Nitrogen gas sparging prior to chlorination shows no qualitative or quantitative difference (8% increase in total ECD area) with the untreated sample (chlorinated, but not sparged).

The sample which was ozonated for four hours without chlorination shows very little gas chromatographable compounds (FID and ECD). This only means that the breakdown products were not analyzable by the used analytical procedures. Evaluation of ozone as a disinfectant was beyond the scope of this research work.

The use of ozone in water treatment is a complex and broad field. These crude experiments were only meant to screen the possible utility of ozone for the reduction of the observed NVCO. Ozone was found to alter the precursors so as to change the chlorination breakdown products. The significance and utility of this observation can only be judged if the breakdown products after ozonation were found to be less harmful than without ozonation.

6.5 Dechlorination

The discovery that sodium sulfite is reactive with some of the observed halogenated organics (discussed in Chapter 5) was initially very exciting as it appeared to be a solution to their elimination. A two stage chlorination

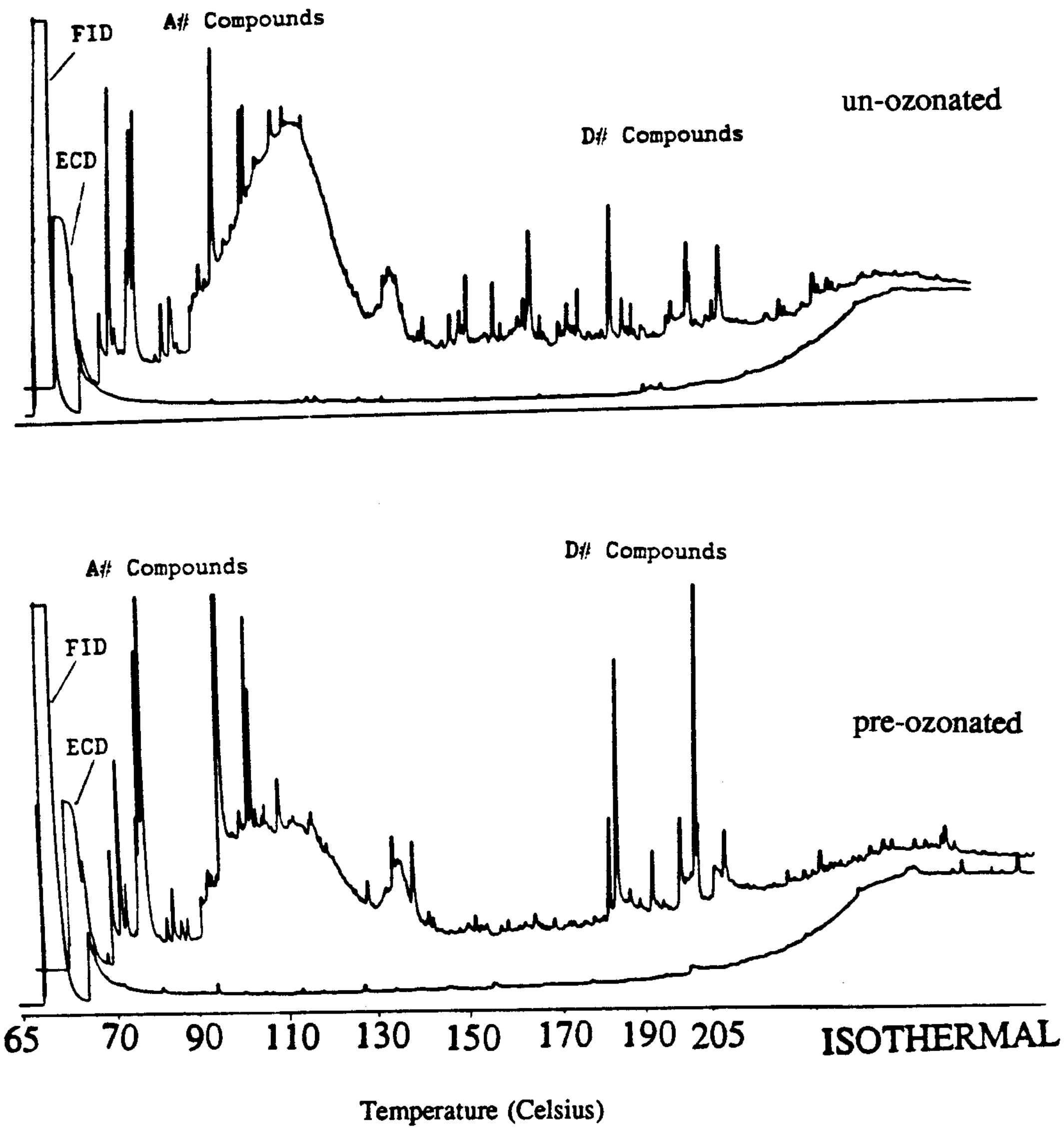


Fig. 46: GC's of the effect of pre-ozonation on NVCO formation. GC conditions as described in Section 6.4. Axes labeled for ECD.

procedure was envisioned, whereby the first chlorination would produce the halogenated by-products and dechlorination would eliminate some of these NVCO. The second chlorination should not produce any chlorination products since the precursors would have been eliminated. This scheme, however, has shown very little success. Apparently, the NVCO are reduced by sodium sulfite and rendered unchromatographable, but a subsequent chlorination oxidizes them to their previous chromatographable state. Figure 47 is a schematic of proposed reactions.

This procedure has been attempted nearly fifty times with very little success. The carbon adsorption effluent from the San Diego Wastewater Treatment Plant, as well as the aquaculture XAD8 extract were the chlorinated samples. The initial chlorination (the precursor consumption step) was attempted at pH 3, 7 and 11. High chlorine doses (10, 20, 40 and 100 mg/L) were used as well as long contact times (4-24 hours). The high chlorine doses and long contact times were intended to maximize the reaction of the precursors with chlorine. The second chlorination was always done for two hours at pH 7 using a 10 mg/L chlorine dose. The chromatograph of this twice chlorinated extract is then compared to a sample which was chlorinated for two hours at pH 7 using a 10 mg/L chlorine dose. The sodium sulfite addition step was done at various pH values since the $SO_3^=$ ion has different redox potentials at the various pH's. In summary, no set of conditions was found which yields any significant treatment. Figure 48 serves as an illustrative example of the limited success shown by this method. The sample used to generate Figure 48 was chlorinated for 4 hours at pH 11, dechlorinated at pH 11 with excess sulfite (five fold excess), then chlorinated again at pH 7 with 10 milligrams of chlorine for two hours. The figure shows the sizeable total ECD area drop after dechlorination and its subsequent reappearance after the second chlorination.

Dechlorination has been shown to be a viable treatment for reducing the levels of the produced NVCO (Sections 5.2 and 5.3). Since it is necessary to maintain a chlorine residual in discharged waters, the effect of partial dechlorination on the observed halogenated organics was investigated. One liter of carbon adsorption effluent from the San Diego Wastewater Treatment plant was chlorinated using a 10 mg/L dose at pH 7 for two hours. The extractable organics were analyzed after partial and full dechlorination. Partial dechlorination (4 mg/L total available chlorine) results in a 65% decrease in the total ECD area and total dechlorination results in a 90% decrease in total ECD area. Partial dechlorination is consequently a desirable unit operation which is capable of significant reduction in the observed halogenated organics levels.

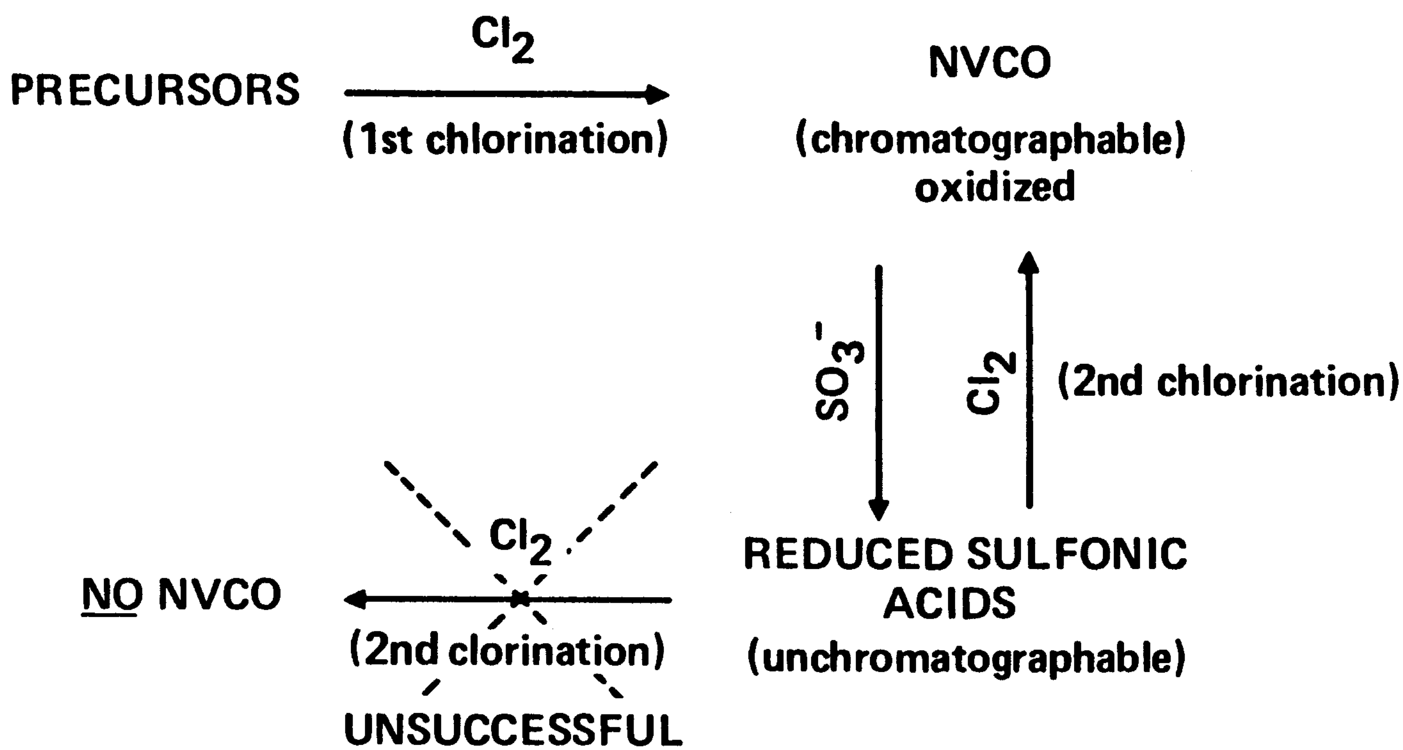


Fig. 47 Schematic of the Proposed 2-Stage Chlorination Scheme

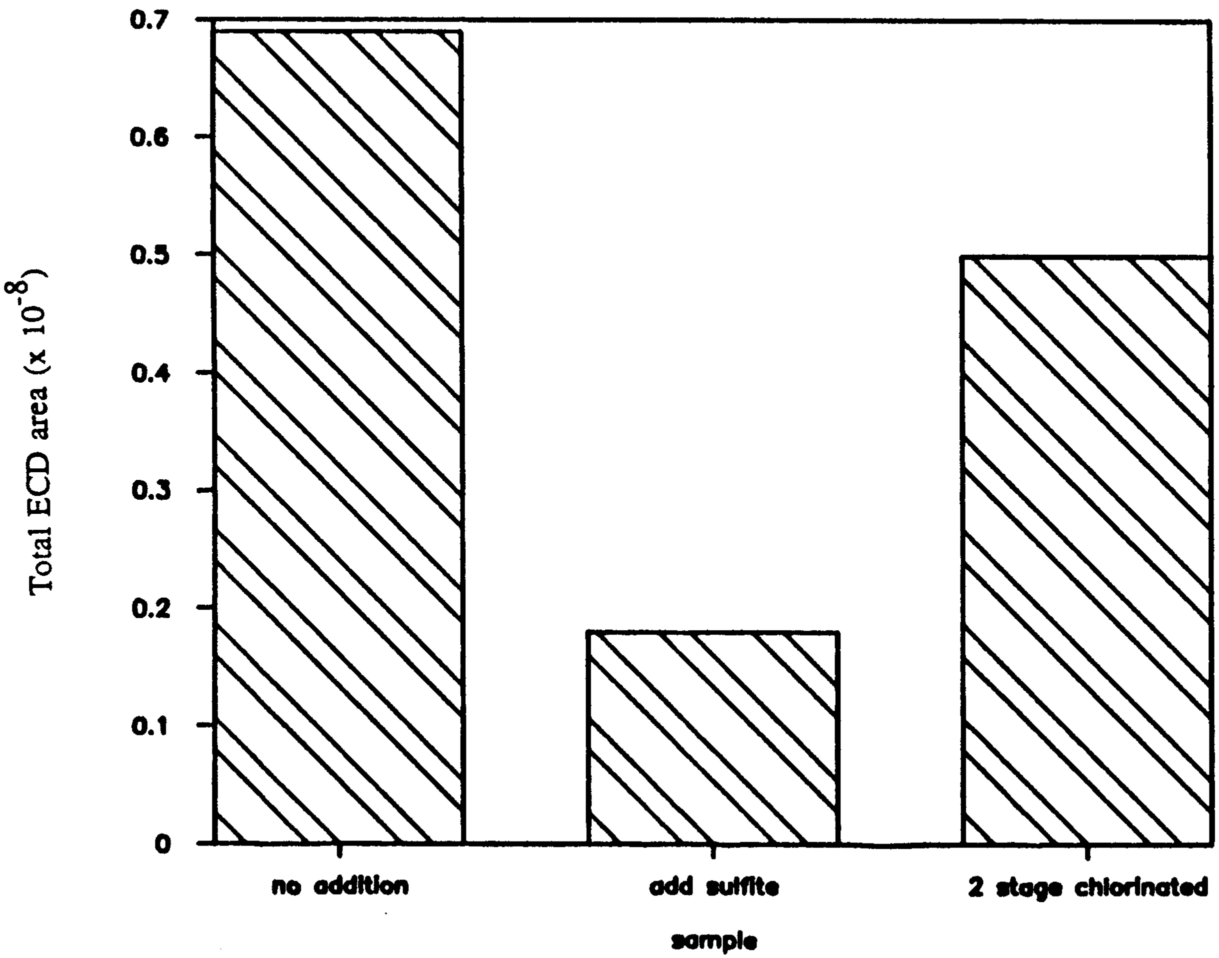


Fig. 48 Treatment of NVCO Levels by 2-Stage Chlorination

V. SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

This research work has focussed on the gas chromatographable non-volatile halogenated organics produced during the disinfection of water. Analysis, formation and treatment of these compounds were investigated. An improved analytical technique for the analysis of these compounds was developed which indicated that dechlorination prior to sample analysis is undesirable. The major precursors to the observed halogenated compounds are characterized. Third, some of the formed NVCO are identified. Fourth, chlorination parameters were varied to assess their importance for NVCO formation. Last, several treatment alternatives were screened for their abilities to reduce NVCO levels. The results from each of these five goals are listed below.

1. It was observed that many of the produced compounds are reactive with dechlorinating agents (sodium sulfite and sodium thiosulfate) and that they had escaped detection by workers who dechlorinated their samples prior to extraction. It is postulated that the sulfite ion undergoes a substitution reaction with halogen atoms. The most reactive group of compounds towards the sulfite ion was found to be the unsaturated, halogenated aliphatics. The sulfite ion was shown to be reactive with aqueous solutions of pure unsaturated halogenated compounds.

   If knowledge of the exact reaction time between chlorine and the TOC in the water samples is not required, then use of dechlorinating agents is unnecessary. Researchers who require exact knowledge of reaction times in their analytical laboratory experiments may remove residual chlorine by rotoevaporation (Kringstad 1985) or perform the extraction in a time period which is small compared to the studied reaction times. Dechlorinating agents should only be added if the compounds of interest are known to not be reactive with the sulfite ion.

2. The major precursors to the observed halogenated compounds were found to be slightly organic solvent (methylene chloride) soluble and to have molecular weights less than 1000 daltons. The precursors were found to be collectible in the fraction that many workers call aquatic fulvic acid (Thurman and Malcolm 1983). The fact that these compounds are organic solvent soluble however, makes it difficult to continue to call them fulvic acids simply because they are yellow and are collectible by an adsorption method designed to collect humic and 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 observed compounds.

Table 22 lists the characteristics of the precursors and cites the section in the Results and Discussion chapter in which the experiment is discussed.

Flavones and flavenols provide good laboratory models of the precursors since they give similar chlorination patterns upon chlorination to the observed NVCO at the San Diego plant. The tested flavone compounds also possess similar MW and solubility properties to the

Table 22 Precursors Characteristics

Observation	Reason	Section in Results and Discussion
1. Precursors are acidic	XAD8 adsorbable in acid	3.1
2. Precursors are polar	column chromatography polar fraction	3.2
3. Precursors can't 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	3.7
5. Precursors are common to water	present in tested water samples	3.8
6. Precursors may be colored	all NVCO productive fractions were pale yellow to bright yellow	3.1,3.3-3.9
7. Flavenols and flavones provide good precursor models	similar properties similar GC pattern	3.1-3.9

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 which the molecules may undergo.

3. The unavailability of a mass spectrophotometer on a routine basis made positive identification of the observed halogenated compounds a difficult task. In general, three categories of compounds were observed. Unsaturated, heavily chlorinated compounds which were reactive with sodium sulfite were identified. Chlorinated furan structures, as well as chlorinated phenolics, were also observed. The chlorinated furans were slightly reactive with sodium sulfite but the chlorophenols were unaffected by dechlorination.

4. It was observed that pH, chlorine dose, contact time, as well as bromide ion concentration greatly affect the relative distribution, as well as the total amounts of the chlorination by-products. A general recommendation of chlorination conditions is intentionally not presented; however, minimization of the observed NVCO occurred at low pH, long contact time and medium chlorine doses.

The NVCO which were monitored in this study are only a fraction of the total TOX formed upon chlorination. A recommendation of general chlorination conditions is dependent on the minimization of the most harmful components of TOX. A study which would address the formation of all the components of TOX and their relative toxicity would be needed to properly recommend chlorination conditions. Studies in the past which have recommended low chlorine dose in order to minimize THM formation would maximize the formation of some of the compounds observed in this study.

In addition to minimizing the harmful chlorination by-products, pH, chlorine dose and contact time can potentially be used to form components of TOX which are amenable to a subsequent treatment step. Conditions which maximize THM formation and minimize NPTOX formation can be used if aeration is used as a final polishing step. Conditions which lead to the formation of heavier components should be used if carbon adsorption is used as a final treatment step.

5. Several treatment schemes were screened for their ability to minimize the formation of the observed halogenated compounds. Carbon adsorption after chlorination was found to be the most effective treatment scheme. Chlorination using chloramines as well as partial dechlorination were also found to be effective treatment alternatives. Aeration was not found to be an effective treatment scheme since even the lightest components of the formed NVCO were not easily purged. Ozone treatment prior to chlorination changes the relative amounts of the formed halogenated organics. The importance of this latter observation depends on the relative toxicity of the various components.

The San Diego wastewater treatment plant effectively removes 97% of the extractable organics from the secondary effluent after carbon adsorption. The problematic treatment step at the plant is chlorination. Chlorination prior to carbon adsorption would be recommended.

This chlorination step would be consumptive of the organic precursors and the carbon adsorption process is capable of removing a sizeable fraction of the formed TOX. Carbon adsorption will also dechlorinate the water which would necessitate a second chlorination after carbon treatment. This second chlorination should not be as TOX productive as the initial chlorination since much of the precursors would have been consumed in the initial chlorination. Partial dechlorination shall be performed after this second chlorination step.

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Appendix 1

In order to better select the most desirable membranes for the proposed expansion of the San Diego Aquaculture treatment system, a "cocktail" composed of various compounds was prepared. These compounds were selected to represent several classes of chemicals. Each class was selected with several similar compounds with different substitutions.

Several iterations of the cocktail formulation were made. Finally the list of compounds shown in Table A1 was selected. These were all soluble enough to be conveniently introduced in the RO feedwater. The compounds were also selected to be identifiable by the previously described GC procedure. The concentration was adjusted to provide approximately 100 μg/l in the RO feedwater, so the product water will remain above minimum detection levels.

The cocktail containing the selected compounds was solubilized in 5 gallons of methanol. The methanol was then diluted to 100 gallons with warm tap water. The tap water was then injected into the RO feedwater pump suction line at 5.0 GPM for 18 minutes. This flow represented approximately 10% of the RO feedwater flow. Brine and product water samples were collected after 25 minutes of operation. This sampling time was determined by using a salt tracer, which showed that 25 minutes was sufficient to allow the cocktail to reach the RO brine water.

A cocktail for selenate and selenite was also used. This cocktail consisted of a 100 gallon solution of each compound. Each tank was injected as described previously. Initial selenate or selenite concentration in the feed water containing the cocktail was 300 μg/l.

At the time of the survey, the RO plant was arranged into three stages of 14, 7 and 3 membranes (pyramid fashion). The last three membranes were changed from the CA membranes traditionally used to the three test low pressure membranes by adding a pressure reducing value. By collecting the brine and product water from each type of membrane, four evaluations were made.

Table A1 shows the results of the survey. In general, all four membranes provided excellent rejection. The ketones were not rejected by the cellulose acetate membranes, and as a result, no analysis of the low pressure membranes could be made. An interference to the aniline analysis occurred, and the data shown in Table A1 for aniline are spurious.

Table A1. Contaminant Mass Rejected by Membrane Type[1]

Compound	Cellulose Acetate	Membrane Type Film Tech	Fluid Systems	Desalination
2-octanone	-8.44	ND	ND	ND
2-nonanone	12.54	ND	ND	ND
tetradecane	100.	98.26	100.	95.10
tetradecene	100.	97.33	100.	95.08
hexadecane	100.	97.89	100.	92.16
hexadecene	100.	98.23	100.	95.03
aniline	-149.71	ND	ND	ND
decanol	93.34	100.	100.	100.
octadecane	100.	98.64	100.	95.93
chlorophenol	58.20	98.43	97.12	97.37
octadecene	100.	98.53	100.	95.58
phenol	27.20	97.46	96.64	95.46
eicosane	100.	98.59	100.	98.02
2,5-dimethylphenol	51.65	ND	ND	ND
m-cresol	29.82	96.24	96.54	92.16
hexadecanone	100.	98.43	99.88	96.28
propyl phenol	88.60	96.75	98.17	92.15
2,3 dimethylphenol	65.57	94.88	93.17	88.98
butyl phenol	87.20	98.05	99.19	94.95
2,4,6 trichlorophenol	99.98	98.44	99.97	98.06
hexadecanol	97.55	99.12	100.	97.11
2,4,5 trichlorophenol	99.95	98.47	99.87	88.45
octadecanol	97.77	98.92	100.	97.46
selenate	97.48	99.18	99.35	97.72
selenite	97.62	97.95	95.42	96.31

Key: ND not detected, due to interferences or too low concentration in the feed-water to the third stage.

1 Table values calculated as follows:

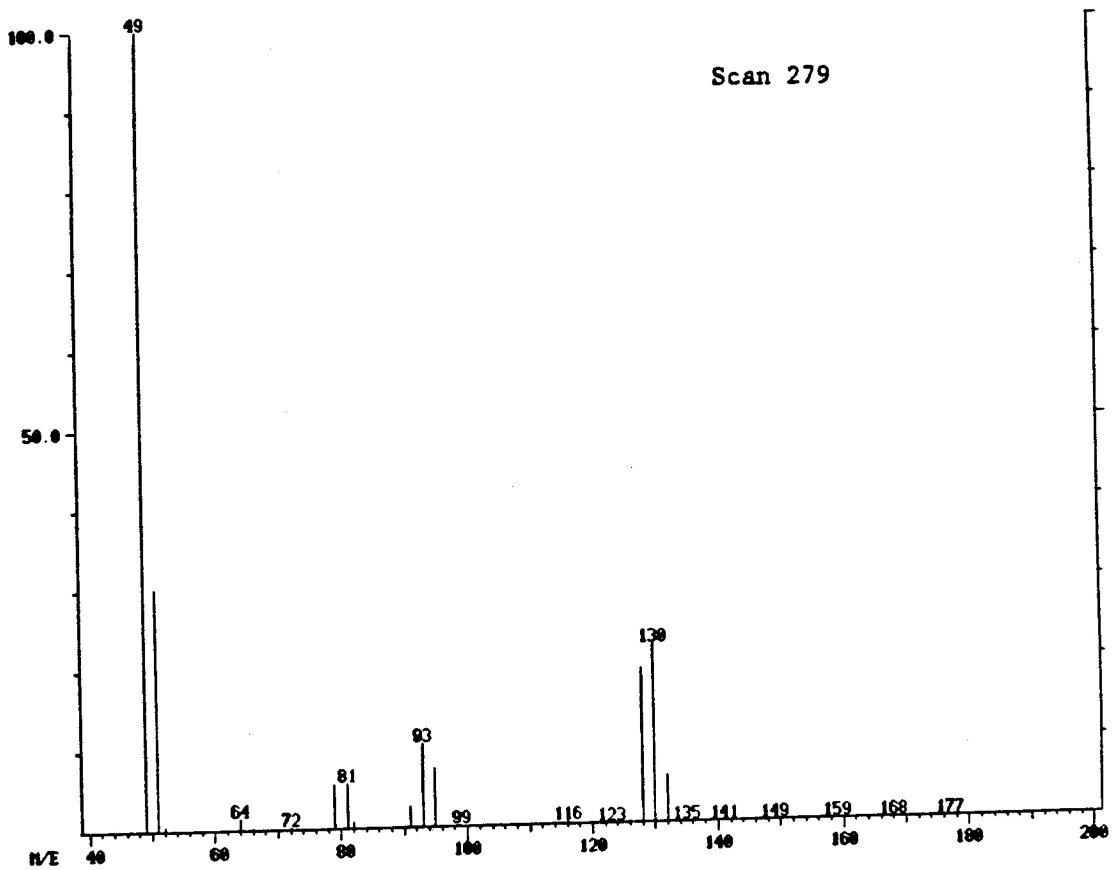
$$Rejection = 100\left[1. - \frac{Q_p\, C_p}{Q_f\, C_f}\right]$$

where

Q_f = Feed flow rate
Q_p = Product flow rate
C_f = Feed concentration
C_p = Product concentration

Appendix 2

Computer reconstructed electron impact mass spectra (MS) of some of the halogenated compounds listed in Table 14 are shown in the following pages.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50.0
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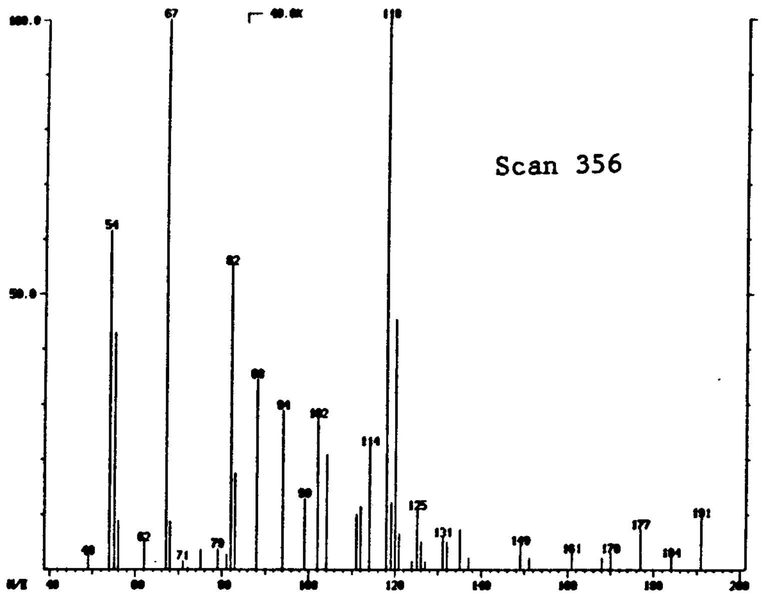
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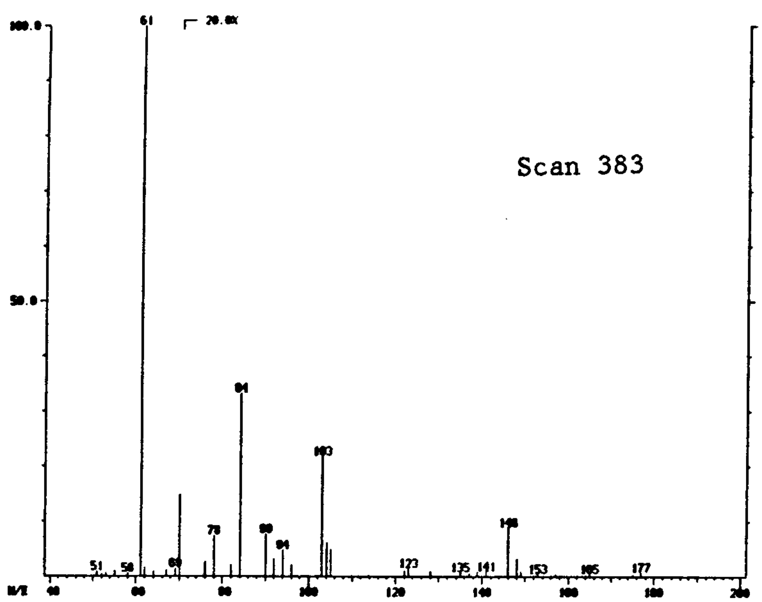
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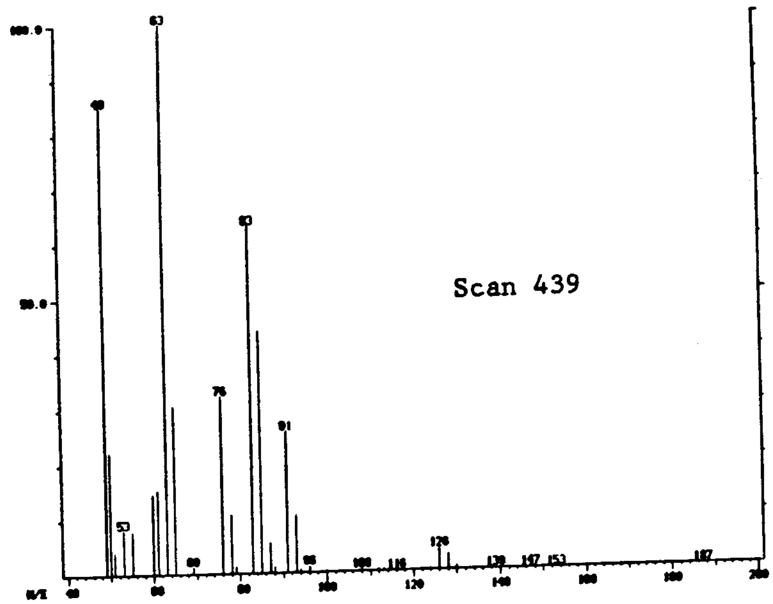
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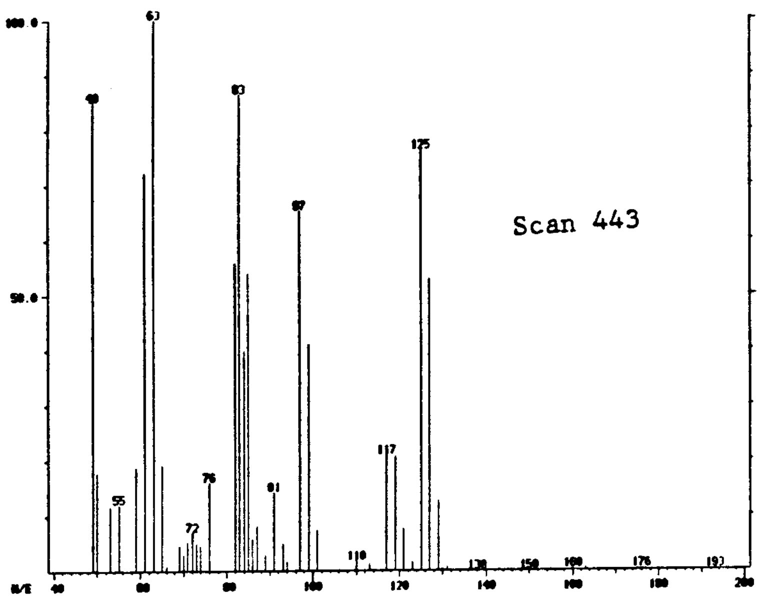
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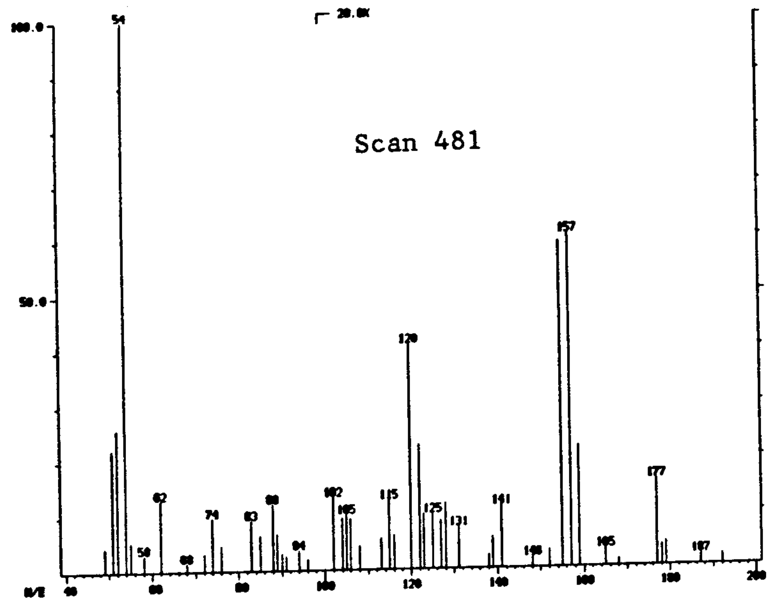
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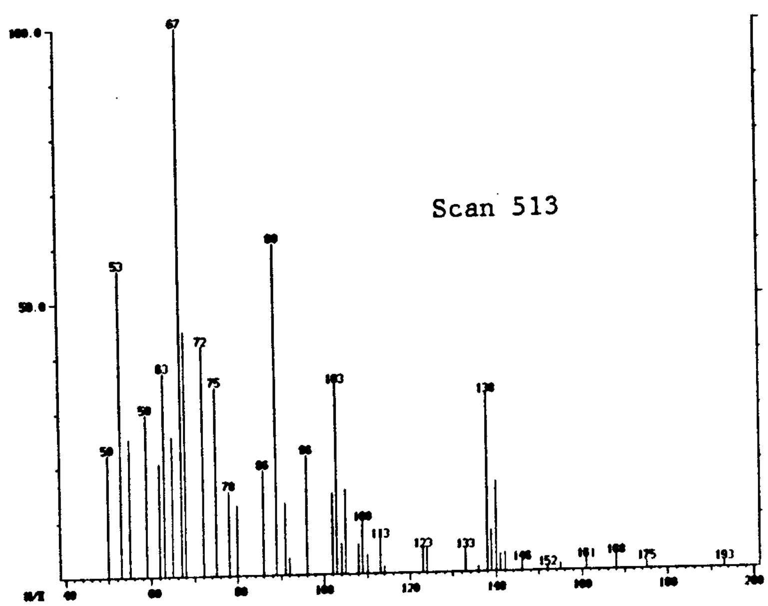
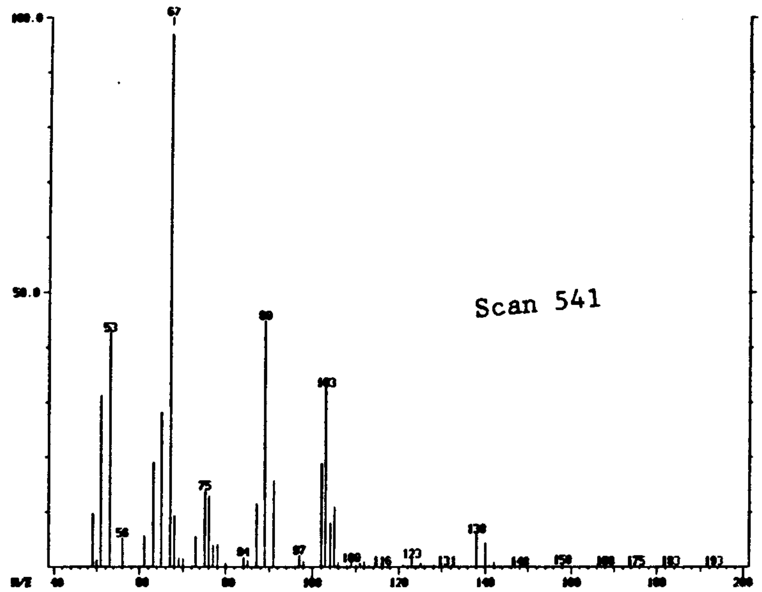
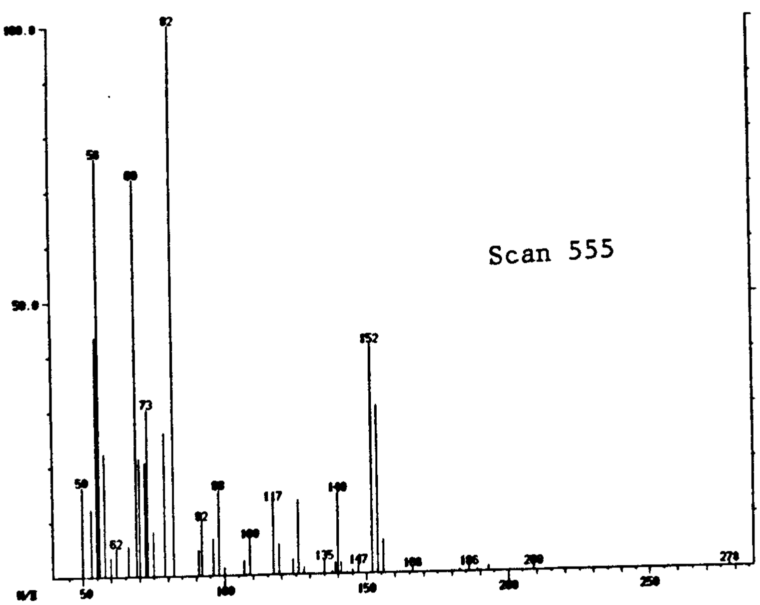
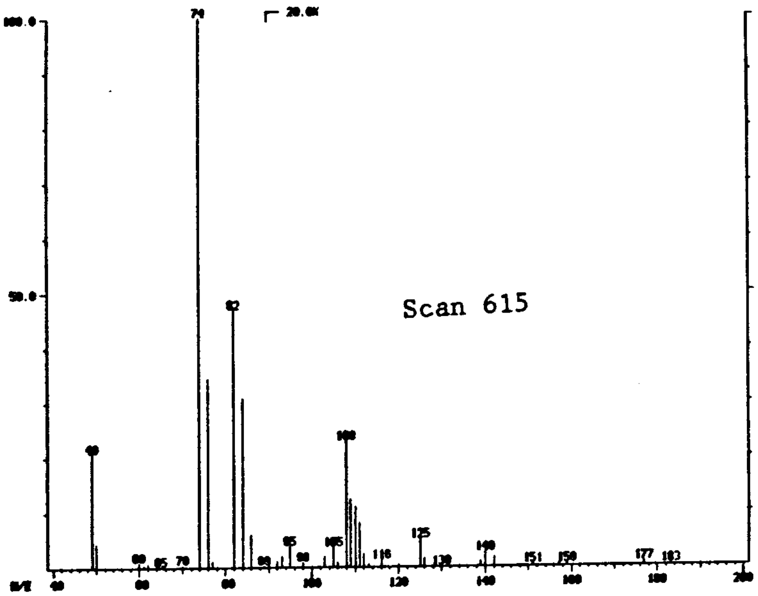
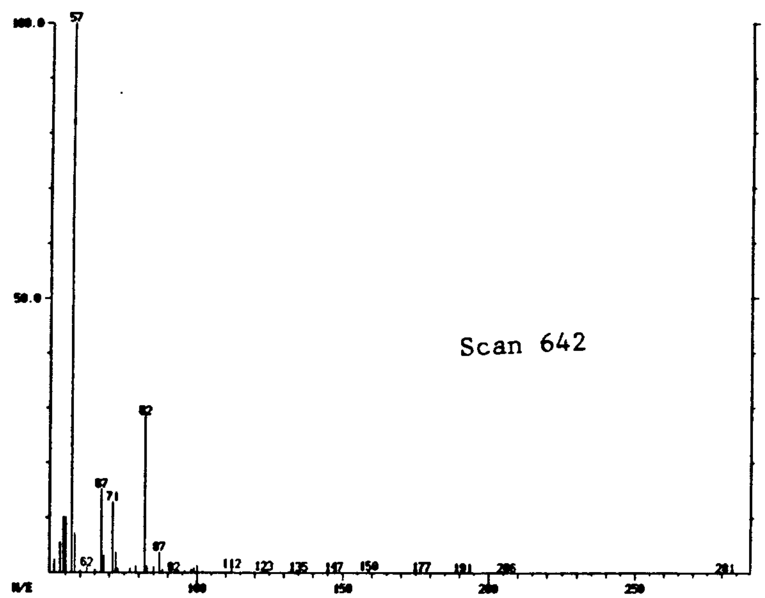
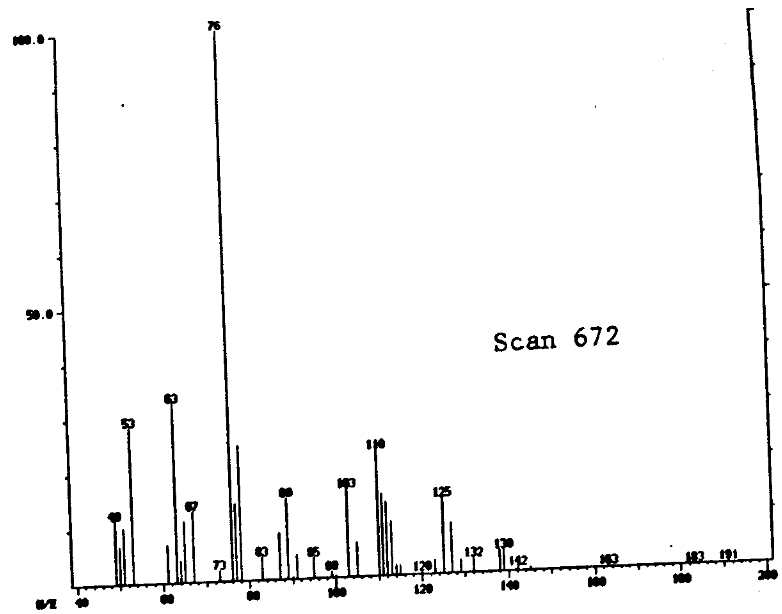

Scan 513

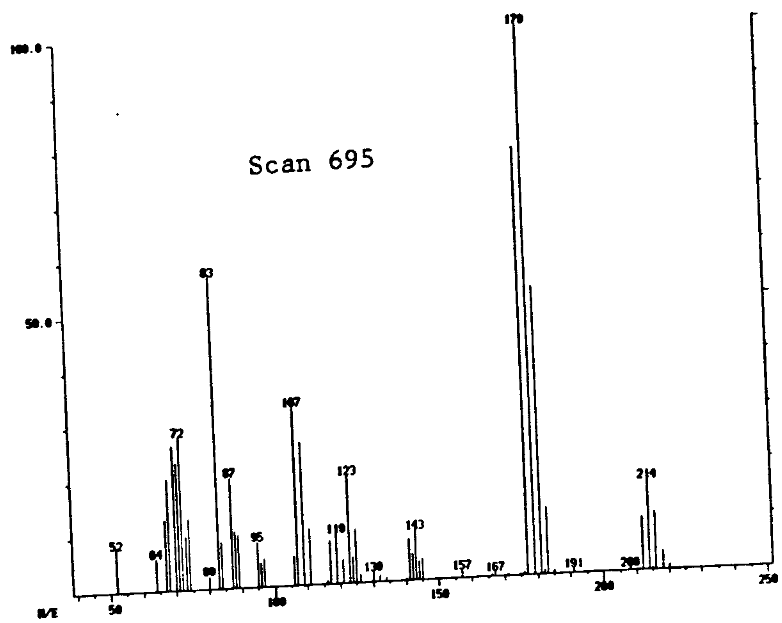

Scan 541

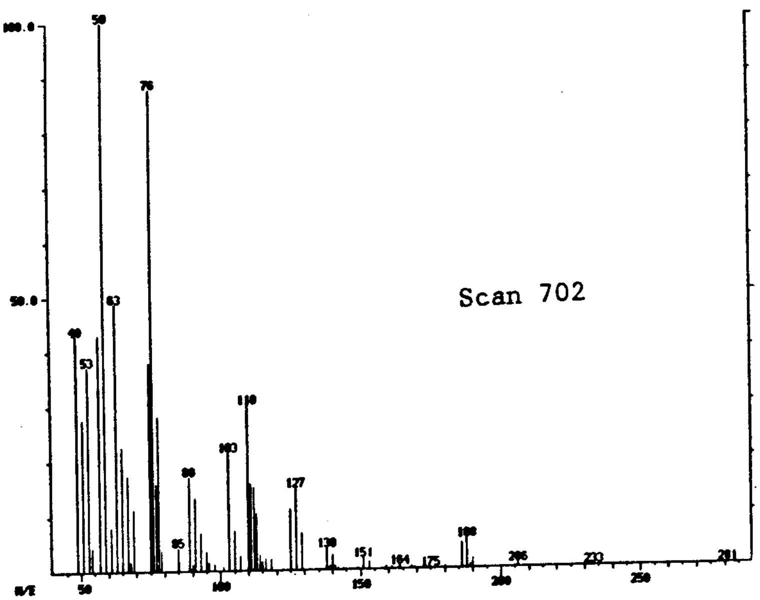

Scan 555


Scan 615
100.0
50.0
74
82
108
125
140
151
159
177
183

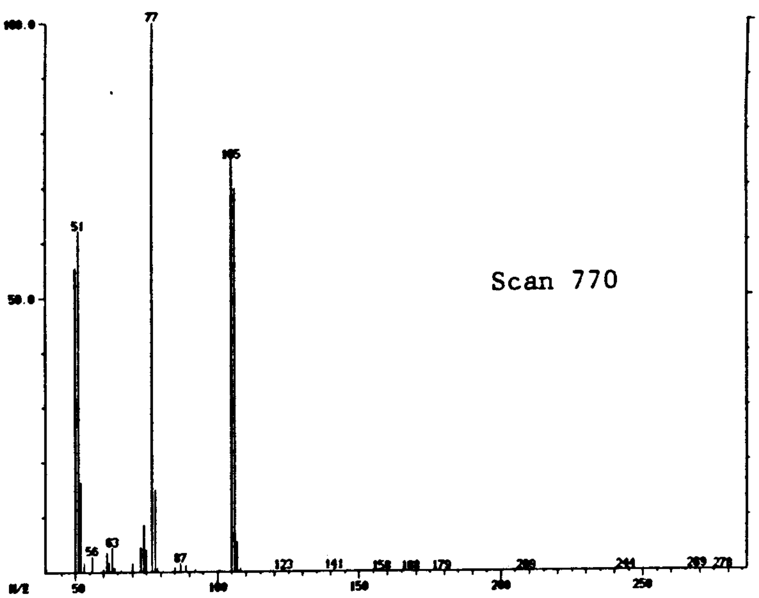

Scan 642
100.0
50.0
57
82
67
71
87
62
92
112
123
135
147
159
177
191
206
281


Scan 672

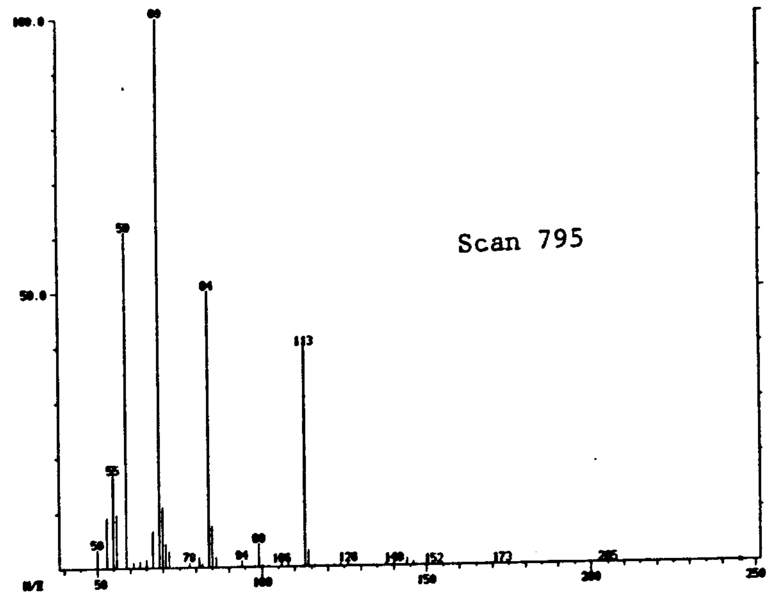

Scan 695

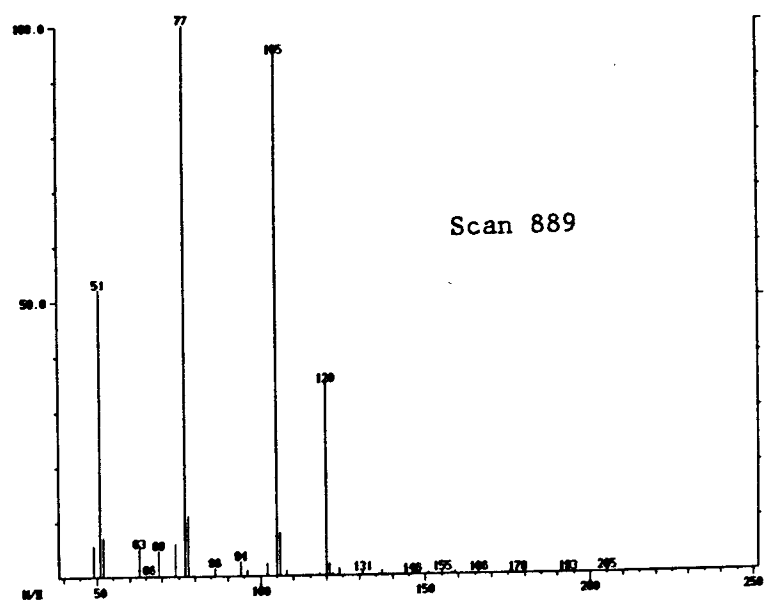


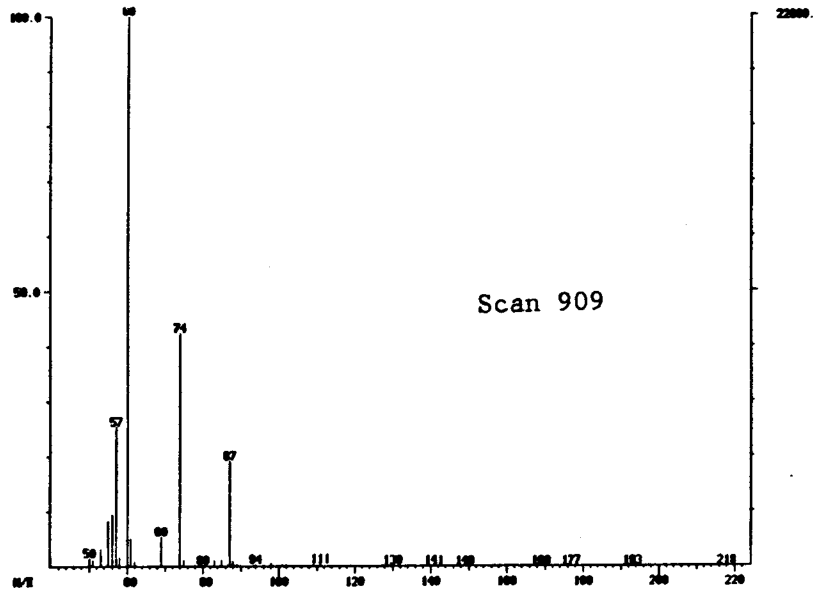
Scan 702

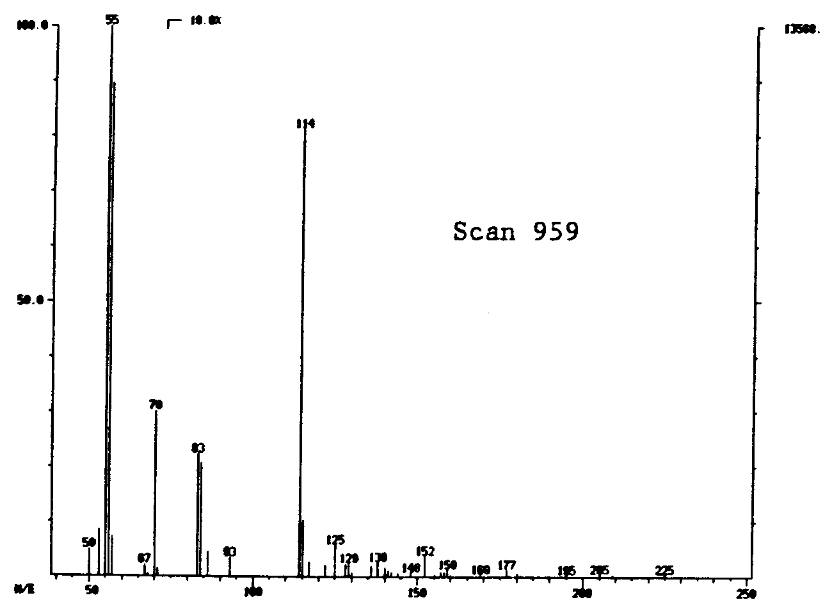


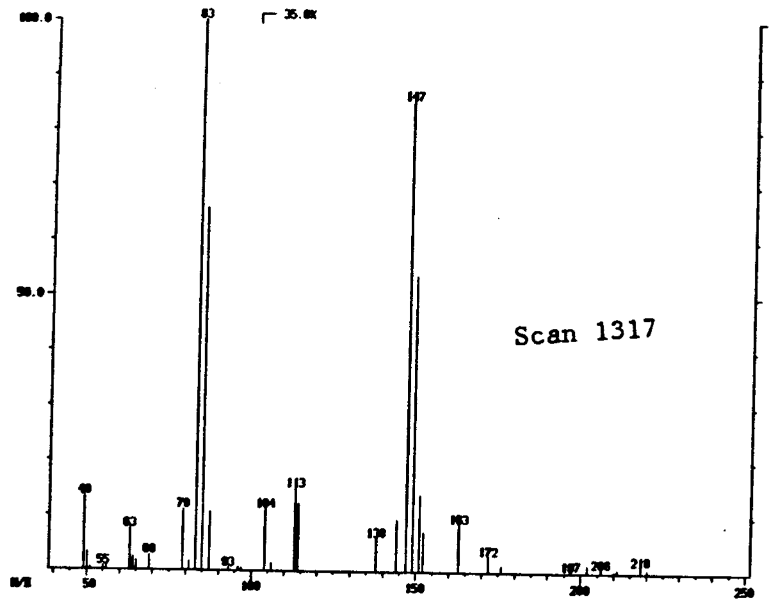
Scan 770

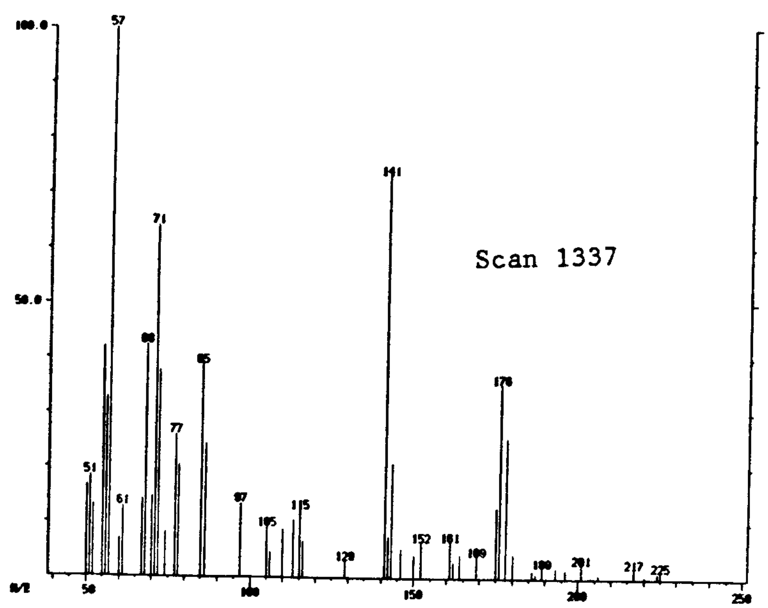

Scan 795

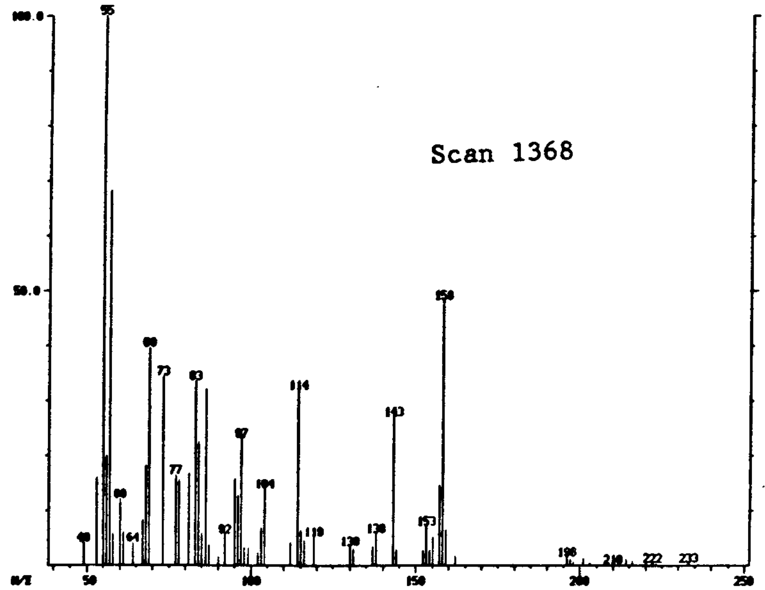

Scan 889

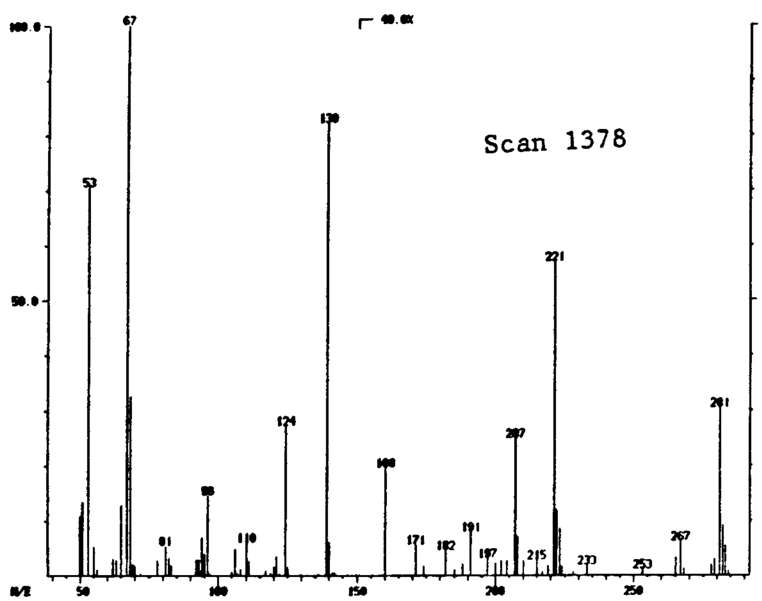

Scan 909
57
74
87
111
177

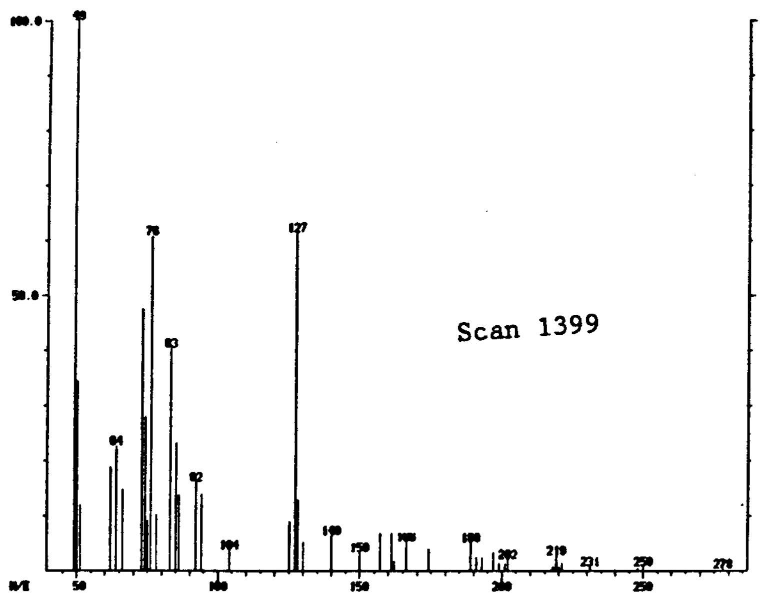

Scan 959
55
114
83
93
125

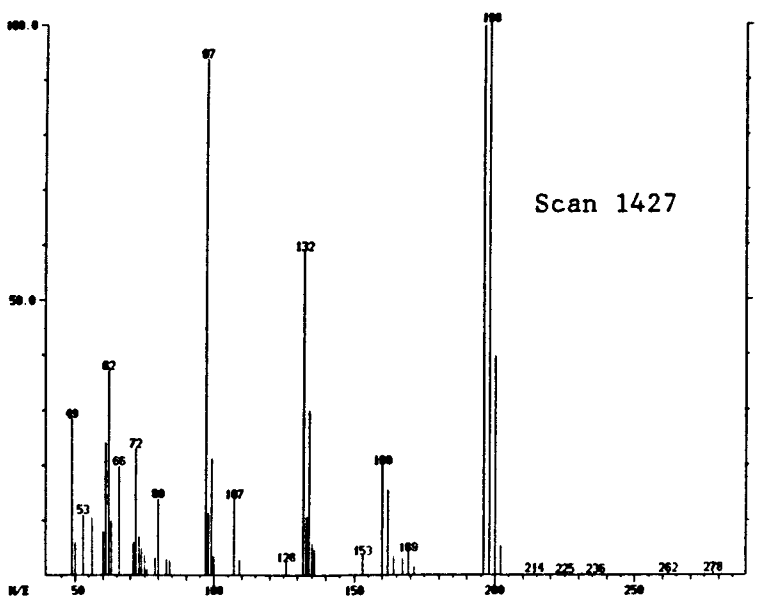

Scan 1317

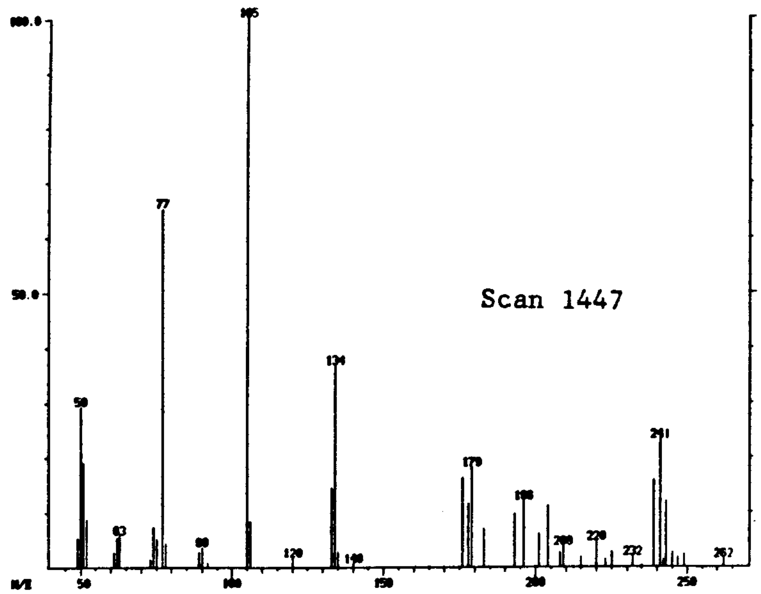

Scan 1337

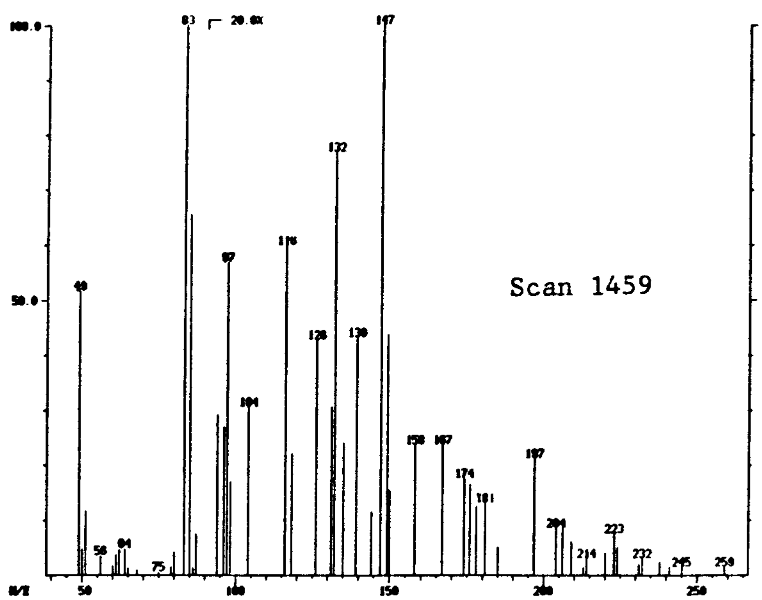

Scan 1368

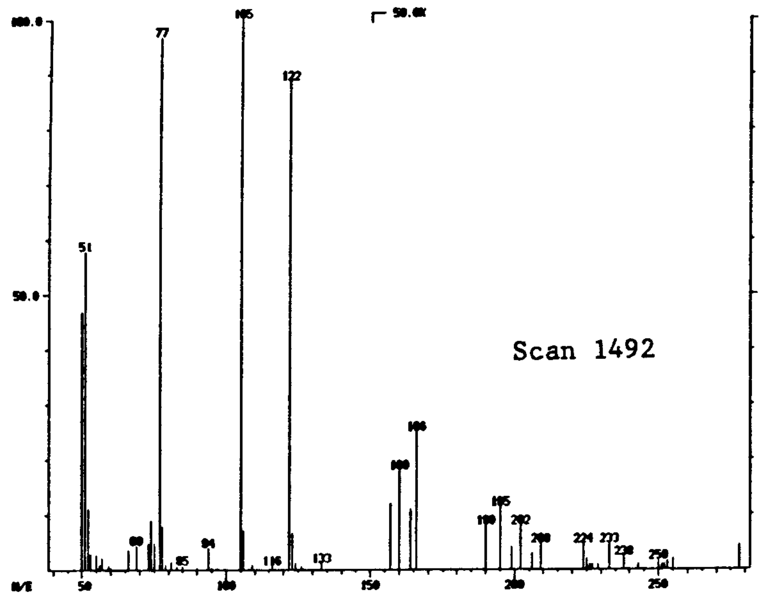

Scan 1378

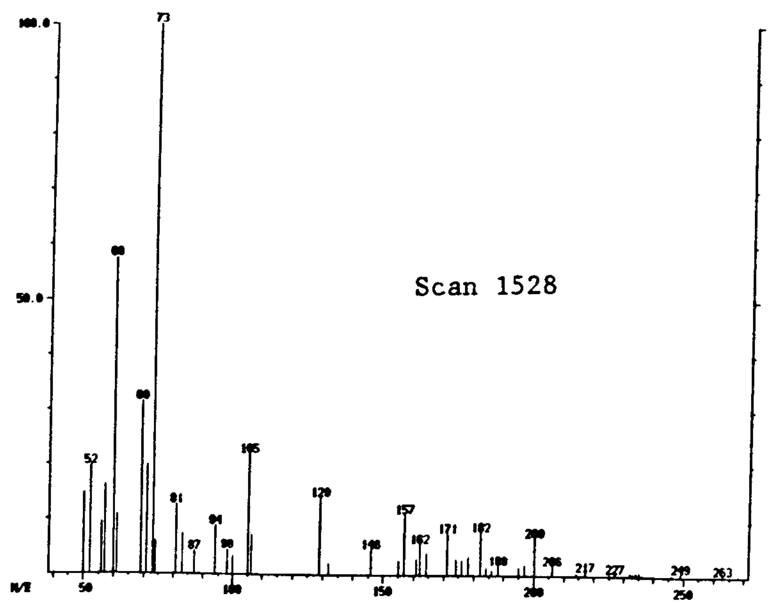

Scan 1399

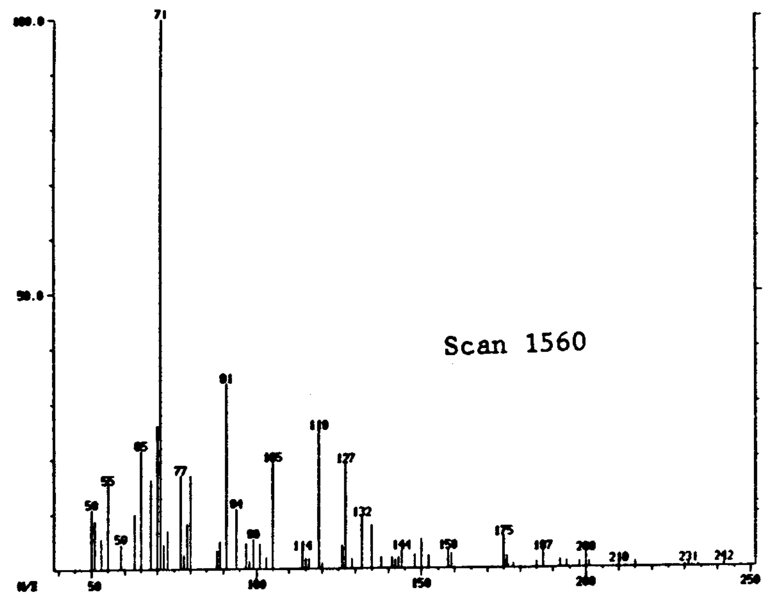

Scan 1427

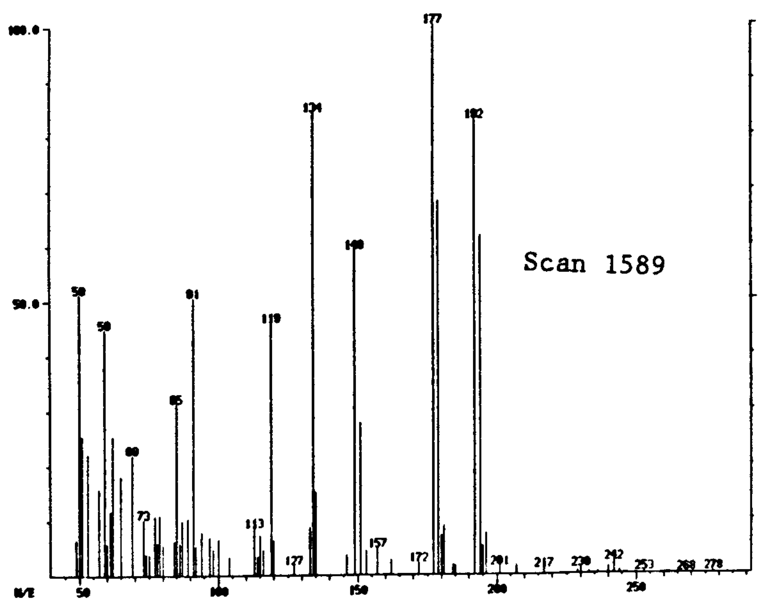

Scan 1447

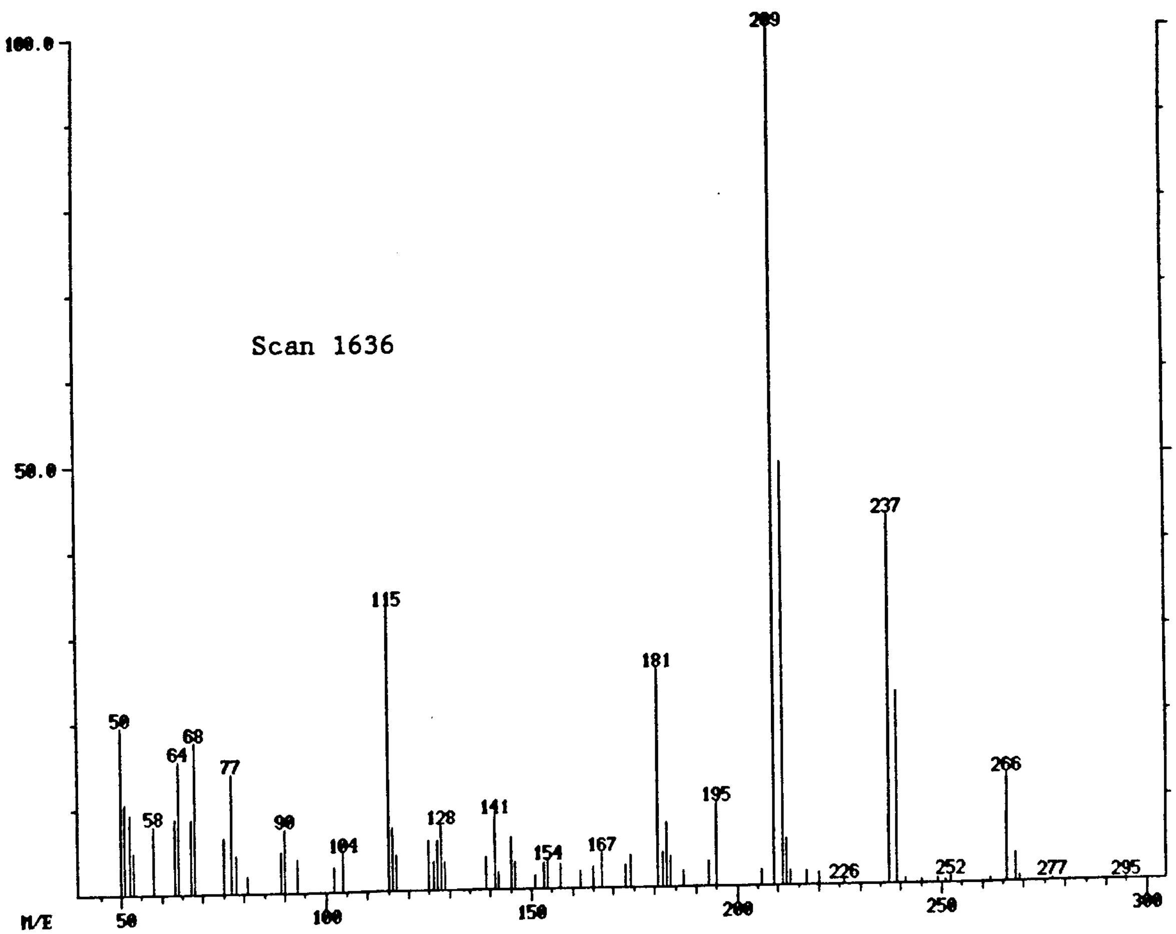

Scan 1459


Scan 1492


Scan 1528


Scan 1560


Scan 1589


Scan 1636
100.0
50.0
M/E
50
100
150
200
250
300
209
237
115
181
50
68
64
77
58
90
104
128
141
154
167
195
226
252
266
277
295

APPENDIX 3

Some of the Hewlett Packard integrator output from one of the experiments designed to assess the effects of chlorine dose, contact time and pH on the formation of the observed halogenated compounds is provided in this appendix. 1 mg TOC (XAD8 aquaculture extract) was chlorinated at varying chlorine doses, contact times and pH values.

The base conditions of 2.5 mg chlorine, pH 7, and two hour contact time are shown below (Table A3). The identified peaks are labeled by reference numbers in this chromatograph (see Table 14). The formation of these compounds may be followed in subsequent chromatographs by retention time matching (RT). The retention times usually match within a 0.04 minute window. The subsequent chromatographs include checkpoints to aid the interested reader in matching the retention times. The checkpoints indicate the difference (RT) at that point in the chromatograph from the base conditions. The retention time difference for peaks between checkpoints from the base conditions (Table A3) can be evaluated by interpolation.

These files were not edited so as to allow for calculation of total areas within desired retention time regions. For example, it is possible to group the areas of compounds eluting before a given retention time or of 'A#' compounds or in any other desired fashion. The area rejection was set at 10,000 counts. All chromatographs were run at identical dilutions and the area counts are directly comparable. Table A2 lists the chlorination conditions of the chromatographs shown in this appendix.

Table A2 List of Chlorination Conditions and Table Numbers

Table Number	pH	Chlorine dose (mg)	Time (hours)	Bromide (mg)	TOC (mg)
A3	7.0	2.5	2.0	0.0	1.0
A4	7.0	5.0	2.0	0.0	1.0
A5	7.0	10.0	2.0	0.0	1.0
A6	7.0	20.0	2.0	0.0	1.0
A7	7.0	40.0	2.0	0.0	1.0
A8	7.0	1.0	2.0	0.0	1.0
A9	7.0	0.5	2.0	0.0	1.0
A10	7.0	2.5	0.25	0.0	1.0
A11	7.0	2.5	0.5	0.0	1.0
A12	7.0	2.5	1.0	0.0	1.0
A13	7.0	2.5	4.0	0.0	1.0
A14	7.0	2.5	8.0	0.0	1.0
A15	7.0	2.5	24.0	0.0	1.0
A16	3.0	2.5	2.0	0.0	1.0
A17	5.0	2.5	2.0	0.0	1.0
A18	9.0	2.5	2.0	0.0	1.0
A19	11.0	2.5	2.0	0.0	1.0
A20	7.0	10.0	2.0	5.0	1.0

Table A3

Base chlorination conditions

RUN # 782, APR/29/86 ,20:15:38
WORKFILE ID: C ,WORKFILE NAME:
ID: 000
AREA%

RT	AREA	TYPE	AR/HT	AREA%	Reference Number
5.48	2019300	BB	0.149	2.285	A1
6.59	1117300	BV	0.084	1.264	A2
6.63	2039300 D	VV	0.154	2.308	A3
7.21	278390	VP	0.207	0.315	
7.61	10631	PP	0.086	0.012	
7.86	3.1797E+07	PV	0.219	35.982	A4
8.05	2.3110E+07 D	VB	0.236	26.152	A5,6
9.84	98496	BV	0.155	0.112	A9
10.18	302310	VV	0.172	0.342	A10
10.69	512090	VV	0.111	0.580	A11
10.86	1252300	VV	0.135	1.417	
11.09	402370	VP	0.169	0.455	A12
11.95	55371	VV	0.163	0.063	A13
12.06	44917	VV	0.127	0.051	
12.58	63395	PV	0.171	0.072	
12.93	43996	PP	0.089	0.050	
13.37	3457300	PB	0.119	3.912	A14
14.09	20853	VV	0.078	0.024	
14.21	56096	VV	0.098	0.064	
14.40	79262	VV	0.106	0.090	
14.48	78979	VV	0.082	0.089	
14.62	460620	VV	0.205	0.521	
14.88	445210	VV	0.221	0.504	
15.06	77692 D	VV	0.044	0.088	
15.22	349180	VV	0.158	0.395	
15.33	586110	VV	0.256	0.663	A16
15.71	2233400	VV	0.143	2.527	A17
16.09	803960	VB	0.212	0.910	
16.93	1809300	BB	0.121	2.047	A18
17.69	15194	PV	0.108	0.017	
17.95	80018	VV	0.103	0.091	A19
18.15	25342	VV	0.151	0.029	
19.13	13955	PV	0.123	0.016	
19.38	42634	BP	0.074	0.048	A21
19.67	21352	PP	0.117	0.024	
20.99	24074	PP	0.083	0.027	
21.55	15257	PH	0.078	0.017	
21.78	27450	HH	0.154	0.031	
22.09	20657	HP	0.108	0.023	
22.64	50717	HP	0.087	0.057	A23
23.48	10601	PH	0.128	0.012	A24
23.57	14676	HH	0.095	0.017	
23.70	22503	HH	0.082	0.026	
23.81	47347	HH	0.126	0.054	
24.05	10941	HV	0.072	0.012	
24.16	41245	VV	0.087	0.047	
24.27	48377	VV	0.143	0.055	
24.48	12008	VV	0.087	0.014	
24.72	47344	VV	0.123	0.054	
25.19	111340	VV	0.141	0.126	
25.41	335870	VV	0.134	0.380	A25
25.60	115100	VV	0.133	0.130	
25.78	60222	VV	0.102	0.068	
26.05	67571	VV	0.150	0.077	
26.26	27283	VV	0.119	0.031	
26.37	25479	VV	0.112	0.029	
26.50	27069	VV	0.135	0.031	
26.76	11784	VV	0.107	0.013	
27.02	41624	VV	0.157	0.047	
27.30	42170	VV	0.170	0.048	
27.49	13768	VV	0.069	0.016	
27.56	13523	VV	0.061	0.015	
27.78	12904	VV	0.084	0.015	
27.91	53072	VV	0.118	0.060	
28.07	29939	VV	0.098	0.034	
28.21	64137	VV	0.151	0.073	
28.44	60400	VV	0.121	0.068	
28.88	30381	VV	0.160	0.034	
29.13	49602	VV	0.207	0.056	
29.57	22100	VV	0.106	0.025	
29.75	15152	VV	0.098	0.017	
29.87	19662	VV	0.104	0.022	
29.97	32946	VV	0.113	0.037	
30.18	11005	VV	0.075	0.013	
30.29	14316	VV	0.120	0.016	
30.61	66318	VV	0.143	0.075	
30.87	16042	VV	0.111	0.018	
31.12	12564	VV	0.102	0.014	
31.26	93445	VV	0.105	0.106	
31.42	41837	VV	0.099	0.047	
31.75	17537	VV	0.090	0.020	
31.89	20457	VV	0.082	0.023	
32.01	20227	VV	0.105	0.023	
32.20	31312	VV	0.134	0.035	
32.30	18458	VV	0.089	0.021	
32.63	70876	VV	0.140	0.080	
32.90	37464	VV	0.105	0.042	
33.09	84656	VV	0.095	0.096	
33.28	26200	VP	0.074	0.030	
33.46	23445	PV	0.081	0.027	
34.30	88092	VV	0.141	0.100	
34.45	32263	VV	0.082	0.037	
34.92	22381	BP	0.076	0.025	
35.30	53063	PH	0.101	0.060	
35.51	12980	HH	0.109	0.015	
35.73	12848	HH	0.108	0.015	
35.82	19076	HH	0.097	0.022	
35.95	21447	HH	0.085	0.024	
36.07	100920	HH	0.173	0.114	

36.47	200330	HH	0.138	0.227	D1
36.73	201390	HH	0.134	0.228	D2
37.01	896660	HH	0.092	1.015	D3
37.25	42306	HH	0.091	0.048	
37.40	268870	HH	0.139	0.304	
37.63	159790	HH	0.125	0.181	D4
38.06	35389	HH	0.129	0.040	
38.23	111580	HH	0.118	0.126	
38.44	94485	HH	0.142	0.107	
38.89	56219	HH	0.169	0.064	D5
39.11	1042200	HV	0.099	1.179	D6
39.34	304190	VV	0.200	0.344	
39.85	405050	VV	0.180	0.458	D7
40.07	418600	VV	0.161	0.474	
40.33	64641	VV	0.081	0.073	
40.39	96067	VV	0.120	0.109	
40.58	114230	VV	0.146	0.129	
40.81	192220	VV	0.149	0.218	D8
41.10	48908	VV	0.109	0.055	
41.46	1274000	VV	0.168	1.442	D9
41.75	97637	VV	0.112	0.111	
42.25	10557	VV	0.075	0.012	
42.54	13494	VV	0.113	0.015	
42.84	117030	VV	0.191	0.132	
42.99	92710	VV	0.176	0.105	D10
43.38	51834	VV	0.129	0.059	
43.53	30531	VV	0.101	0.035	
43.78	88720	VV	0.112	0.100	
43.96	19936	VP	0.101	0.023	
44.23	68401	PV	0.093	0.077	
44.47	148110	VV	0.156	0.168	D11
44.75	324470	VV	0.110	0.367	
44.96	23476	VV	0.101	0.027	
45.21	47977	VV	0.100	0.054	D12
45.59	18900	VV	0.107	0.021	
45.98	39080	VV	0.125	0.044	
46.15	34089	VV	0.143	0.039	
46.33	66889	VV	0.152	0.076	D13
46.51	26700	VV	0.115	0.030	
46.69	13461	VV	0.087	0.015	
46.91	125580	VV	0.213	0.142	
47.22	75214	VV	0.141	0.085	
47.44	55872	VV	0.082	0.063	
47.59	35937	VV	0.051	0.041	D14
47.65	37648	VV	0.052	0.043	
47.79	229280	VV	0.125	0.260	
48.12	751790	VV	0.093	0.851	
48.34	118740	VV	0.118	0.134	
48.75	112950	VV	0.230	0.128	
48.85	12260	VV	0.036	0.014	
49.02	101150	VV	0.166	0.115	
49.17	81881	VP	0.175	0.093	
49.60	50403	PV	0.143	0.057	
50.07	67105	VV	0.176	0.076	

50.36	29738	VV	0.123	0.034
50.53	28750	VV	0.104	0.033
50.78	48336	VV	0.119	0.055
50.93	62105	VV	0.132	0.070
51.54	74513	PV	0.132	0.084
51.79	10632	VV	0.090	0.012
51.99	19407	VV	0.101	0.022
52.53	62300	PV	0.138	0.071
52.76	31795	VV	0.152	0.036
53.00	13150	VV	0.072	0.015
53.17	31474	VV	0.129	0.036
53.79	24621	PV	0.115	0.028
54.26	36416	VV	0.162	0.041
55.57	51881	VV	0.167	0.059
56.29	58185	VV	0.137	0.066
56.51	53883	VV	0.174	0.061
56.78	100670	VV	0.180	0.114
57.32	14396	VV	0.109	0.016
57.72	54020	VP	0.179	0.061
58.80	13931	VV	0.138	0.016
59.99	15253	VV	0.144	0.017
60.29	109560	VV	0.187	0.124
61.03	112250	VV	0.164	0.127
62.30	22512	VV	0.216	0.026
63.25	17332	VP	0.168	0.020
64.20	24938	VV	0.144	0.028
65.07	16867	VV	0.147	0.019
65.17	25658	VP	0.151	0.029
65.59	128030	PP	0.174	0.145
67.13	63340	VV	0.254	0.072
67.94	25417	VV	0.085	0.029
68.06	53678	VV	0.095	0.061
68.14	48937	VV	0.078	0.055
68.20	48557	VV	0.067	0.055
68.27	71217	VV	0.093	0.081
68.36	66125	D VV	0.104	0.075
69.28	13214	PV	0.104	0.015
69.52	41280	VV	0.111	0.047
69.55	42550	D VV	0.106	0.048
70.42	49801	PV	0.102	0.056
73.43	28311	PV	0.184	0.032
73.99	17457	VV	0.121	0.020
74.56	31137	VV	0.129	0.035
77.38	118280	PV	0.119	0.134
77.43	58729	VV	0.054	0.067
79.58	38124	VV	0.282	0.043
83.12	70826	PV	0.149	0.080
83.16	29703	VV	0.055	0.034
83.21	23297	D VV	0.048	0.026
83.26	51611	D VV	0.128	0.058
85.12	22112	PV	0.110	0.025
85.18	13352	VV	0.054	0.015
88.88	133350	VV	0.531	0.151
89.70	13403	VV	0.133	0.015

95.12	21384	PV	0.106	0.024
95.23	30702	VV	0.095	0.035
95.26	12577	D VV	0.037	0.014
95.31	33945	D VV	0.103	0.038
95.99	78093	BV	0.129	0.088
96.03	36532	VV	0.053	0.041
96.12	23766	D VV	0.040	0.027

TOTAL AREA= 8.8367E+07
MUL FACTOR= 1.0000E+00

Table A4

5 mg Chlorine dose

RUN # 783, APR/29/86 ,22:01:39
WORKFILE ID: C ,WORKFILE NAME:
ID: 000
AREA%

checkpoint: next peak is A1; RT is off because peak is broad.

RT	AREA	TYPE	AR/HT	AREA%
5.55	3290700	BV	0.145	3.880
5.81	126620	VV	0.093	0.149
5.97	58658	VB	0.094	0.069
6.65	3666300	BV	0.174	4.323
7.07	315880	VV	0.177	0.372
7.27	366760	VP	0.182	0.432
7.67	64857	PV	0.089	0.077
7.94	2.0632E+07	VV	0.187	24.327
8.11	1.6152E+07	VV	0.186	19.044
8.36	9807500	VB	0.220	11.564
9.26	17521	BP	0.087	0.021
9.53	14883	VP	0.094	0.018
9.87	188600	PV	0.158	0.222
10.21	490980	VV	0.171	0.579
10.41	289250	VV	0.165	0.341
10.72	916350	VV	0.114	1.080
10.88	761590	VV	0.128	0.898
11.13	395360	VV	0.150	0.466
11.37	162140	VP	0.124	0.191
11.98	103310	VP	0.199	0.122
12.32	17876	PP	0.106	0.021
12.61	83931	PV	0.167	0.099
12.76	12692	VV	0.065	0.015
12.95	77467	PV	0.086	0.091
13.16	14728	VV	0.077	0.017

checkpoint: next peak is A14 subtract 0.02 minutes

13.39	3966600	VB	0.115	4.677
13.87	45216	BV	0.152	0.053
14.08	14082	VV	0.052	0.017
14.12	13577	VV	0.039	0.016
14.23	97211	VV	0.141	0.115
14.36	58977	VV	0.077	0.070
14.62	664250	VV	0.231	0.783
14.85	587750	VV	0.214	0.693
15.02	228030 D	VV	0.099	0.269
15.24	862640	VV	0.137	1.017
15.35	847720	VV	0.175	1.000

checkpoint: next peak is A17; subtract 0.02 minutes

15.73	1721100	VV	0.195	2.029
16.11	1113700	VP	0.187	1.313
16.76	19291	PV	0.059	0.023
16.94	2594700	VB	0.117	3.059
17.58	10989	BV	0.080	0.013
17.72	47349	VV	0.096	0.056
17.87	20249	VV	0.065	0.024
17.97	114940	VV	0.099	0.136
18.17	46803	VV	0.214	0.055
18.73	42731	VP	0.129	0.050
19.17	55122	PV	0.130	0.065
19.21	22096 D	VV	0.054	0.026
19.39	119580	VV	0.098	0.141
19.68	113110	VV	0.182	0.133
20.20	21461	VV	0.150	0.025
21.00	17037	VV	0.085	0.020
21.19	14790	VP	0.090	0.017
21.58	13102	VV	0.112	0.016
21.82	36065	VV	0.168	0.043
22.10	71980	VV	0.136	0.085
22.49	28953	VV	0.104	0.034
22.65	63568	VV	0.112	0.075
22.82	16533	VV	0.176	0.020
23.70	19778	BV	0.077	0.023
23.82	36501	VV	0.129	0.043
24.06	17436	VV	0.073	0.021
24.17	39690	VV	0.086	0.047
24.38	26583	VV	0.097	0.031
24.73	51616	VP	0.140	0.061
25.20	68215	PV	0.136	0.080

checkpoint: next peak is A25; subtract 0.01 minute

25.42	77738	VV	0.133	0.092
25.62	76970	VV	0.119	0.091
26.06	53703	VP	0.091	0.063
27.01	36791	VV	0.120	0.043
27.23	27858	VV	0.174	0.033
27.62	23178	VP	0.140	0.027
27.93	74043	PV	0.106	0.087
28.09	23859	VV	0.096	0.028
28.22	59953	VV	0.139	0.071
28.44	38208	VV	0.104	0.045
28.89	24998	BV	0.091	0.030
29.14	47077	VV	0.152	0.056
29.58	12469	VP	0.083	0.015
29.86	24442	PV	0.111	0.029
29.98	23796	VP	0.078	0.028
30.62	48196	PH	0.096	0.057
30.88	24774	HH	0.145	0.029
31.11	25651	HH	0.134	0.030
31.28	165230	HV	0.106	0.195
31.43	63619	VV	0.112	0.075
31.61	14877	VV	0.081	0.018
31.77	36327	VV	0.103	0.043
31.89	21115	VV	0.079	0.025
32.04	23668	VV	0.121	0.028
32.21	21722	VV	0.084	0.026
32.32	36368	VV	0.101	0.043
32.64	73580	VV	0.183	0.087

32.92	59109	VV	0.112	0.070
33.10	187950	VV	0.096	0.222
33.29	16086	VP	0.077	0.019
33.47	23098	PV	0.090	0.027
34.26	100310	VV	0.178	0.118
34.81	54733	VV	0.078	0.065
34.93	27779	VV	0.093	0.033
35.31	30657	VV	0.101	0.036
35.50	18472	VV	0.148	0.022
35.73	16542	VV	0.103	0.020
35.84	18514	VV	0.090	0.022
35.95	18442	VV	0.075	0.022
36.09	63517	VV	0.122	0.075
36.16	30221 D	VV	0.065	0.036
36.39	64618	VV	0.094	0.076
36.49	124630	VV	0.094	0.147
36.73	73864	VV	0.047	0.087
36.75	125390 D	VV	0.078	0.148
checkpoint: next peak is D3; RT exact				
37.01	1632400	VV	0.089	1.925
37.41	305670	VV	0.130	0.360
37.64	77643	VV	0.117	0.092
37.87	32350	VV	0.148	0.038
38.07	16526	VV	0.100	0.020
38.25	53664	VV	0.089	0.063
38.44	51502	VV	0.143	0.061
38.68	12011	VV	0.087	0.014
38.88	11224	VP	0.098	0.013
39.12	574750	PV	0.089	0.678
39.34	132050	VV	0.102	0.156
39.94	257090	VV	0.187	0.303
40.06	325020	VV	0.235	0.383
40.40	88916	VV	0.118	0.105
40.57	70533	VV	0.127	0.083
40.83	125870	VV	0.172	0.148
41.10	28739	VV	0.088	0.034
41.21	80620	VV	0.112	0.095
41.45	1642100	VV	0.149	1.936
41.78	171280	VV	0.167	0.202
42.24	12019	VP	0.097	0.014
42.82	57948	VV	0.105	0.068
checkpoint: next peak is d10; add 0.04				
43.03	252160	VV	0.138	0.297
43.39	75607	VV	0.100	0.089
43.52	79639	VV	0.114	0.094
43.78	38242	VV	0.138	0.045
43.99	14532	VP	0.114	0.017
44.46	113340	VV	0.137	0.134
44.75	97354	VV	0.153	0.115
44.98	30706	VV	0.138	0.036
45.22	34494	VV	0.112	0.041
45.86	21176	PV	0.134	0.025
46.00	27859	VV	0.098	0.033
46.35	30265	VV	0.080	0.036

46.69	21160	VV	0.105	0.025
46.84	13880	VV	0.082	0.016
47.21	63012	VV	0.115	0.074
47.48	37395	VV	0.095	0.044
47.54	26288	VV	0.059	0.031
47.64	50421	VV	0.095	0.060
47.80	91139	VV	0.142	0.108
48.03	42723	VV	0.143	0.050
48.36	87268	VP	0.122	0.103
48.74	41993	VV	0.143	0.050
49.03	156950	VV	0.183	0.185
49.64	38522	PV	0.128	0.045
50.09	59958	BV	0.139	0.071
50.29	13460 D	VV	0.039	0.016
50.34	33868	VV	0.094	0.040
50.79	15071	VV	0.074	0.018
50.93	90187	VV	0.167	0.106
51.12	34445	VV	0.094	0.041
51.34	18805	VV	0.056	0.022
51.54	155010	VV	0.204	0.183
51.66	65030	VV	0.110	0.077
51.98	95205	VV	0.164	0.112
52.26	109690	VV	0.167	0.129
52.55	166030	VV	0.213	0.196
52.78	48798	VV	0.106	0.058
53.14	97000	VV	0.207	0.114
53.39	23642	VV	0.109	0.028
53.82	17094	PV	0.118	0.020
54.29	24364	VV	0.131	0.029
54.60	12690	VV	0.111	0.015
55.57	95402	VV	0.207	0.113
56.30	96742	VV	0.144	0.114
56.79	71555	VV	0.169	0.084
57.72	67908	VV	0.166	0.080
58.67	16487	VV	0.091	0.019
58.80	22321	VV	0.104	0.026
59.27	128590	VV	0.266	0.152
60.30	196340	VV	0.237	0.232
60.80	18691	VV	0.105	0.022
61.04	83785	VV	0.182	0.099
61.83	31426	VP	0.222	0.037
62.79	24880	VV	0.164	0.029
63.40	27016	BV	0.201	0.032
65.60	63818	BP	0.169	0.075
67.07	12040	VV	0.101	0.014
67.16	29484	VV	0.184	0.035
68.30	23763	VV	0.132	0.028
68.67	50402	VV	0.252	0.059
69.57	38805	VV	0.182	0.046
70.49	136060	VV	0.222	0.160
70.61	38330	VV	0.068	0.045
70.66	45114	VV	0.079	0.053
71.49	23696	VV	0.110	0.028
74.59	22125	PV	0.104	0.026

77.37	45926	VV	0.093	0.054
77.43	48674	VV	0.091	0.057
79.71	331840	PV	0.468	0.391
83.09	28000	VV	0.122	0.033
83.20	26080	VV	0.104	0.031
83.24	13774	VV	0.049	0.016
85.19	14135	PV	0.132	0.017
85.24	24535	VV	0.183	0.029
87.08	355830 I	VH	0.530	0.420

TOTAL AREA= 8.4812E+07

Table A5

10 mg Chlorine dose

RUN # 778, APR/29/86 ,13:04:45
WORKFILE ID: C ,WORKFILE NAME:
ID: 000
AREA%

RT	AREA	TYPE	AR/HT	AREA%
5.49	1400800	BP	0.141	1.700
5.76	102740	PV	0.086	0.125
5.93	284030	VP	0.160	0.345
checkpoint: next peak is A2; add 0.03 minutes				
6.60	5161200	PV	0.189	6.264
7.00	404650	VV	0.162	0.491
7.19	464480	VP	0.190	0.564
7.60	158980	PV	0.092	0.193
7.83	1.9016E+07	VV	0.193	23.077
8.04	1.3754E+07	VV	0.177	16.692
8.29	1.1580E+07	VB	0.234	14.054
9.21	18242	BP	0.088	0.022
9.43	20326	PP	0.127	0.025
9.80	243720	PV	0.159	0.296
10.14	407290	VV	0.170	0.494
10.32	183340	VV	0.159	0.223
10.65	751570	VV	0.110	0.912
10.82	1638900	VV	0.127	1.989
11.04	351840	VV	0.152	0.427
11.30	157670	VP	0.133	0.191
11.72	11420	VV	0.086	0.014
11.90	62603	VV	0.133	0.076
12.23	32450	VP	0.107	0.039
12.52	49577	PV	0.119	0.060
12.72	28453	VV	0.119	0.035
12.88	68668	VV	0.102	0.083
13.08	36968	VV	0.089	0.045
checkpoint: next peak is A14; add 0.05 minutes				
13.32	4058600	VB	0.127	4.925
13.79	23502	BP	0.127	0.029
14.15	42313	VV	0.158	0.051
14.42	73795	VV	0.125	0.090
14.56	366300	VV	0.178	0.445
14.81	535060	VV	0.260	0.649
15.16	976850	VV	0.122	1.186
15.27	765990	VV	0.150	0.930
15.65	842150	VV	0.149	1.022
15.80	389370	VV	0.145	0.473
16.02	622750	VV	0.171	0.756
checkpoint: next peak is A18; add 0.05 minutes				
16.87	3844200	PB	0,131	4.665
17.64	19518	PV	0.083	0.024
17.78	14567	VV	0.064	0.018
17.89	66424	VP	0.080	0.081
18.63	12580	VV	0.089	0.015
19.06	46462	PV	0.123	0.056
19.31	99212	VV	0.108	0.120
19.59	139620	VV	0.184	0.169
20.14	17006	VV	0.079	0.021
20.91	17433	VV	0.089	0.021
21.51	11203	PV	0.116	0.014
21.73	41496	VV	0.130	0.050
22.02	106120	VB	0.098	0.129
22.41	18328	BH	0.099	0.022
22.57	30211	HP	0.098	0.037
23.01	13524	VP	0.080	0.016
23.30	22308	PH	0.150	0.027
23.62	18984	HH	0.090	0.023
23.74	23697	HH	0.110	0.029
23.98	12852	HH	0.078	0.016
24.09	65810	HH	0.117	0.080
24.31	19822	HH	0.084	0.024
24.41	14851	HH	0.084	0.018
24.65	50929	HP	0.150	0.062
25.12	71942	PH	0.140	0.087
checkpoint: next peak is A25; add 0.07 minutes				
25.34	107360	HH	0.147	0.130
25.53	99432	HH	0.134	0.121
25.81	16577	HH	0.084	0.020
25.98	126300	HH	0.114	0.153
26.71	23981	HH	0.129	0.029
26.80	18106	HH	0.085	0.022
26.93	63528	HH	0.146	0.077
27.14	27518	HH	0.091	0.033
27.48	85094	HH	0.235	0.103
27.84	152920	HH	0.136	0.186
28.00	47656	HH	0.102	0.058
28.18	95325	HH	0.178	0.116
28.33	49886	HH	0.116	0.061
28.48	43525	HH	0.131	0.053
28.81	38990	HH	0.102	0.047
28.91	26008	HH	0.080	0.032
29.08	80302	HH	0.222	0.098
29.77	46956	HH	0.129	0.057
29.89	35304	HH	0.107	0.043
30.54	73211	HV	0.109	0.089
30.80	17246	VV	0.115	0.021
30.89	12304	VV	0.088	0.015
31.00	19523	VV	0.103	0.024
31.18	150180	VV	0.118	0.182
31.34	66433	VV	0.126	0.081
31.52	15075	VV	0.078	0.018
31.67	55879	VV	0.123	0.068
31.81	26584	VV	0.085	0.032
31.93	40829	VV	0.144	0.050
32.14	23112	VV	0.099	0.028
32.23	36049	VV	0.098	0.044
32.61	63611	VV	0.177	0.077
32.83	58892	VV	0.125	0.072

33.01	211990	VV	0.092	0.257
33.19	27459	VP	0.078	0.033
33.39	14696	PV	0.096	0.018
33.58	11056	VV	0.088	0.013
34.05	26578	VV	0.081	0.032
34.21	83541	VV	0.162	0.101
34.37	34353	VV	0.122	0.042
34.72	58381	VV	0.086	0.071
34.83	24644	VP	0.108	0.030
35.22	18685	VV	0.098	0.023
35.40	15476	VV	0.120	0.019
35.63	16949	VV	0.081	0.021
35.74	50946	VV	0.091	0.062
35.85	18337	VV	0.066	0.022
35.99	118070	VV	0.168	0.143
36.29	65092	VV	0.100	0.079
36.40	160760	VV	0.099	0.195
36.64	221600	VV	0.130	0.269
checkpoint: next peak is D3; add 0.08 minutes				
36.93	1978000	VV	0.091	2.401
37.16	45285	VV	0.085	0.055
37.32	333120	VV	0.151	0.404
37.55	120670	VV	0.146	0.146
37.96	33938	VV	0.144	0.041
38.15	42860	VV	0.113	0.052
38.35	29522	VV	0.162	0.036
38.58	30780	VV	0.092	0.037
39.03	287410	PV	0.096	0.349
39.24	147690	VV	0.123	0.179
39.78	82188	VV	0.096	0.100
39.98	178560	VV	0.215	0.217
40.31	52218	VV	0.103	0.063
40.47	42392	VV	0.106	0.052
40.73	79225	VP	0.109	0.096
41.11	25646	PV	0.071	0.031
41.31	1598000	VV	0.159	1.939
41.68	88847	VV	0.110	0.108
42.12	12984	VP	0.099	0.016
42.48	18949	VV	0.095	0.023
42.80	90441	VV	0.170	0.110
42.92	208380	VV	0.136	0.253
43.30	57851	VV	0.107	0.070
43.41	87433	VV	0.118	0.106
43.71	30877	VV	0.168	0.038
44.33	106460	PV	0.183	0.129
44.66	73408	VV	0.173	0.089
44.88	22334	VV	0.147	0.027
45.16	35593	VV	0.147	0.043
45.69	24357	BV	0.124	0.030
45.90	19016	VV	0.088	0.023
45.99	19779	VV	0.078	0.024
46.10	44037	VV	0.143	0.053
46.27	84171	VV	0.181	0.102
46.59	12517	VV	0.095	0.015
47.11	53058	VV	0.098	0.064
47.25	17877	VV	0.074	0.022
47.37	29681	VV	0.083	0.036
47.50	66924	VV	0.149	0.081
47.69	46798	VV	0.120	0.057
47.93	57779	VV	0.158	0.070
48.25	56612	VV	0.172	0.069
48.65	34422	VV	0.132	0.042
48.94	250820	VV	0.159	0.304
49.55	123970	PV	0.115	0.150
49.97	74786	VV	0.184	0.091
50.24	72243	VV	0.197	0.088
50.45	33579	VV	0.143	0.041
50.60	14857	VV	0.091	0.018
50.82	76683	VV	0.176	0.093
50.97	13698	VV	0.059	0.017
51.43	45849	VV	0.126	0.056
51.66	81064	VV	0.211	0.098
52.13	31803	BV	0.103	0.039
52.41	59270	VP	0.129	0.072
53.04	87046	PV	0.146	0.106
53.67	11566	PV	0.119	0.014
54.15	17401	VV	0.124	0.021
54.48	18556	VV	0.115	0.023
54.72	15275	VV	0.128	0.019
55.45	40030	VV	0.140	0.049
56.14	20821	VV	0.129	0.025
56.37	43422	VV	0.180	0.053
56.63	87953	VV	0.220	0.107
57.16	15251	VV	0.108	0.019
57.57	72883	VP	0.176	0.089
59.02	16755	VV	0.117	0.020
60.11	91091	PV	0.149	0.111
60.85	81862	VV	0.135	0.099
61.62	16837	VV	0.136	0.020
62.11	16029	PV	0.170	0.020
62.40	11950	VV	0.130	0.015
63.13	11959	PV	0.107	0.015
63.97	20082	BP	0.140	0.024
65.38	115340	PP	0.161	0.140
66.90	17249	VV	0.096	0.021
67.14	15050	VV	0.090	0.018
67.31	41845	VV	0.104	0.051
67.34	31768	VV	0.071	0.039
67.44	31022	VV	0.077	0.038
67.50	11841 D	VV	0.034	0.014
67.54	15776	VV	0.047	0.019
67.59	33998 D	VB	0.104	0.041
69.26	55441	BV	0.172	0.067
70.17	53106	BV	0.128	0.065
77.04	103130	PV	0.120	0.125
77.09	158070	VV	0.157	0.192
79.18	49638	PV	0.129	0.060
79.28	141020	VV	0.335	0.171
80.10	19698	VV	0.149	0.024
80.25	24790	VV	0.138	0.030
82.68	35731	VV	0.118	0.043
82.75	30088	VV	0.070	0.037
82.85	28955 D	VV	0.065	0.035
84.74	28731	VV	0.143	0.035
84.84	13795	VV	0.060	0.017
86.63	178110	PV	0.457	0.216
88.36	10658	VV	0.189	0.013
94.66	15577	VV	0.089	0.019
94.77	15566	VV	0.053	0.019
95.45	56394	BV	0.115	0.068
95.51	46675	VV	0.079	0.057
95.61	20148 D	VV	0.040	0.025
98.55	12282	VV	0.177	0.015

TOTAL AREA= 8.2402E+07
MUL FACTOR= 1.0000E+00

Table A6

20 mg chlorine dose

RUN # 784, APR/30/86 ,10:36:08
WORKFILE ID: C ,WORKFILE NAME:
ID: 000
AREA%

RT	AREA	TYPE	AR/HT	AREA%
checkpoint: next peak is A1; subtract 0.03 minutes				
5.51	762690	BP	0.146	1.381
5.78	84239	PV	0.083	0.153
5.95	339930	VP	0.179	0.616
6.61	2930600	PV	0.170	5.306
7.03	285390	VV	0.162	0.517
7.22	401830	VP	0.188	0.728
7.62	166590	PV	0.097	0.302
7.88	1.1286E+07	VV	0.195	20.434
8.08	9329100	VV	0.167	16.892
8.33	9046700	VB	0.220	16.380
9.27	39209	BV	0.128	0.071
9.47	26083	VP	0.135	0.047
9.83	199780	PV	0.169	0.362
10.17	125180	VV	0.147	0.227
10.38	71565	VV	0.125	0.130
10.69	471920	VV	0.117	0.855
10.85	416380	VV	0.121	0.754
11.09	176310	VV	0.149	0.319
11.35	91752	VP	0.125	0.166
11.94	69284	VP	0.178	0.126
12.28	25243	PP	0.099	0.046
12.49	59492	PP	0.117	0.108
12.77	43361	PV	0.098	0.079
12.93	31105	VP	0.088	0.056
13.12	11998	PV	0.080	0.022
checkpoint: the next peak is A14; subtract 0.01 minute				
13.38	2144600	VB	0.116	3.883
13.83	24784	BP	0.150	0.045
14.24	30493	PV	0.148	0.055
14.46	66708	VV	0.146	0.121
14.61	268590	VV	0.176	0.486
14.82	259690	VV	0.177	0.470
15.01	66004	VV	0.062	0.120
15.22	1117400	VV	0.114	2.023
15.32	706400	VV	0.126	1.279
15.71	597000	VV	0.131	1.081
15.86	249370	VV	0.125	0.452
16.08	210740	VP	0.128	0.382
checkpoint: the next peak is A18; add 0.01 minute				
16.92	5625700	PB	0.200	10.186
17.57	16660	BV	0.064	0.030
17.68	16653	VV	0.084	0.030
17.85	29600	VV	0.073	0.054
17.94	23896	VP	0.075	0.043
18.16	10937	PP	0.101	0.020
18.76	17644	VP	0.123	0.032
19.38	29477	VV	0.078	0.053
19.47	16318	VV	0.085	0.030
19.66	90131	VV	0.200	0.163
19.99	22856	VV	0.100	0.041
21.26	12582	VP	0.094	0.023
21.57	10549	VV	0.106	0.019
21.80	26526	VV	0.141	0.048
22.09	163490	VV	0.094	0.296
22.46	25331	VV	0.116	0.046
22.63	27319	VV	0.117	0.050
23.38	21448	BP	0.117	0.039
23.88	28413	VV	0.211	0.052
24.04	12877	VV	0.078	0.023
24.15	36484	VV	0.089	0.066
24.48	11707	VV	0.095	0.021
24.71	58423	VP	0.153	0.106
25.19	55826	PV	0.145	0.101
25.41	81617	VV	0.145	0.148
25.60	70167	VV	0.113	0.127
26.05	110370	VV	0.105	0.200
26.42	13765	VV	0.105	0.025
27.00	25941	VV	0.128	0.047
27.91	58219	PV	0.094	0.105
28.25	17936	BV	0.100	0.033
29.16	45883	VV	0.180	0.083
29.86	33736	PV	0.119	0.061
30.20	18935	VV	0.155	0.034
30.62	46953	PV	0.105	0.085
31.25	45294	PV	0.108	0.082
31.42	33187	VV	0.168	0.060
31.75	32134	VV	0.104	0.058
31.88	12277	VV	0.079	0.022
32.01	40067	VV	0.123	0.073
32.31	54871	VV	0.190	0.099
32.69	40020	VV	0.167	0.073
32.91	38747	VV	0.122	0.070
33.09	44488	VV	0.121	0.081
33.27	21548	VP	0.075	0.039
34.12	28324	PV	0.098	0.051
34.30	52376	VV	0.184	0.095
34.45	17767	VV	0.089	0.032
35.29	16398	PV	0.120	0.030
35.48	10327	VV	0.125	0.019
35.72	10181	VV	0.071	0.018
35.81	82271	VV	0.099	0.149
36.07	52532	VP	0.139	0.095
36.37	14133	PV	0.075	0.026
36.48	111860	VV	0.086	0.203
36.72	110730	VP	0.113	0.201
checkpoint: the next peak is D3; add 0.01 minute				
37.00	1601600	PB	0.105	2.900
37.40	101590	BV	0.112	0.184

37.63	34728	VP	0.090	0.063
38.22	14957	VV	0.099	0.027
38.66	36179	VV	0.083	0.066
39.10	127150	PV	0.094	0.230
39.33	49454	VV	0.090	0.090
39.85	55613	BV	0.169	0.101
40.14	29224	VV	0.155	0.053
40.39	25229	VV	0.094	0.046
40.56	14230	VV	0.081	0.026
40.81	35163	VV	0.122	0.064
41.08	13888	VV	0.092	0.025
41.18	30325	VV	0.119	0.055
41.42	470480	VV	0.163	0.852
41.77	51947	VV	0.118	0.094
42.56	26009	VV	0.097	0.047
42.76	36518	VV	0.120	0.066
42.87	29834	VV	0.101	0.054
43.01	55592	VV	0.155	0.101
43.38	62743	VV	0.135	0.114
43.50	90412	VV	0.189	0.164
43.74	43178	VV	0.144	0.078
44.43	61591	VV	0.174	0.112
44.74	24353	VV	0.146	0.044
45.24	20547	VV	0.141	0.037
45.76	12385	PV	0.096	0.022
46.05	27924	VV	0.154	0.051
46.14	24370	VV	0.129	0.044
46.35	30255	VV	0.150	0.055
46.56	12022	VV	0.096	0.022
47.19	40023	PV	0.102	0.073
47.35	18431	VV	0.092	0.033
47.62	78636	VV	0.183	0.142
47.99	28263	VV	0.127	0.051
48.32	23194	VV	0.158	0.042
48.72	90032	VV	0.131	0.163
49.03	126860	VV	0.146	0.230
49.36	16956	VP	0.098	0.031
49.64	55704	PV	0.113	0.101
50.07	40695	VV	0.157	0.074
50.31	31101	VV	0.158	0.056
50.90	25296	VV	0.135	0.046
51.54	60180	BV	0.146	0.109
51.64	11441	VV	0.037	0.021
51.73	50294	VV	0.138	0.091
52.23	46909	VV	0.139	0.085
52.51	199760	VV	0.293	0.362
53.12	102810	VV	0.182	0.186
53.38	67140	VV	0.175	0.122
53.75	115000	VV	0.200	0.208
54.26	42971	VV	0.211	0.078
55.57	37277	PP	0.210	0.068
56.51	17358	VV	0.118	0.031
56.76	38306	VV	0.156	0.069
57.69	50043	PV	0.188	0.091
60.24	55982	VV	0.187	0.101
61.03	20589	BP	0.155	0.037
65.55	30761	VV	0.192	0.056
67.07	19433	VV	0.224	0.035
68.26	14352	PV	0.209	0.026
69.51	14282	VV	0.164	0.026
70.42	42752	VP	0.305	0.077
71.77	13210	VV	0.121	0.024
71.95	17900	VV	0.121	0.032
77.38	50070	PV	0.220	0.091
79.50	61915	VV	0.399	0.112
80.59	35799	VV	0.187	0.065
80.68	22208	VV	0.101	0.040
80.78	25064	VV	0.122	0.045
83.09	29365	BV	0.237	0.053
85.16	10888	PV	0.165	0.020
86.76	16488	VV	0.125	0.030
86.87	37201	VV	0.238	0.067
91.94	10157	VV	0.126	0.018
92.19	19782	VV	0.155	0.036

TOTAL AREA= 5.5229E+07
MUL FACTOR= 1.0000E+00

Table A7

40 mg chlorine dose

RUN # 787, APR/30/86 ,16:37:12
WORKFILE ID: C ,WORKFILE NAME:
ID: 000
AREA%

RT	AREA	TYPE	AR/HT	AREA%
5.55	669780	BP	0.148	0.861
5.82	123290	PV	0.086	0.159
6.00	825890	VP	0.228	1.062
checkpoint: the next peak is A2; subtract 0.03 minutes				
6.66	3491800	PV	0.176	4.488
7.07	369730	VV	0.167	0.475
7.25	465820	VP	0.175	0.599
7.66	232150	PV	0.095	0.298
7.89	7276700	VV	0.097	9.354
7.92	8714600 D	VV	0.119	11.202
8.09	9736400	VV	0.178	12.515
8.36	9950400	VB	0.219	12.790
9.26	19888	BP	0.108	0.026
9.53	29757	PV	0.122	0.038
9.87	280020	PV	0.166	0.360
10.21	84714	VV	0.153	0.109
10.41	93411	VV	0.132	0.120
10.72	639910	VV	0.112	0.823
10.87	418490	VV	0.111	0.538
11.12	173990	VV	0.139	0.224
11.37	240340	VP	0.117	0.309
11.85	59083	PV	0.155	0.076
11.96	116360	VP	0.187	0.150
12.29	25128	PV	0.100	0.032
12.53	37122	VV	0.119	0.048
12.79	200520	VV	0.158	0.258
12.95	167560	VV	0.131	0.215
checkpoint: the next peak is A14; subtract 0.01 minute				
13.38	2878100	VV	0.150	3.700
13.72	214970	VV	0.139	0.276
13.82	67398	VV	0.047	0.087
14.05	75590	VV	0.060	0.097
14.25	241080	VV	0.164	0.310
14.33	71893	VV	0.049	0.092
14.47	253230	VV	0.132	0.326
14.62	619470	VV	0.192	0.796
14.84	1025500	VV	0.277	1.318
15.22	1750700	VV	0.119	2.250
15.33	1903200	VV	0.155	2.446
15.72	761790	VV	0.173	0.979
15.86	681640	VV	0.162	0.876
16.11	902530	VP	0.258	1.160
checkpoint: the next peak is A18; add 0.01 minute				
16.92	7113500	PB	0.143	9.144
17.57	10869	BP	0.054	0.014
17.71	19626	PV	0.081	0.025
17.85	121360	VV	0.079	0.156
17.94	49449	VV	0.067	0.064
18.15	16932	PV	0.099	0.022
18.74	44929	VP	0.176	0.058
19.14	26574	VV	0.106	0.034
19.28	55957	VV	0.092	0.072
19.38	70576	VV	0.085	0.091
19.48	41940	VV	0.090	0.054
19.67	244330	VV	0.229	0.314
20.00	80829	VV	0.137	0.104
20.29	110120	VV	0.146	0.142
20.97	33989	VV	0.142	0.044
21.18	18386	VV	0.075	0.024
21.25	32355	VP	0.107	0.042
21.56	14215	PP	0.098	0.018
21.81	63301	PV	0.093	0.081
22.08	400330	VB	0.087	0.515
22.47	21120	PH	0.092	0.027
22.63	27017	HP	0.097	0.035
22.91	24003	PP	0.083	0.031
23.09	11785	PP	0.074	0.015
23.38	39020	PP	0.120	0.050
23.96	58745	HH	0.149	0.076
24.15	59420	HH	0.084	0.076
24.28	21497	HH	0.086	0.028
24.48	10302	HH	0.072	0.013
24.59	13251	HH	0.072	0.017
24.71	65401	HP	0.161	0.084
25.19	83492	PH	0.147	0.107
25.42	155140	HH	0.133	0.199
25.60	112010	HH	0.117	0.144
25.77	16685	HH	0.069	0.022
26.05	185310	HH	0.134	0.238
26.42	70662	HH	0.194	0.091
26.78	104130	HH	0.104	0.134
27.00	82979	HH	0.143	0.107
27.22	29414	HH	0.076	0.038
27.28	43675	HH	0.100	0.056
27.40	44281	HH	0.101	0.057
27.56	73265	HH	0.143	0.094
27.73	79494	HH	0.113	0.102
27.91	224330	HH	0.121	0.288
28.12	81466	HH	0.122	0.105
28.23	105990	HH	0.125	0.136
28.37	80295	HV	0.136	0.103
28.56	24476	VV	0.096	0.032
28.68	23350	VV	0.106	0.030
28.87	27603	VV	0.123	0.036
29.16	107250	VV	0.130	0.138
29.41	30861	VV	0.139	0.040
29.85	61020	VV	0.104	0.078
29.96	24882	VV	0.078	0.032
30.15	11946	VV	0.101	0.015

30.29	17843	VV	0.111	0.023
30.63	262730	VV	0.100	0.338
30.87	31871	VV	0.094	0.041
30.97	27101	VV	0.098	0.035
31.25	89934	VV	0.121	0.116
31.39	103890	VV	0.144	0.134
31.60	13696	VV	0.050	0.018
31.69	164970	VV	0.110	0.212
31.87	29920	VV	0.076	0.039
31.99	187930	VV	0.112	0.242
32.23	33161	VV	0.090	0.043
32.30	48897	VV	0.089	0.063
32.40	32286	VV	0.065	0.042
32.67	90776	VV	0.190	0.117
32.90	77345	VV	0.130	0.099
33.09	122250	VV	0.108	0.157
33.27	40482	VP	0.074	0.052
33.67	20888	VV	0.098	0.027
34.11	52934	VV	0.096	0.068
34.24	89506	VV	0.181	0.115
34.44	26732	VV	0.095	0.034
34.60	19747	VV	0.111	0.025
34.91	29512	VV	0.115	0.038
35.20	16236	PV	0.105	0.021
35.49	28736	VV	0.129	0.037
35.71	23974	VV	0.073	0.031
35.82	181710	VV	0.090	0.234
36.06	149560	VV	0.149	0.192
36.37	66824	VV	0.113	0.086
36.47	148850	VV	0.100	0.191
36.71	251950	VV	0.123	0.324
checkpoint: the next peak is D3; add 0.02 minutes				
36.99	2391200	VV	0.090	3.074
37.23	46022	VV	0.090	0.059
37.41	213770	VV	0.154	0.275
37.63	80449	VV	0.127	0.103
38.08	41337	VV	0.092	0.053
38.23	19849	VV	0.090	0.026
38.34	13689	VV	0.123	0.018
38.65	45256	PV	0.079	0.058
39.10	193420	VV	0.109	0.249
39.32	115520	VV	0.111	0.149
39.83	139840	VV	0.149	0.180
40.14	33244	VV	0.099	0.043
40.28	11958	VV	0.087	0.015
40.39	39811	VV	0.099	0.051
40.55	30826	VV	0.104	0.040
40.80	27940	VP	0.112	0.036
41.05	26434	PV	0.098	0.034
41.19	69192	VV	0.107	0.089
41.38	1685600	VV	0.153	2.167
41.74	172000	VV	0.175	0.221
42.21	17914	VV	0.130	0.023
42.44	11385	VV	0.071	0.015

42.55	35842	VV	0.100	0.046
42.75	60148	VV	0.117	0.077
42.88	39972	VV	0.081	0.051
42.99	287030	VV	0.137	0.369
43.37	59567	VV	0.103	0.077
43.48	91625	VV	0.124	0.118
43.77	19624	VV	0.095	0.025
43.84	25462	VV	0.107	0.033
44.40	38776	VV	0.136	0.050
44.66	26482	VV	0.118	0.034
44.94	45576	VV	0.117	0.059
45.19	28203	VV	0.128	0.036
45.75	67271	PV	0.101	0.087
45.97	22158	VV	0.094	0.029
46.15	21059	VV	0.122	0.027
46.34	16500	VV	0.088	0.021
47.19	48247	PV	0.094	0.062
47.40	46111	VV	0.125	0.059
47.62	63209	VV	0.155	0.081
48.72	39856	BV	0.136	0.051
49.02	223360	VV	0.131	0.287
49.36	22378	VV	0.092	0.029
49.63	155990	PV	0.101	0.201
50.07	76808	PV	0.192	0.099
50.22	19669	VV	0.064	0.025
50.28	41910	VV	0.136	0.054
50.91	40104	VV	0.124	0.052
51.52	31601	VV	0.089	0.041
51.73	113600	VV	0.192	0.146
52.22	82781	VV	0.159	0.106
52.51	71305	VV	0.153	0.092
53.12	55232	VP	0.135	0.071
53.38	26901	PV	0.111	0.035
53.77	16940	VP	0.129	0.022
54.25	26483	VV	0.188	0.034
54.84	16458	VP	0.142	0.021
55.57	33142	BV	0.124	0.043
56.48	13420	PV	0.070	0.017
56.76	45197	VV	0.172	0.058
57.29	15405	PP	0.129	0.020
57.68	51291	PP	0.166	0.066
60.27	134570	VV	0.263	0.173
61.01	67889	VV	0.159	0.087
62.56	29250	PV	0.168	0.038
64.17	13587	PP	0.159	0.018
65.56	73115	BP	0.161	0.094
68.21	13429	PV	0.118	0.017
69.51	58436	VP	0.200	0.075
70.36	25981	PV	0.099	0.033
71.15	10293	BV	0.146	0.013
71.36	20049	VV	0.109	0.026
71.44	14953	VV	0.068	0.019
71.49	14819	VV	0.059	0.019
71.64	12124	VV	0.056	0.016

73.98	20614	VP	0.305	0.027
76.42	18888	VV	0.269	0.024
77.30	59140	PV	0.102	0.076
77.36	43812	VV	0.063	0.056
83.08	54314	PV	0.184	0.070
83.18	37940	VV	0.135	0.049
85.15	39655	VP	0.317	0.051
95.12	19868	VV	0.118	0.026
95.17	10732	VV	0.055	0.014
95.90	58931	VV	0.162	0.076
95.98	78700	VP	0.188	0.101

TOTAL AREA= 7.7797E+07
MUL FACTOR= 1.0000E+00

Table A8

1 mg chlorine dose

RUN # 779, APR/29/86 ,14:52:39
WORKFILE ID: C ,WORKFILE NAME:
ID: 000
AREA%

RT	AREA	TYPE	AR/HT	AREA%
checkpoint: RT nearly identical				
6.60	1087200	BV	0.155	1.083
6.91	242470	VV	0.215	0.242
7.85	5.6748E+07	SPB	0.351	56.530
10.12	22769	TBV	0.135	0.023
10.66	192450	BV	0.104	0.192
10.82	952590	VV	0.119	0.949
11.06	255360	VP	0.163	0.254
11.83	16579	PV	0.130	0.017
12.03	51714	VP	0.157	0.052
12.60	12035	PV	0.162	0.012
12.89	93299	VV	0.165	0.093
checkpoint: next peak is A14; add 0.05 minutes				
13.32	950720	VV	0.127	0.947
13.60	230540	VV	0.167	0.230
14.02	54024	VV	0.084	0.054
14.14	190090	VV	0.198	0.189
14.56	314350	VV	0.225	0.313
14.83	203570	VV	0.191	0.203
15.32	204090	VV	0.225	0.203
15.66	439100	VV	0.150	0.437
16.06	191980	VB	0.199	0.191
checkpoint: next peak is A18; add 0.05 minutes				
16.88	1466400	PB	0.112	1.461
17.87	14503	PV	0.101	0.015
18.07	15912	VP	0.124	0.016
18.42	11118	PV	0.091	0.011
19.31	76281	VV	0.089	0.076
20.92	14560	VP	0.086	0.015
21.71	29544	BV	0.173	0.029
22.51	19780	VV	0.159	0.020
23.03	17432	PV	0.104	0.017
23.64	25677	VV	0.092	0.026
23.76	82602	VV	0.221	0.082
24.09	39133	VV	0.089	0.039
24.65	53412	VP	0.112	0.053
25.09	612350	PV	0.107	0.610
25.32	5080600	VV	0.138	5.061
25.81	104220	D VV	0.079	0.104
26.16	118390	VV	0.146	0.118
26.31	69894	VV	0.104	0.070
26.40	60895	VV	0.104	0.061
26.64	48039	VV	0.098	0.048
26.72	24323	D VV	0.050	0.024
26.82	47109	VV	0.108	0.047
26.89	14646	VV	0.032	0.015
26.92	21289	VV	0.043	0.021
27.18	56080	VV	0.102	0.056
27.44	26385	VV	0.075	0.026
27.50	18861	VV	0.048	0.019
28.37	23064	PV	0.078	0.023
29.89	40904	VP	0.119	0.041
30.22	10339	VP	0.095	0.010
30.53	19138	VV	0.094	0.019
30.71	17926	VP	0.120	0.018
31.20	114330	VV	0.106	0.114
31.35	32126	VV	0.090	0.032
31.68	11101	VV	0.077	0.011
31.94	13491	VV	0.108	0.013
32.12	43639	VV	0.166	0.044
32.54	81625	VV	0.140	0.081
32.83	26354	VV	0.101	0.026
33.01	48741	VV	0.104	0.049
33.26	17019	VV	0.094	0.017
34.19	22336	VV	0.120	0.022
34.63	16647	VV	0.165	0.017
34.85	35882	VV	0.136	0.036
35.23	82862	VV	0.147	0.083
35.86	39449	VV	0.119	0.039
36.07	26348	VV	0.098	0.026
36.30	22740	VV	0.088	0.023
36.41	33575	VV	0.097	0.034
36.65	54569	VV	0.084	0.054
checkpoint:next peak is D3; add 0.08 minutes				
36.93	999280	VV	0.095	0.996
37.17	42800	VV	0.102	0.043
37.33	94348	VV	0.141	0.094
37.55	97369	VV	0.137	0.097
37.82	29398	VV	0.102	0.029
37.94	92752	VV	0.127	0.092
38.15	37179	VV	0.134	0.037
38.36	111270	VV	0.169	0.111
38.87	28769	VV	0.117	0.029
39.03	1534100	VV	0.101	1.528
39.77	381870	VV	0.126	0.380
39.99	140170	VV	0.160	0.140
40.23	30230	VV	0.067	0.030
40.65	77798	VV	0.163	0.078
40.75	89738	VV	0.173	0.089
41.00	64139	VV	0.150	0.064
41.26	1.8362E+07	SHB	0.176	18.292
42.69	35094	TPV	0.095	0.035
42.79	50307	TVV	0.109	0.050
42.92	271270	TVP	0.118	0.270
43.26	24496	TPV	0.076	0.024
43.40	210910	TVV	0.134	0.210
43.69	122240	TVV	0.099	0.122
43.90	84990	TVB	0.097	0.085
44.31	660440	BV	0.159	0.658

44.77	30391	VV	0.117	0.030
44.91	45575	VV	0.119	0.045
45.13	105200	VV	0.106	0.105
45.23	122920	VV	0.122	0.123
45.50	40427	VV	0.111	0.040
45.72	13756	VV	0.125	0.014
45.90	22824	VV	0.091	0.023
46.05	33195	VV	0.103	0.033
46.28	35084	VV	0.143	0.035
46.50	19617	VV	0.093	0.020
46.62	26277	VV	0.103	0.026
46.74	26341	VV	0.088	0.026
46.85	37728	VV	0.110	0.038
47.09	51082	VV	0.135	0.051
47.27	98720	VV	0.123	0.098
47.55	646170	VV	0.322	0.644
48.09	66155	VV	0.129	0.066
48.24	117080	VV	0.155	0.117
48.43	45738	VV	0.097	0.046
48.64	144460	VV	0.169	0.144
48.82	66472	VV	0.115	0.066
49.04	119990	VV	0.230	0.120
49.50	85317	VV	0.149	0.085
49.64	35326	VV	0.089	0.035
49.71	24893	VV	0.058	0.025
49.90	13796	VV	0.033	0.014
49.96	55765	VV	0.111	0.056
50.27	73847	VV	0.141	0.074
50.45	75544	VV	0.121	0.075
50.58	122860	VV	0.185	0.122
50.82	98476	VV	0.161	0.098
50.98	83552	VV	0.161	0.083
51.25	62373	VV	0.124	0.062
51.43	148590	VV	0.165	0.148
51.64	282150	VV	0.267	0.281
51.96	60450	VV	0.114	0.060
52.14	144970	VV	0.176	0.144
52.43	166460	VV	0.223	0.166
52.85	86615	VV	0.165	0.086
53.16	86024	VV	0.244	0.086
53.68	45669	VV	0.134	0.046
54.42	24288	BP	0.130	0.024
55.46	90717	VV	0.199	0.090
55.77	18144	VV	0.094	0.018
55.87	39905	VV	0.169	0.040
56.15	55605	VV	0.175	0.055
56.37	44320	VV	0.147	0.044
57.57	29685	PP	0.149	0.030
58.00	11125	PV	0.096	0.011
58.82	20542	PV	0.174	0.021
60.85	58438	VP	0.155	0.058
61.61	29836	VP	0.196	0.030
62.18	10765	VV	0.134	0.011
63.95	11978	PV	0.163	0.012
65.38	56962	VP	0.155	0.057
66.70	42161	VV	0.148	0.042
67.18	17285	VV	0.065	0.017
67.24	13523	VV	0.047	0.014
67.29	15675	VV	0.043	0.016
67.39	58030	VV	0.136	0.058
67.55	55914	VV	0.164	0.056
68.99	10355	PV	0.156	0.010
69.30	41358	VV	0.218	0.041
70.18	56535	PV	0.159	0.056
72.31	268280	PV	0.573	0.267
74.55	38700	VV	0.213	0.039
76.99	39315	BV	0.097	0.039
77.07	88430	VP	0.170	0.088
82.70	38225	PV	0.166	0.038
82.79	56192	VV	0.229	0.056
86.53	19620	VV	0.217	0.020
88.47	123650	PV	0.475	0.123
94.70	46709	VV	0.227	0.047
95.42	39815	VV	0.135	0.040
95.53	16036	VV	0.050	0.016

TOTAL AREA= 1.0038E+08
MUL FACTOR= 1.0000E+00

Table A9

0.5 mg chlorine dose

RUN # 781, APR/29/86 ,18:26:29
WORKFILE ID: C ,WORKFILE NAME:
ID: 000
AREA%

RT	AREA	TYPE	AR/HT	AREA%
checkpoint: RT nearly identical				
6.60	792070	BV	0.164	1.005
6.90	157660	VV	0.114	0.200
7.03	318150 D	VB	0.247	0.404
7.85	4.6985E+07	BV	0.319	59.610
10.13	92980	VV	0.232	0.118
10.35	59203	VV	0.170	0.075
10.66	141580	VV	0.115	0.180
10.82	1126400	VV	0.128	1.429
11.05	206900	VV	0.174	0.263
11.84	35062	VV	0.131	0.045
12.88	16627	PV	0.099	0.021
checkpoint: next peak is A14; add 0.04 minutes				
13.33	389070	PV	0.116	0.494
13.59	53243	VV	0.141	0.068
14.14	28554	VV	0.154	0.036
14.40	15318	VV	0.162	0.019
14.56	67224	VV	0.173	0.085
14.82	56562	VV	0.216	0.072
15.34	15243	VP	0.169	0.019
checkpoint: next peak is A17; add 0.06 minutes				
15.65	3543100	PB	0.097	4.495
16.88	642820	BB	0.114	0.816
17.88	15083	BV	0.111	0.019
18.06	13162	VP	0.124	0.017
19.31	25120	BB	0.085	0.032
20.48	18547	PB	0.150	0.024
21.71	24268	BV	0.166	0.031
22.50	13764	BV	0.158	0.018
23.02	13800	BV	0.103	0.018
23.62	16635	BV	0.084	0.021
23.74	33895	VV	0.129	0.043
24.09	28864	VV	0.080	0.037
24.64	33636	PV	0.097	0.043
25.08	470600	PV	0.095	0.597
checkpoint: next peak is A25				
25.31	4430100	VB	0.127	5.620
26.93	10001	VV	0.078	0.013
27.21	43540	VV	0.148	0.055
27.47	20215	VV	0.102	0.026
27.56	15381	VV	0.076	0.020
28.36	42285	VV	0.093	0.054
29.88	33622	VP	0.117	0.043
30.24	20865	VV	0.098	0.027
30.50	23847	VV	0.111	0.030
31.18	324180	VV	0.100	0.411
31.33	58990 D	VV	0.109	0.075
31.67	13441	VV	0.108	0.017
31.96	15509	VV	0.129	0.020
32.10	38642	VV	0.167	0.049
32.40	16825	VV	0.100	0.021
32.53	72507	VV	0.148	0.092
33.03	12052	VV	0.138	0.015
33.25	14359	VV	0.095	0.018
33.38	10277	VP	0.085	0.013
34.64	10788	VV	0.145	0.014
34.83	23582	VB	0.089	0.030
35.24	19818	BP	0.159	0.025
35.85	20133	VV	0.091	0.026
35.98	23751	VP	0.133	0.030
36.33	13751	PV	0.081	0.018
36.39	17031	VP	0.088	0.022
36.69	73739	PV	0.125	0.094
checkpoint: next peak is D3; add 0.10 minutes				
36.91	380320	VV	0.105	0.483
37.16	17771	VV	0.081	0.023
37.34	44131	VV	0.136	0.056
37.54	33954	VV	0.112	0.043
37.94	62776	VV	0.109	0.080
38.09	65043	VV	0.116	0.083
38.36	53173	VV	0.120	0.068
38.49	17962	VP	0.101	0.023
39.02	810890	PB	0.089	1.029
39.61	12096	PV	0.064	0.015
39.76	263610	VV	0.100	0.334
39.98	58507	VV	0.107	0.074
40.71	22954	VV	0.159	0.029
41.30	7967300	PB	0.148	10.108
42.79	214850	PV	0.124	0.273
42.93	125320	VV	0.118	0.159
43.29	30344	VV	0.108	0.039
43.43	89801	VV	0.132	0.114
43.69	113770	VV	0.105	0.144
43.90	36609	VV	0.096	0.047
44.34	388410	PV	0.173	0.493
44.89	28006	VV	0.200	0.036
45.22	156430	VV	0.187	0.199
45.50	20354	VP	0.102	0.026
45.72	15074	PV	0.103	0.019
45.90	12758	VV	0.107	0.016
46.05	17177	VP	0.117	0.022
46.47	23927	VV	0.126	0.030
46.74	48992	VV	0.218	0.062
46.96	12766	VV	0.102	0.016
47.10	15509	VV	0.106	0.020
47.56	571300	VV	0.359	0.725
47.91	35772 D	VV	0.091	0.045
48.03	65121	VV	0.114	0.083
48.20	17683	VV	0.119	0.022

48.65	71502		PV	0.139	0.091
48.84	21548		VV	0.098	0.027
49.05	37024		VV	0.140	0.047
49.25	15606		VV	0.115	0.020
49.50	19463		PV	0.076	0.025
49.98	14526		PV	0.081	0.018
50.26	22634		VV	0.111	0.029
50.44	29864		VV	0.099	0.038
50.60	80443		VV	0.162	0.102
50.81	47733		VV	0.128	0.061
50.96	34678		VV	0.170	0.044
51.25	32301		VV	0.106	0.041
51.43	100810		VV	0.165	0.128
51.79	135350		VV	0.274	0.172
52.13	57681		VV	0.182	0.073
52.43	50211		VV	0.118	0.064
52.83	10894		VV	0.079	0.014
53.81	141290		PV	0.162	0.179
54.41	95148		VV	0.322	0.121
55.45	42948		VV	0.148	0.055
56.41	39053		VV	0.152	0.050
56.56	29468		VV	0.128	0.037
57.17	18779		BV	0.114	0.024
57.57	20339		PV	0.140	0.026
58.12	28333		PV	0.164	0.036
58.88	59174		VV	0.243	0.075
60.09	53051		VV	0.138	0.067
60.46	410650		VV	0.306	0.521
60.85	278010		VV	0.204	0.353
61.57	13297		VV	0.194	0.017
62.07	11474		VV	0.130	0.015
63.07	27332		VV	0.186	0.035
63.96	42696		VV	0.155	0.054
64.96	34760		VP	0.145	0.044
65.38	212000		PV	0.157	0.269
66.88	106310		VV	0.305	0.135
67.33	91206		VV	0.340	0.116
69.05	37906		PV	0.159	0.048
69.28	152270		VV	0.202	0.193
70.18	189380		BV	0.239	0.240
72.11	612000		PV	0.218	0.776
72.19	1053700		VB	0.380	1.337
76.13	10344		VV	0.087	0.013
76.19	28512		VP	0.184	0.036
77.00	112000		PV	0.093	0.142
77.05	65115		VV	0.045	0.083
77.08	60616		VV	0.038	0.077
77.13	83264		VV	0.049	0.106
77.16	123290	D	VB	0.083	0.156
78.27	21485		BV	0.130	0.027
79.17	26466		PV	0.161	0.034
82.64	56219		PV	0.116	0.071
82.72	46642		VV	0.067	0.059
82.76	27201	D	VV	0.037	0.035
82.79	44169		VV	0.054	0.056
84.70	21378		BV	0.075	0.027
84.76	22575		VV	0.066	0.029
84.80	13909	D	VV	0.039	0.018
88.44	103380		PV	0.448	0.131
89.25	11226		BV	0.124	0.014
90.49	16520		BV	0.197	0.021
92.66	41038		PV	0.246	0.052
94.64	57107		VV	0.144	0.073
94.77	63108		VV	0.108	0.080
94.82	24881	D	VV	0.045	0.032
94.87	23278		VV	0.046	0.030
95.28	15418		VV	0.072	0.020
95.40	50498		VV	0.084	0.064
95.50	102550		VV	0.104	0.130
95.56	24152		VV	0.025	0.031
95.59	181680		VB	0.161	0.231
96.32	15138		PV	0.167	0.019
98.50	25826		VV	0.215	0.033

TOTAL AREA= 7.8821E+07
MUL FACTOR= 1.0000E+00

Table A10

0.25 hour contact time

RUN # 777, APR/29/86 ,11:12:33
WORKFILE ID: C ,WORKFILE NAME:
ID: 000
AREA%

RT	AREA	TYPE	AR/HT	AREA%
CHECKPOINT: THE NEXT PEAK IS A1; SUBTRACT 0.03 MINUTES				
5.51	872120	BB	0.090	1.067
6.58	3907800	BV	0.162	4.780
6.91	668980	VV	0.234	0.818
7.19	345350	VV	0.193	0.423
7.61	10427	VP	0.071	0.013
7.85	2.6913E+07	PV	0.193	32.923
8.04	2.1774E+07	VB	0.246	26.636
9.80	400960	BV	0.131	0.491
10.15	215630	VV	0.157	0.264
10.34	110520	VV	0.136	0.135
10.65	420660	VV	0.097	0.515
10.83	3145300	VV	0.123	3.848
11.04	488980	VV	0.158	0.598
11.77	14779	PV	0.127	0.018
11.91	30722	VV	0.127	0.038
12.01	30675	VV	0.108	0.038
12.55	72814	PV	0.186	0.089
12.75	26925	VV	0.131	0.033
12.88	86419	VV	0.124	0.106
13.08	26963	VV	0.082	0.033
checkpoint: the next peak is A14; add 0.06 minutes				
13.31	2862200	VV	0.122	3.501
14.14	39374	VV	0.171	0.048
14.55	207470	BV	0.168	0.254
14.83	199390	VV	0.245	0.244
15.16	167270	VV	0.133	0.205
15.27	221500	VV	0.180	0.271
15.65	1613100	VV	0.128	1.973
16.03	424760	VP	0.193	0.520
checkpoint: the next peak is A18; add 0.06 minutes				
16.87	2454000	PB	0.118	3.002
17.64	26218	VV	0.084	0.032
17.88	80078	VV	0.092	0.098
18.64	13222	BP	0.090	0.016
19.05	59549	PV	0.214	0.073
19.31	68516	VV	0.106	0.084
19.60	28358	VV	0.183	0.035
19.93	11958	VV	0.095	0.015
20.17	17544	VP	0.135	0.022
20.91	12307	VP	0.087	0.015
21.72	28294	VV	0.183	0.035
22.04	23123	VV	0.178	0.028
22.57	54451	VV	0.087	0.067
23.74	55893	BV	0.212	0.068
23.97	13134	VV	0.072	0.016
24.09	33326	VV	0.091	0.041
24.64	57403	VP	0.121	0.070
25.09	198060	PV	0.128	0.242
25.34	712030	VV	0.195	0.871
25.96	51547	VV	0.136	0.063
26.28	55428	VV	0.274	0.068
26.96	14956	PV	0.133	0.018
27.20	10221	VP	0.088	0.013
27.55	33704	BP	0.109	0.041
27.84	15662	PH	0.080	0.019
28.14	24957	HH	0.112	0.031
28.37	23761	HH	0.096	0.029
28.48	16110	HP	0.110	0.020
29.05	11008	PH	0.086	0.014
29.89	22205	VV	0.094	0.027
30.52	31165	PV	0.110	0.038
31.18	107570	VV	0.111	0.132
31.35	59972	VV	0.111	0.073
31.68	16713	VV	0.091	0.021
31.81	13148	VV	0.090	0.016
31.93	21746	VV	0.120	0.027
32.14	48558	VV	0.218	0.059
32.54	76401	VV	0.169	0.094
32.83	29394	VV	0.105	0.036
33.01	49843	VV	0.111	0.061
33.38	12290	PV	0.088	0.015
33.83	11494	VP	0.163	0.014
34.17	26156	PV	0.170	0.032
34.60	14568	VV	0.213	0.018
34.84	22999	VV	0.078	0.028
35.22	40204	PV	0.122	0.049
35.99	54702	VP	0.199	0.067
36.30	58981	PV	0.090	0.072
36.39	77809	VV	0.099	0.095
36.64	136540	VV	0.140	0.167
checkpoint: the next peak is D3; add 0.08 minutes				
36.93	1161900	VV	0.099	1.421
37.17	49430	VV	0.091	0.061
37.32	133780	VV	0.134	0.164
37.55	70630	VV	0.111	0.086
37.79	18916	VV	0.148	0.023
38.15	25629	PV	0.084	0.031
38.36	79735	VV	0.130	0.098
39.03	965730	PV	0.090	1.181
39.24	124950	VV	0.099	0.153
39.76	411880	VV	0.124	0.504
39.98	232310	VV	0.142	0.284
40.24	47430	VV	0.095	0.058
40.30	60715	VV	0.101	0.074
40.47	80750	VV	0.143	0.099
40.73	201820	VV	0.122	0.247
41.00	31697	VV	0.132	0.039
41.31	1485800	VV	0.157	1.818

41.68	110440	VV	0.131	0.135
42.14	13120	VV	0.110	0.016
42.70	34020	PV	0.087	0.042
42.80	55288	VV	0.125	0.068
42.91	115320	VV	0.145	0.141
43.29	36347	VV	0.125	0.045
43.42	42342	VV	0.126	0.052
43.68	58084	VV	0.133	0.071
43.88	19837	VV	0.128	0.024
44.16	28435	VV	0.105	0.035
44.32	157400	VV	0.161	0.193
44.66	245670	VV	0.110	0.301
44.88	25683	VV	0.112	0.031
45.13	62003	VV	0.143	0.076
45.28	15548	VV	0.098	0.019
45.88	12405	BV	0.087	0.015
46.10	15312	VV	0.099	0.019
46.26	31712	VV	0.142	0.039
46.61	17559	VV	0.099	0.022
46.78	14504	VV	0.079	0.018
46.98	14124	VV	0.105	0.017
47.10	14833	VV	0.071	0.018
47.40	83210	VV	0.163	0.102
47.44	21632	VV	0.041	0.027
47.60	121660	VV	0.176	0.149
47.71	102640	VV	0.143	0.126
47.92	37694	VV	0.103	0.046
48.03	92628	VV	0.118	0.113
48.25	118460	VV	0.140	0.145
48.64	102130	VV	0.265	0.125
48.92	126670	VV	0.197	0.155
49.06	77452 D	VV	0.170	0.095
49.50	115940	VV	0.192	0.142
49.76	40683	VV	0.096	0.050
49.97	144400	VV	0.203	0.177
50.27	122910	VV	0.190	0.150
50.45	85225	VV	0.128	0.104
50.68	164230	VV	0.183	0.201
50.83	117670	VV	0.145	0.144
51.43	191460	VV	0.200	0.234
51.68	185240	VV	0.216	0.227
51.85	101660	VV	0.132	0.124
52.13	87450	VV	0.125	0.107
52.42	207460	VV	0.229	0.254
53.31	55291	VV	0.129	0.068
53.67	113590	VV	0.238	0.139
53.94	48825	VV	0.146	0.060
54.15	54501	VV	0.153	0.067
54.62	13893	VV	0.088	0.017
54.74	39549	VV	0.210	0.048
55.10	19545	VV	0.172	0.024
55.46	47351	VV	0.172	0.058
56.16	57608	VV	0.129	0.071
56.40	69230	VV	0.199	0.085
56.63	75334	VV	0.195	0.092
57.17	12921	PV	0.101	0.016
57.57	28497	VP	0.125	0.035
58.63	12814	VV	0.119	0.016
60.11	118960	VV	0.193	0.146
60.86	103940	VP	0.149	0.127
63.08	10688	PV	0.122	0.013
63.99	47300	VV	0.208	0.058
64.98	30976	VV	0.160	0.038
65.40	146120	VP	0.157	0.179
66.93	57041	VP	0.220	0.070
69.04	24042	BV	0.140	0.029
69.28	56435	VV	0.111	0.069
70.19	118760	PV	0.220	0.145
70.65	14712	VV	0.112	0.018
70.92	53704	VV	0.166	0.066
71.08	18003	VV	0.064	0.022
73.19	30169	PV	0.247	0.037
73.75	26453	PP	0.290	0.032
74.50	19157	VV	0.125	0.023
74.63	14065	VV	0.086	0.017
76.16	10336	BV	0.103	0.013
77.11	217880	BV	0.169	0.267
77.16	114700 D	VP	0.096	0.140
79.17	16520	PV	0.112	0.020
82.71	66060	BV	0.132	0.081
82.78	40067	VV	0.070	0.049
84.78	36757	PV	0.132	0.045
84.86	24417	VV	0.074	0.030
88.38	36546	PV	0.179	0.045
89.26	17053	VV	0.172	0.021
93.39	34786	PV	0.300	0.043
94.61	17702	VV	0.085	0.022
94.70	26491	VV	0.075	0.032
94.74	17037 D	VV	0.047	0.021
94.80	12476	VV	0.036	0.015
94.85	70587	VB	0.170	0.086
95.43	52392	BV	0.111	0.064
95.50	39403	VV	0.062	0.048
95.60	133880	VV	0.159	0.164
98.56	16360	VV	0.164	0.020

TOTAL AREA= 8.1747E+07
MUL FACTOR= 1.0000E+00

Table A11

0.5 hour contact time

RUN # 775, APR/28/86 ,18:35:19
WORKFILE ID: C ,WORKFILE NAME:
ID: 000
AREA%

RT	AREA	TYPE	AR/HT	AREA%
checkpoint: the next peak is A1; subtract 0.04 minutes				
5.52	2977900	BB	0.138	3.057
6.60	7608100	BV	0.177	7.810
6.90	938900	D VV	0.187	0.964
7.19	148940	VV	0.056	0.153
7.61	18033	VP	0.080	0.019
7.87	2.5632E+07	PV	0.193	26.311
8.06	1.5362E+07	VV	0.179	15.769
8.29	7656200	VB	0.217	7.859
9.83	229380	PV	0.141	0.236
10.17	337870	VV	0.168	0.347
10.68	433310	PV	0.088	0.445
10.84	8467100	VB	0.145	8.691
11.95	26692	PV	0.102	0.027
12.05	47255	VV	0.112	0.049
12.54	114150	PV	0.174	0.117
12.91	52462	PP	0.088	0.054
checkpoint: the next peak is A14; add 0.02 minutes				
13.35	3147900	PB	0.123	3.231
14.08	11492	VV	0.064	0.012
14.15	20088	VV	0.051	0.021
14.18	33156	VV	0.077	0.034
14.59	448470	VV	0.249	0.460
14.87	415210	VV	0.212	0.426
15.20	312060	VV	0.148	0.320
15.30	455270	VV	0.214	0.467
15.68	2984900	VV	0.132	3.064
16.06	740530	VV	0.160	0.760
checkpoint: the next peak is A18; add 0.03 minutes				
16.90	2278000	VB	0.129	2.338
17.67	14122	PV	0.092	0.015
17.92	98026	VV	0.090	0.101
18.10	13636	VP	0.117	0.014
18.60	34018	VP	0.171	0.035
19.09	47010	PV	0.144	0.048
19.35	62926	VP	0.092	0.065
19.65	42018	PV	0.109	0.043
19.96	18276	VV	0.092	0.019
20.20	24588	VP	0.136	0.025
20.97	47351	PB	0.090	0.049
21.51	43142	BH	0.076	0.044
21.76	37060	HP	0.136	0.038
22.60	47705	HP	0.080	0.049
23.41	24755	PH	0.212	0.025
23.66	24110	HH	0.089	0.025
23.77	66344	HH	0.163	0.068
24.13	58823	HH	0.089	0.060
24.24	37773	HH	0.099	0.039
24.68	109500	HH	0.122	0.112
25.13	114740	HH	0.159	0.118
25.38	103350	HH	0.138	0.106
25.56	49820	HH	0.131	0.051
25.74	132300	HH	0.088	0.136
26.00	39801	HH	0.130	0.041
26.21	20898	HH	0.124	0.022
26.46	12136	HP	0.097	0.013
26.97	28610	HH	0.121	0.029
27.14	69691	HH	0.126	0.072
27.57	52697	HH	0.145	0.054
27.87	90922	HH	0.112	0.093
28.03	29185	HH	0.103	0.030
28.17	55191	HH	0.147	0.057
28.39	58082	HH	0.120	0.060
28.82	32006	HH	0.158	0.033
29.09	30009	HH	0.113	0.031
29.52	31268	HH	0.134	0.032
29.70	20999	HH	0.116	0.022
29.81	18279	HV	0.085	0.019
29.93	42568	VV	0.121	0.044
30.12	15053	VV	0.102	0.016
30.57	90333	VV	0.117	0.093
30.84	19901	VV	0.128	0.020
31.07	16455	VV	0.102	0.017
31.21	884800	VV	0.125	0.908
31.71	37506	VV	0.109	0.039
31.85	24952	VV	0.092	0.026
31.96	25749	VV	0.101	0.026
32.14	40810	VV	0.145	0.042
32.26	17442	VV	0.075	0.018
32.58	80629	VV	0.139	0.083
32.85	34390	VV	0.098	0.035
33.04	190150	VV	0.087	0.195
33.23	10672	VV	0.077	0.011
33.40	16644	VV	0.090	0.017
34.23	38726	VV	0.153	0.040
34.54	13070	VV	0.123	0.013
34.86	31204	VP	0.091	0.032
35.25	60149	PV	0.122	0.062
35.76	10174	VV	0.083	0.010
35.89	23954	VV	0.106	0.025
36.09	53514	VV	0.167	0.055
36.32	56769	VV	0.074	0.058
36.41	176240	VV	0.103	0.181
36.67	169710	VV	0.124	0.174
checkpoint: the next peak is D3; add 0.06 minutes				
36.95	1039300	VV	0.085	1.067
37.20	56333	VV	0.092	0.058
37.35	172070	VV	0.139	0.177
37.58	132820	VV	0.101	0.136

38.18	62777	VV	0.090	0.064
38.38	103560	VV	0.154	0.106
39.05	1229100	PV	0.095	1.262
39.26	259980	VV	0.164	0.267
39.80	265660	VV	0.165	0.273
40.01	266980	VV	0.148	0.274
40.25	40343	VV	0.080	0.041
40.33	60001	VV	0.105	0.062
40.51	62700	VV	0.127	0.064
40.75	421060	VP	0.094	0.432
41.13	20563	VP	0.077	0.021
41.38	3036200	PB	0.162	3.117
42.75	111720	PV	0.203	0.115
42.97	222010	VV	0.130	0.228
43.31	46939	VV	0.135	0.048
43.47	65041	VV	0.126	0.067
43.71	114970	VV	0.119	0.118
43.94	27564	VP	0.114	0.028
44.17	60552	VV	0.115	0.062
44.40	179590	VV	0.139	0.184
44.68	309050	VV	0.112	0.317
45.13	76471	VV	0.101	0.079
45.25	71985	VV	0.147	0.074
45.52	13350	VP	0.102	0.014
45.72	25634	PV	0.104	0.026
45.92	27054	VV	0.115	0.028
46.11	55618	VV	0.124	0.057
46.26	36722	VV	0.132	0.038
46.45	41642	VV	0.099	0.043
47.14	18425	VV	0.108	0.019
47.41	50892	VV	0.129	0.052
47.72	238090	VV	0.215	0.244
47.94	22134	VV	0.067	0.023
48.05	164890	VV	0.109	0.169
48.28	104320	VV	0.118	0.107
48.53	30855	VV	0.121	0.032
48.60	17009	VV	0.063	0.018
48.68	34645	VV	0.106	0.036
48.95	71737	VV	0.132	0.074
49.12	45424	VV	0.120	0.047
49.30	10797	VV	0.055	0.011
49.41	27049	VV	0.087	0.028
49.51	90188	VV	0.164	0.093
50.01	44603	PV	0.114	0.046
50.28	17365	VV	0.111	0.018
50.71	32328	BV	0.084	0.033
50.84	43164	VV	0.123	0.044
51.45	88825	VV	0.151	0.091
51.69	14012	VV	0.058	0.014
51.88	117800	VV	0.213	0.121
52.16	100620	VV	0.171	0.103
52.45	110110	VV	0.190	0.113
52.70	48759	VV	0.135	0.050
52.80	30465	VV	0.079	0.031
53.08	54903	VV	0.168	0.056
53.68	61941	VV	0.164	0.064
53.92	14979	VV	0.080	0.015
54.01	32356	VV	0.133	0.033
54.18	51180	VV	0.167	0.053
54.42	18678	VV	0.093	0.019
55.10	11873	VV	0.080	0.012
55.47	79349	VV	0.216	0.082
56.19	86685	VV	0.154	0.089
56.37	16123	VV	0.060	0.017
56.65	63761	VV	0.159	0.066
57.18	21530	VV	0.128	0.022
57.57	79876	VV	0.227	0.082
58.15	16535	VV	0.156	0.017
58.54	18001	VV	0.112	0.019
58.62	10790	VV	0.058	0.011
58.66	18328	VV	0.086	0.019
60.12	84791	VV	0.175	0.087
60.87	73066	VV	0.141	0.075
62.12	16512	PV	0.221	0.017
63.74	11029	VV	0.145	0.011
64.02	33860	VV	0.211	0.035
64.65	35138	VV	0.230	0.036
64.98	17361	VV	0.130	0.018
65.40	99174	VP	0.164	0.102
66.92	28136	VV	0.113	0.029
69.07	14438	PV	0.153	0.015
69.30	36866	VV	0.112	0.038
70.22	82423	VP	0.236	0.085
73.77	10011	PV	0.102	0.010
75.59	15609	VV	0.123	0.016
77.12	235230	PV	0.260	0.242
77.42	29417	VV	0.122	0.030
79.26	13600	PV	0.144	0.014
79.59	69175	VV	0.398	0.071
81.40	15846	VV	0.248	0.016
82.83	63253	VV	0.173	0.065
84.79	52074	BV	0.295	0.054
86.92	40405	BV	0.220	0.042
88.43	24125	PV	0.146	0.025
93.33	77218	VV	0.184	0.079
94.71	128180	VV	0.207	0.132
94.76	37371	VV	0.051	0.038
94.89	43145	VV	0.050	0.044
95.30	167600	VP	0.163	0.172

TOTAL AREA= 9.7421E+07
MUL FACTOR= 1.0000E+00

Table A12

1.0 hour contact time

RUN # 776, APR/29/86 ,09:28:33
WORKFILE ID: C ,WORKFILE NAME:
ID: 000
AREA%

RT	AREA	TYPE	AR/HT	AREA%
5.48	1848800	BB	0.139	3.502
checkpoint: the next peak is A2; add 0.03 minutes.				
6.60	3777700	PV	0.166	7.155
6.86	413810	VV	0.134	0.784
7.18	474880	VV	0.213	0.899
7.58	24081	VV	0.092	0.046
7.86	6727300	VV	0.169	12.741
8.06	8105600	VV	0.176	15.352
8.29	5819000	VB	0.228	11.021
9.40	82080	VP	0.156	0.156
9.79	96149	PV	0.144	0.182
10.13	271740	VV	0.150	0.515
10.34	84196	VV	0.139	0.160
10.65	432830	VV	0.105	0.820
10.82	3938900	VV	0.123	7.460
11.89	23982	VV	0.112	0.045
12.02	28885	VV	0.114	0.055
12.49	79554	PV	0.152	0.151
12.88	48708	PV	0.093	0.092
checkpoint: the next peak is A14; add 0.04 minutes				
13.33	2303900	PB	0.117	4.364
14.15	76716	VV	0.164	0.145
14.56	512040	VV	0.291	0.970
14.82	278630	VV	0.189	0.528
15.17	274990	VV	0.144	0.521
15.28	366270	VV	0.204	0.694
15.66	2243700	VV	0.128	4.250
16.03	586290	VV	0.191	1.110
checkpoint: the next peak is A18; add 0.05 minutes				
16.88	4097000	VV	0.224	7.760
17.63	96971	VV	0.130	0.184
17.78	28963	VV	0.066	0.055
17.89	104120	VV	0.116	0.197
18.06	30470	VP	0.147	0.058
18.58	49331	VP	0.140	0.093
19.31	40588	BP	0.083	0.077
19.58	17365	VV	0.241	0.033
20.95	70329	VB	0.076	0.133
21.49	74107	PV	0.078	0.140
21.73	21000	VV	0.193	0.040
22.03	11721	VV	0.094	0.022
22.57	41642	VV	0.075	0.079
23.74	23639	VV	0.112	0.045
23.98	10931	VV	0.071	0.021
24.09	32052	VV	0.081	0.061
24.20	24498	VV	0.115	0.046
24.66	66542	BP	0.114	0.126
25.10	118690	PV	0.147	0.225
checkpoint: the next peak is A25; add 0.06 minutes				
25.35	310520	VV	0.148	0.588
25.71	310020	VV	0.091	0.587
25.97	48309	VV	0.141	0.092
26.95	23884	VV	0.167	0.045
27.14	13079	VV	0.091	0.025
27.32	15770	VV	0.095	0.030
27.54	48874	VV	0.174	0.093
27.84	74229	VV	0.126	0.141
27.99	22425	VV	0.103	0.043
28.15	53188	VV	0.158	0.101
28.36	31356	VV	0.117	0.059
28.51	60049	VV	0.185	0.114
28.81	44245	VV	0.199	0.084
29.06	20962	VV	0.097	0.040
29.49	20181	VV	0.124	0.038
29.66	20605	VV	0.122	0.039
29.78	20443	VV	0.098	0.039
29.89	47449	VV	0.131	0.090
30.51	19834	VV	0.125	0.038
31.19	127790	VV	0.115	0.242
31.35	64964	VV	0.130	0.123
31.68	24012	VV	0.116	0.046
31.82	17083	VV	0.092	0.032
31.94	17238	VV	0.106	0.033
32.14	39502	VV	0.201	0.075
32.56	27980	VV	0.090	0.053
32.84	25782	VV	0.109	0.049
33.01	84413	VV	0.096	0.160
33.38	19243	VV	0.095	0.037
34.17	43016	PP	0.190	0.082
34.72	99953	PV	0.078	0.189
34.84	18592	VV	0.079	0.035
35.23	32394	VV	0.121	0.061
36.00	23547	VV	0.093	0.045
36.30	41866	PV	0.088	0.079
36.41	78132	VV	0.085	0.148
36.64	93412	VP	0.128	0.177
checkpoint: the next peak is D3; add 0.08 minutes				
36.93	1067600	PB	0.100	2.022
37.32	74786	BP	0.110	0.142
37.55	38005	PP	0.080	0.072
38.15	23410	VV	0.086	0.044
38.36	29704	VV	0.106	0.056
39.03	661700	PV	0.093	1.253
39.25	90018	VV	0.095	0.171
39.77	294200	VV	0.126	0.557
39.98	89656	VV	0.167	0.170
40.31	95656	VV	0.194	0.181
40.48	49473	VV	0.129	0.094
40.75	76172	VV	0.235	0.144

41.01	27857	VV	0.114	0.053
41.39	609260	VV	0.159	1.154
41.68	69532	VV	0.113	0.132
41.82	62062	VV	0.152	0.118
42.16	10737	VV	0.128	0.020
42.80	78342	PV	0.184	0.148
42.95	58348	VV	0.203	0.111
43.46	209250	VV	0.241	0.396
43.67	106240	VV	0.146	0.201
43.94	12084	VV	0.116	0.023
44.23	31184	VV	0.092	0.059
44.39	24024	VV	0.074	0.046
44.60	34864	VV	0.126	0.066
44.74	29981	VV	0.123	0.057
44.88	23108	VV	0.131	0.044
45.11	133710	VV	0.130	0.253
45.70	35380	PV	0.097	0.067
45.95	23037	VV	0.094	0.044
46.05	40061	VV	0.152	0.076
46.27	30796	VV	0.134	0.058
46.44	91175	VV	0.097	0.173
46.62	11485	VV	0.098	0.022
47.13	21847	PV	0.121	0.041
47.44	36916	VV	0.131	0.070
47.53	28747	VV	0.075	0.055
47.58	22745	VV	0.056	0.043
47.71	84526	VV	0.113	0.160
47.93	35552	VV	0.135	0.067
48.26	54583	VV	0.088	0.103
48.64	76652	PV	0.134	0.145
48.93	41910	VV	0.140	0.079
49.09	51110	VP	0.130	0.097
49.49	27799	PV	0.097	0.053
50.00	50478	PV	0.103	0.096
50.27	21461	VV	0.115	0.041
50.46	13168	VV	0.086	0.025
50.70	24183	VV	0.129	0.046
50.82	22817	VV	0.116	0.043
50.99	10620	VV	0.092	0.020
51.43	88998	VV	0.145	0.169
51.81	16016	VV	0.105	0.030
52.46	37014	PV	0.098	0.070
52.66	34621	VV	0.148	0.066
53.42	20716	VV	0.184	0.039
53.67	85565	VV	0.145	0.162
54.14	27558	VV	0.155	0.052
54.75	11317	PP	0.138	0.021
55.43	15731	VV	0.069	0.030
56.16	71447	PV	0.116	0.135
56.64	62105	VV	0.147	0.118
57.57	32994	VV	0.142	0.063
58.56	14281	VV	0.114	0.027
58.94	12569	VV	0.124	0.024
60.13	91590	VV	0.181	0.174
60.61	22267	VV	0.142	0.042
60.86	101810	VV	0.177	0.193
61.66	20750	PV	0.174	0.039
64.97	17064	VP	0.147	0.032
65.39	107200	PP	0.174	0.203
66.94	44913	VV	0.233	0.085
69.28	28942	VV	0.090	0.055
70.17	33498	VV	0.104	0.063
70.22	49853 D	VV	0.146	0.094
72.15	16996	VV	0.134	0.032
72.36	25110	VV	0.104	0.048
72.46	30598	VV	0.111	0.058
72.57	25832	VV	0.083	0.049
73.78	12713	PV	0.119	0.024
73.90	24738	VV	0.185	0.047
76.21	19739	VP	0.229	0.037
77.10	130430	BV	0.138	0.247
77.14	92953 D	VV	0.106	0.176
78.33	18295	PV	0.201	0.035
79.18	13668	VV	0.126	0.026
82.75	51334	PV	0.152	0.097
82.82	31860	VV	0.078	0.060
88.38	32392	PV	0.233	0.061
93.32	126410	PV	0.439	0.239
94.65	13128	VV	0.073	0.025
94.78	30889	VV	0.112	0.059
95.33	15288	VV	0.095	0.029
95.47	41331	VV	0.093	0.078
95.52	21818	VV	0.048	0.041
95.60	43205 D	VV	0.085	0.082

TOTAL AREA= 5.2800E+07
MUL FACTOR= 1.0000E+00

Table A13

4.0 hours contact time

RUN # 789, APR/30/86 ,20:12:05
WORKFILE ID: C ,WORKFILE NAME:
ID: 000
AREA%

RT	AREA	TYPE	AR/HT	AREA%
checkpoint: the next peak is A1; add 0.06 minutes				
5.54	2793900	BB	0.149	3.491
6.63	1856400	PB	0.159	2.320
7.27	106630	BP	0.142	0.133
7.67	19074	PV	0.084	0.024
7.91	5.5541E+07	VV	0.372	69.395
9.25	239110	VV	0.166	0.299
9.48	115070	VV	0.109	0.144
9.87	212340	VV	0.251	0.265
10.22	287330	VV	0.201	0.359
10.39	177760	VV	0.178	0.222
10.72	464900	VV	0.113	0.581
10.87	471150	VV	0.130	0.589
11.13	243370	VV	0.150	0.304
11.37	42065	VP	0.124	0.053
11.97	56210	VV	0.229	0.070
12.64	54352	PV	0.133	0.068
12.96	145550	VV	0.159	0.182
checkpoint: the next peak is A14; subtract 0.01				
13.38	2630700	VV	0.135	3.287
13.83	61662	VV	0.052	0.077
14.10	137340	VV	0.117	0.172
14.19	99207	VV	0.076	0.124
14.22	147110	VV	0.111	0.184
14.36	83443	VV	0.063	0.104
14.62	757490	VV	0.324	0.947
14.91	381640	VV	0.196	0.477
15.23	366160	VV	0.178	0.458
15.34	427410	VV	0.211	0.534
15.72	460110	VV	0.200	0.575
15.88	326390	VV	0.158	0.408
16.10	584220	VV	0.166	0.730
checkpoint: the next peak is A18; RT exact				
16.93	1462400	PB	0.108	1.827
17.72	18421	VV	0.110	0.023
17.95	74105	VV	0.115	0.093
18.15	38843	VV	0.198	0.049
18.75	19947	VP	0.135	0.025
19.14	24437	PV	0.120	0.031
19.38	80041	VV	0.113	0.100
19.66	41651	VV	0.199	0.052
20.98	13873	PP	0.080	0.017
21.78	13900	BV	0.124	0.017
22.09	19800	VV	0.110	0.025
22.63	37155	VP	0.090	0.046
23.70	10897	BV	0.073	0.014
23.82	31845	VV	0.119	0.040
24.15	34395	VV	0.087	0.043
24.26	31772	VV	0.143	0.040
24.70	58617	VP	0.107	0.073
25.18	86955	PV	0.129	0.109
checkpoint; the next peak is A25; RT exact				
25.41	390840	VV	0.130	0.488
25.60	123020	VV	0.143	0.154
26.04	40412	VV	0.116	0.051
27.00	16932	PV	0.113	0.021
27.29	10376	VV	0.118	0.013
27.91	28717	VV	0.101	0.036
28.06	17872	VV	0.094	0.022
28.20	38385	VV	0.135	0.048
28.41	29399	VV	0.119	0.037
28.87	18253	VV	0.161	0.023
29.12	24481	VV	0.161	0.031
29.85	16711	VV	0.102	0.021
29.97	17132	VV	0.087	0.021
30.60	42962	PV	0.113	0.054
30.86	16741	VV	0.152	0.021
31.25	38819	VV	0.104	0.049
31.41	31660	VV	0.100	0.040
31.74	14552	VV	0.091	0.018
31.87	17956	VV	0.080	0.022
32.00	16289	VV	0.092	0.020
32.19	33544	VV	0.153	0.042
32.29	16094	VV	0.090	0.020
32.62	46099	VV	0.170	0.058
32.90	28372	VV	0.103	0.036
33.08	38034	VV	0.100	0.048
33.27	20584	VP	0.070	0.026
33.45	22525	PV	0.090	0.028
34.28	80998	PV	0.150	0.101
34.44	31186	VV	0.107	0.039
34.91	15573	BV	0.073	0.020
35.28	43481	PV	0.096	0.054
35.47	14814	VV	0.146	0.019
35.80	12009	VV	0.099	0.015
35.92	13496	VV	0.083	0.017
36.06	73469	VV	0.168	0.092
36.37	31112	VV	0.087	0.039
36.47	85646	VV	0.094	0.107
36.71	153280	VV	0.123	0.192
checkpoint: the next peak is D3; add 0.02 minutes				
36.99	789490	VV	0.086	0.986
37.24	24328	VV	0.100	0.030
37.40	171740	VV	0.130	0.215
37.62	92736	VV	0.103	0.116
38.02	14705	VV	0.119	0.018
38.22	76720	VV	0.105	0.096
38.43	43905	VV	0.137	0.055
39.09	688590	VV	0.093	0.860

39.33	163900	VV	0.168	0.205
39.83	307490	VV	0.147	0.384
40.06	297150	VV	0.153	0.371
40.30	40634	VV	0.081	0.051
40.38	62028	VV	0.120	0.078
40.57	59870	VV	0.121	0.075
40.80	106850	VV	0.149	0.134
41.09	54163	VV	0.176	0.068
41.40	869410	VV	0.158	1.086
41.74	58361	VV	0.112	0.073
42.80	42797	PV	0.095	0.054
42.99	55094	VV	0.183	0.069
43.36	41547	VV	0.134	0.052
43.51	42630	VV	0.122	0.053
43.75	71725	VV	0.140	0.090
44.22	24793	PV	0.093	0.031
44.43	43414	VV	0.128	0.054
44.74	135110	VV	0.121	0.169
45.20	32247	VV	0.114	0.040
45.37	40103	VV	0.143	0.050
45.96	16053	VV	0.106	0.020
46.16	10248	VV	0.134	0.013
46.52	19404	VV	0.100	0.024
46.92	22893	PV	0.163	0.029
47.19	25229	VV	0.105	0.032
47.45	22696	VV	0.075	0.028
47.50	14916	VV	0.045	0.019
47.61	64789	VV	0.130	0.081
47.78	139270	VV	0.125	0.174
47.99	13804	VV	0.057	0.017
48.11	207510	VV	0.099	0.259
48.33	71508	VV	0.105	0.089
48.72	39163	VV	0.150	0.049
49.00	62090	VV	0.139	0.078
49.17	50902	VP	0.175	0.064
49.58	26028	PV	0.112	0.033
49.86	22334	VV	0.136	0.028
50.07	70060	VV	0.224	0.088
50.35	29115	VV	0.135	0.036
50.52	30364	VV	0.132	0.038
50.77	30557	VV	0.150	0.038
50.92	50737	VV	0.145	0.063
51.50	61387	BV	0.161	0.077
51.84	25433	VV	0.117	0.032
52.08	30386	VV	0.126	0.038
52.52	97684	VV	0.202	0.122
52.95	30070	VV	0.130	0.038
53.15	50162	VV	0.181	0.063
53.40	13487	VV	0.106	0.017
53.77	38900	VV	0.172	0.049
54.04	11426	VV	0.092	0.014
54.25	42887	VV	0.200	0.054
54.83	28141	VV	0.189	0.035
55.56	22025	PP	0.139	0.028

56.25	41063	PV	0.142	0.051
56.51	24737	VV	0.141	0.031
56.73	62898	VV	0.179	0.079
57.65	10310	BV	0.067	0.013
57.69	18169	VV	0.096	0.023
60.26	62066	VV	0.183	0.078
61.00	56418	PV	0.147	0.071
64.95	16499	VV	0.161	0.021
65.56	89689	PV	0.180	0.112
67.14	43671	PV	0.271	0.055
69.51	57070	VV	0.205	0.071
70.40	72778	VV	0.245	0.091
73.98	14251	VV	0.134	0.018
74.86	46237	VV	0.198	0.058
77.28	55059	VV	0.100	0.069
77.32	20833 D	VV	0.034	0.026
77.36	20783	VV	0.033	0.026
77.38	80250 D	VB	0.112	0.100
78.63	15004	BV	0.230	0.019
79.54	14209	BV	0.152	0.018
83.05	55140	PV	0.176	0.069
83.12	20570	VV	0.060	0.026
85.11	51496	VP	0.305	0.064
88.90	44509	PV	0.403	0.056

TOTAL AREA= 8.0035E+07
MUL FACTOR= 1.0000E+00

Table A14

8.0 hours contact time

RUN # 790, MAY/01/86 ,13:52:31
WORKFILE ID: C ,WORKFILE NAME:
ID: 000
AREA%

RT	AREA	TYPE	AR/HT	AREA%
5.09	139450	BP	0.156	0.159

checkpoint: the next peak is A1; subtract 0.01 minute

5.49	4287600	PV	0.163	4.879
5.93	43888	VP	0.071	0.050
6.60	1893000	PV	0.161	2.154
7.02	168920	VV	0.172	0.192
7.24	336150	VP	0.176	0.383
7.62	17980	PV	0.093	0.021
7.86	4.5242E+07	VV	0.297	51.486
8.30	1.1377E+07	VV	0.261	12.948
9.44	390590	VV	0.278	0.445
9.80	247140	VV	0.264	0.281
10.16	480620	VV	0.176	0.547
10.37	239950	VV	0.168	0.273
10.68	697520	VV	0.124	0.794
10.83	341670	VV	0.128	0.389
11.08	261680	VV	0.145	0.298
11.34	49270	VP	0.139	0.056
11.93	22750	PV	0.101	0.026
12.05	29758	VP	0.106	0.034
12.26	13138	PP	0.088	0.015
12.55	64020	PV	0.167	0.073
12.92	49050	PP	0.085	0.056

checkpoint: the next peak is A14; add 0.02 minutes

13.35	4101100	PB	0.117	4.667
13.83	13791	BV	0.082	0.016
14.07	39185	VV	0.090	0.045
14.18	64676	VV	0.086	0.074
14.24	47629	VV	0.058	0.054
14.37	120990	VV	0.113	0.138
14.46	105570	VV	0.081	0.120
14.58	648720	VV	0.205	0.738
14.85	329970	VV	0.149	0.376
15.05	109980 D	VV	0.053	0.125
15.19	539920	VV	0.150	0.614
15.31	557730	VV	0.184	0.635
15.68	560990	VV	0.204	0.638
15.84	330660	VV	0.144	0.376
16.06	583420	VV	0.131	0.664

checkpoint: the next peak is A18; add 0.03 minutes

16.90	5008000	VB	0.192	5.699
17.67	88320	BV	0.114	0.101
17.91	27704	VP	0.092	0.032
18.68	11330	PV	0.071	0.013
19.23	97712	VV	0.087	0.111
19.35	57578	VP	0.087	0.066
19.59	18867	VP	0.267	0.022
20.05	26977	PV	0.083	0.031
20.82	12578	VV	0.089	0.014
21.15	17181	VP	0.085	0.020
21.75	25319	VV	0.226	0.029
22.06	26041	VV	0.099	0.030
22.44	10433	VV	0.104	0.012
22.61	63847	VV	0.086	0.073
23.39	23496	PV	0.239	0.027
23.68	15174	VV	0.096	0.017
23.79	43714	VV	0.171	0.050
24.03	20863	VV	0.080	0.024
24.12	37489	VV	0.083	0.043
24.25	36094	VV	0.138	0.041
24.68	79697	VP	0.122	0.091
25.15	110620	VV	0.131	0.126
25.37	430160	VV	0.145	0.490
25.57	136170	VV	0.141	0.155
25.84	21509	VV	0.097	0.025
26.01	74462	VV	0.140	0.085
26.30	27444	VV	0.179	0.031
26.98	30919	PP	0.138	0.035
27.89	55594	VV	0.101	0.063
28.03	14444	VV	0.093	0.016
28.18	31701	VV	0.134	0.036
28.52	41160	VV	0.154	0.047
28.85	22214	VV	0.103	0.025
29.11	12144	VV	0.121	0.014
29.81	16974	PV	0.122	0.019
29.92	24201	VV	0.096	0.028
30.56	21984	PV	0.115	0.025
31.22	19612	VV	0.108	0.022
31.40	53541	VP	0.113	0.061
31.71	11391	PV	0.085	0.013
31.85	14886	VV	0.075	0.017
31.98	16195	VV	0.103	0.018
32.27	10194	VB	0.076	0.012
32.66	14614	BV	0.120	0.017
32.87	18006	VV	0.094	0.021
33.06	23359	VP	0.111	0.027
33.42	21465	VV	0.105	0.024
34.03	15336	PV	0.108	0.018
34.21	111840	VV	0.165	0.127
34.89	18300	VV	0.098	0.021
35.26	25665	PV	0.111	0.029
36.04	189060	VV	0.108	0.215
36.45	67824	VP	0.083	0.077
36.69	89300	PP	0.123	0.102

checkpoint: the next peak is D3; add 0.05 minutes

36.96	1196100	PB	0.105	1.361
37.36	100970	BV	0.109	0.115
37.60	46342	VP	0.078	0.053
37.99	23029	VP	0.092	0.026

38.20	34783	PV	0.085	0.040
38.39	19270	VV	0.127	0.022
39.07	371910	PV	0.094	0.423
39.30	42645	VV	0.093	0.049
39.80	278470	PV	0.120	0.317
40.03	155370	VV	0.187	0.177
40.38	61741	VV	0.128	0.070
40.53	15914	VV	0.070	0.018
40.78	58138	VV	0.175	0.066
41.04	25974	VV	0.102	0.030
41.39	537700	VV	0.174	0.612
41.73	55474	VV	0.105	0.063
41.85	68941	VV	0.131	0.079
42.85	92896	PV	0.177	0.106
43.06	62853	VV	0.202	0.072
43.34	47873	VV	0.154	0.055
43.46	30371	VV	0.112	0.035
43.72	28331	VV	0.121	0.032
44.25	11910	PV	0.090	0.014
44.40	11611	VV	0.099	0.013
44.67	18083	VV	0.134	0.021
45.15	29763	PV	0.128	0.034
45.74	19042	PV	0.109	0.022
45.94	20340	VV	0.124	0.023
46.28	27648	VV	0.132	0.032
46.47	18136	VV	0.102	0.021
47.17	13054	PV	0.102	0.015
47.58	105580	VV	0.215	0.120
47.75	102000	VV	0.115	0.116
47.97	25443	VV	0.101	0.029
48.09	17184	VV	0.090	0.020
48.29	33779	VP	0.094	0.038
48.66	114720	PV	0.136	0.131
48.96	61933	VV	0.167	0.071
49.14	45513	VP	0.148	0.052
49.56	31122	PV	0.097	0.035
49.67	26112	VV	0.074	0.030
49.74	23122	VV	0.065	0.026
50.04	66748	VV	0.153	0.076
50.30	30993	VV	0.136	0.035
50.49	23673	VV	0.098	0.027
50.74	41125	VV	0.181	0.047
50.89	38478	VV	0.126	0.044
51.48	55909	BV	0.142	0.064
52.50	57399	VV	0.141	0.065
53.35	10490	VV	0.099	0.012
53.70	87784	VV	0.156	0.100
54.07	12974	VV	0.135	0.015
54.78	15282	VV	0.131	0.017
55.51	41324	VP	0.196	0.047
56.22	69585	PV	0.123	0.079
56.48	22219	VV	0.142	0.025
56.71	74429	VV	0.180	0.085
57.66	46696	BV	0.157	0.053
58.59	11616	PV	0.117	0.013
60.01	23200	VV	0.166	0.026
60.17	40041	VV	0.176	0.046
60.97	39070	PP	0.152	0.045
61.70	18133	PP	0.196	0.021
62.25	12874	BV	0.170	0.015
64.88	17093	VV	0.108	0.020
65.51	55876	PV	0.168	0.064
67.04	20374	VV	0.156	0.023
69.43	37539	VV	0.185	0.043
70.31	22186	BV	0.118	0.025
71.41	17742	VV	0.155	0.020
73.92	13366	VV	0.132	0.015
74.45	67332	VV	0.203	0.077
77.18	27342	BV	0.086	0.031
77.27	39026	VV	0.080	0.044
77.31	72572	VV	0.138	0.083
77.77	45997	VV	0.189	0.052
77.84	19784	VV	0.066	0.023
77.90	18634	VV	0.063	0.021
82.97	60400	VV	0.226	0.069
88.76	110700	PV	0.484	0.126
90.78	12690	BV	0.147	0.014
93.59	52738	BV	0.485	0.060
94.91	11327	VV	0.089	0.013
95.09	30545	VV	0.150	0.035
95.76	41316	VV	0.140	0.047
95.81	39166	VV	0.113	0.045

TOTAL AREA= 8.7872E+07
MUL FACTOR= 1.0000E+00

Table A15

24 hours contact time

RUN # 788, APR/30/86 ,18:28:35
WORKFILE ID: C ,WORKFILE NAME:
ID: 000
AREA%

RT	AREA	TYPE	AR/HT	AREA%
5.12	82563	BP	0.122	0.088
checkpoint: the next peak is A1; subtract 0.07 minutes				
5.55	1017800	PP	0.150	1.090
6.65	2274300	BV	0.178	2.436
7.04	103450	VV	0.138	0.111
7.26	195580	VP	0.194	0.210
7.89	6.6721E+07	SPB	0.371	71.454
9.36	10352	TVP	0.064	0.011
9.87	28295	VP	0.133	0.030
10.21	168260	PV	0.162	0.180
10.40	84112	VV	0.142	0.090
10.72	350950	VV	0.099	0.376
10.88	1465500	VV	0.125	1.569
11.12	250900	VV	0.143	0.269
11.44	139090	VV	0.125	0.149
11.63	84710	VV	0.128	0.091
11.96	11608	VV	0.081	0.012
12.08	29621	VP	0.113	0.032
12.64	59870	PV	0.181	0.064
12.95	133260	VV	0.143	0.143
13.15	54598	VV	0.088	0.059
checkpoint: the next peak is A14; subtract 0.01 minute				
13.38	2630300	VV	0.138	2.817
13.84	97422	VV	0.059	0.104
14.08	151080	VV	0.088	0.162
14.24	366860	VV	0.188	0.393
14.34	85647	VV	0.044	0.092
14.37	50390	VV	0.026	0.054
14.63	933570	VV	0.301	1.000
14.90	680530	VV	0.239	0.729
15.02	89907	D VV	0.034	0.096
15.06	75900	D VV	0.029	0.081
15.08	94032	D VV	0.036	0.101
15.24	541690	VV	0.188	0.580
15.34	141840	VV	0.051	0.152
15.72	918100	VV	0.161	0.983
15.86	489000	VV	0.161	0.524
16.12	822720	VB	0.234	0.881
checkpoint: the next peak is A18; subtract 0.01 minute				
16.94	1239300	BB	0.117	1.327
17.73	23874	BV	0.127	0.026
17.94	31834	VV	0.134	0.034
18.14	23026	VV	0.123	0.025
18.74	12370	VP	0.129	0.013
19.16	35525	PV	0.184	0.038
19.39	96541	VV	0.104	0.103
19.66	33057	VV	0.199	0.035
20.24	10494	PV	0.103	0.011
20.56	15046	PP	0.164	0.016
20.99	16222	PP	0.082	0.017
21.79	30003	BV	0.117	0.032
22.09	54546	VV	0.125	0.058
22.63	51783	VV	0.165	0.056
22.82	12563	VP	0.167	0.014
23.09	10914	PV	0.090	0.012
23.71	13601	PV	0.072	0.015
23.82	53730	VV	0.162	0.058
24.15	36171	VV	0.083	0.039
24.29	60284	VV	0.175	0.065
24.48	13658	VV	0.086	0.015
24.71	53752	VP	0.117	0.058
25.17	127840	PV	0.125	0.137
25.41	576360	VV	0.140	0.617
25.61	158300	VV	0.138	0.170
26.04	88966	VV	0.146	0.095
26.25	51768	VV	0.147	0.055
26.50	38005	VV	0.149	0.041
27.01	75313	VV	0.144	0.081
27.23	18916	VV	0.070	0.020
27.30	39329	VV	0.107	0.042
27.50	63175	VV	0.230	0.068
27.79	24517	VV	0.112	0.026
27.91	53450	VV	0.103	0.057
28.06	37428	VV	0.118	0.040
28.20	60047	VV	0.144	0.064
28.43	64190	VV	0.122	0.069
28.87	47082	VV	0.133	0.050
29.05	17555	VV	0.077	0.019
29.12	22556	VV	0.087	0.024
29.55	49379	VV	0.203	0.053
29.73	10037	VV	0.082	0.011
29.85	23702	VV	0.107	0.025
29.96	32962	VV	0.114	0.035
30.29	35132	VV	0.210	0.038
30.59	39418	VV	0.112	0.042
31.10	17483	VV	0.143	0.019
31.25	87025	VV	0.104	0.093
31.41	40778	VV	0.096	0.044
31.74	18300	VV	0.086	0.020
31.87	31534	VV	0.082	0.034
32.01	21893	VV	0.116	0.024
32.20	33668	VV	0.133	0.036
32.29	14282	VV	0.067	0.015
32.61	64347	VV	0.138	0.069
32.90	41755	VV	0.113	0.045
33.09	38186	VV	0.110	0.041
33.28	49176	VV	0.093	0.053
33.45	25729	VP	0.090	0.028
34.24	208390	VV	0.140	0.223

34.44	51735	VV	0.107	0.055
34.92	23502	PP	0.081	0.025
35.29	46080	VV	0.090	0.049
35.48	10334	VP	0.105	0.011
35.91	15304	VV	0.073	0.016
36.06	232730	VV	0.114	0.249
36.47	77271	BP	0.085	0.083
36.72	182860	PV	0.115	0.196

checkpoint: the next peak is D3; add 0.02 minute

36.99	984370	VV	0.087	1.054
37.24	16350	VV	0.084	0.018
37.40	224710	VV	0.127	0.241
37.62	124580	VV	0.102	0.133
38.01	105560	VV	0.128	0.113
38.23	94555	VV	0.115	0.101
38.42	60771	VV	0.133	0.065
39.10	824770	VV	0.095	0.883
39.33	121260	VV	0.180	0.130
39.82	792080	VV	0.154	0.848
40.32	105220	VV	0.204	0.113
40.55	26624	VV	0.113	0.029
40.70	23920	VV	0.100	0.026
40.82	26466	VV	0.090	0.028
41.12	35741	VV	0.154	0.038
41.39	845000	VV	0.158	0.905
41.76	43137	VV	0.098	0.046
41.87	43077	VP	0.114	0.046
42.19	19245	PV	0.143	0.021
42.87	122040	PV	0.162	0.131
43.35	62333	VV	0.128	0.067
43.49	38469	VP	0.111	0.041
43.74	46369	PV	0.117	0.050
43.96	11549	VP	0.115	0.012
44.41	16886	VV	0.103	0.018
45.20	14359	PV	0.072	0.015
45.36	12320	VV	0.090	0.013
45.56	11141	VP	0.105	0.012
45.97	14089	VV	0.082	0.015
46.11	13141	VV	0.098	0.014
46.32	15826	VV	0.120	0.017
46.54	19428	VP	0.095	0.021
46.92	20741	VV	0.122	0.022
47.19	26193	VV	0.092	0.028
47.51	47687	PV	0.093	0.051
47.61	105220	VV	0.154	0.113
47.78	147590	VV	0.130	0.158
48.00	28804	VV	0.112	0.031
48.33	54593	VP	0.090	0.059
48.71	33237	BV	0.128	0.036
48.99	59658	VV	0.121	0.064
49.15	49705	VV	0.150	0.053
49.57	11572	PV	0.060	0.012
50.04	48217	PV	0.154	0.052
50.34	31360	VV	0.146	0.034
50.52	24549	VV	0.100	0.026
50.92	45416	VV	0.133	0.049
51.07	17248	VV	0.122	0.019
51.50	50960	PV	0.128	0.055
51.77	10905	VV	0.097	0.012
52.51	40502	PV	0.103	0.043
52.98	20525	VV	0.142	0.022
53.38	30405	VP	0.161	0.033
53.76	31927	PV	0.129	0.034
54.24	29365	VV	0.167	0.032
55.55	35842	VV	0.151	0.038
56.26	51418	PV	0.138	0.055
56.49	46663	VV	0.180	0.050
56.70	22877	VV	0.074	0.025
57.29	13169	VP	0.165	0.014
57.67	39273	PP	0.145	0.042
58.15	10976	VV	0.139	0.012
60.24	69589	VV	0.268	0.075
60.99	57082	BP	0.152	0.061
61.76	10262	BV	0.115	0.011
64.12	17328	BV	0.179	0.019
64.95	59099	VV	0.279	0.063
65.52	28982	VV	0.076	0.031
67.05	13798	VV	0.095	0.015
68.02	35774	VV	0.157	0.038
68.10	25792	VV	0.092	0.028
68.17	46994	VV	0.166	0.050
69.46	23212	VV	0.121	0.025
70.42	79846	VP	0.289	0.086
72.60	50391	BV	0.364	0.054
74.01	13248	VV	0.181	0.014
77.31	79024	VV	0.147	0.085
79.47	18513	BV	0.202	0.020
82.99	24243	PV	0.118	0.026
83.08	51076	VV	0.212	0.055
85.04	11413	VV	0.111	0.012
85.11	23875	VV	0.181	0.026
88.85	84319	VV	0.456	0.090

TOTAL AREA= 9.3376E+07
MUL FACTOR= 1.0000E+00

Table A16

pH 3

RUN # 785, APR/30/86 ,13:10:08
WORKFILE ID: C ,WORKFILE NAME:
ID: 000
AREA%

RT	AREA	TYPE	AR/HT	AREA%
checkpoint: the next peak is A1; subtract 0.07 minutes				
5.55	1431000	BB	0.153	2.733
6.66	1981900	BV	0.203	3.785
7.24	180070	VV	0.211	0.344
7.92	7877000	PV	0.173	15.042
8.10	9579700	VV	0.190	18.294
8.32	5423900	VB	0.231	10.357
9.48	42760	BP	0.155	0.082
9.87	59565	PV	0.142	0.114
10.20	196550	VV	0.211	0.375
10.72	356470	VV	0.115	0.681
10.88	568280	VV	0.121	1.085
11.12	286580	VV	0.151	0.547
11.36	114020	VP	0.144	0.218
11.78	51814	PV	0.135	0.099
11.96	16411	VV	0.079	0.031
12.08	31523	VP	0.139	0.060
12.59	67086	PV	0.192	0.128
12.96	61021	PV	0.113	0.117
13.14	32706	VV	0.092	0.063
checkpoint:the next peak is A14; subtract 0.01 minute				
13.38	2547500	VV	0.126	4.865
13.64	101660	VV	0.110	0.194
14.21	26045	VV	0.108	0.050
14.62	141530	PV	0.153	0.270
14.88	121150	VV	0.184	0.231
15.21	20513	BV	0.077	0.039
15.36	117100	VV	0.204	0.224
15.72	472580	VV	0.115	0.902
15.86	139310	VV	0.124	0.266
16.11	333310	VP	0.162	0.637
checkpoint: the next peak is A18; RT exact				
16.93	4024000	PB	0.136	7.684
17.70	27324	BV	0.079	0.052
17.93	32048	VV	0.099	0.061
18.11	14968	VV	0.147	0.029
18.71	85182	VP	0.122	0.163
19.38	66948	VP	0.094	0.128
19.65	38730	PV	0.179	0.074
20.20	17489	PP	0.201	0.033
20.84	15896	PV	0.080	0.030
21.72	45281	PV	0.304	0.087
22.22	23381	VV	0.173	0.045
22.51	16647	VV	0.135	0.032
22.63	25655	VV	0.097	0.049
22.81	13239	VV	0.134	0.025
23.30	13369	PV	0.112	0.026
23.45	16618	VV	0.161	0.032
23.80	56508	VV	0.196	0.108
24.04	32763	VV	0.077	0.063
24.15	56817	VV	0.166	0.109
24.70	72085	VP	0.122	0.138
25.17	144600	PV	0.141	0.276
25.40	377540	VV	0.135	0.721
25.85	22101	VV	0.117	0.042
26.04	39306	VV	0.127	0.075
26.24	28190	VV	0.163	0.054
26.50	10172	VV	0.092	0.019
26.99	26317	PV	0.119	0.050
27.28	12442	VV	0.144	0.024
27.61	17436	BV	0.108	0.033
27.92	32672	BH	0.134	0.062
28.05	10733	HH	0.076	0.021
28.21	46648	HH	0.176	0.089
28.41	37788	HH	0.121	0.072
28.53	26735	HH	0.117	0.051
28.88	23794	HH	0.141	0.045
29.03	10683	HH	0.085	0.020
29.11	12036	HH	0.091	0.023
29.29	26100	HH	0.166	0.050
29.55	12150	HH	0.115	0.023
29.72	17173	HH	0.117	0.033
29.83	29928	HH	0.098	0.057
29.95	31059	HH	0.103	0.059
30.18	35738	HH	0.197	0.068
30.83	27182	HH	0.095	0.052
31.24	43473	HH	0.113	0.083
31.41	33015	HP	0.088	0.063
31.74	16040	PH	0.077	0.031
32.19	21030	HV	0.131	0.040
32.61	60649	VV	0.142	0.116
32.90	32356	VV	0.098	0.062
33.08	109310	VV	0.091	0.209
33.44	14204	PV	0.077	0.027
33.67	14654	VV	0.132	0.028
33.96	19111	VV	0.212	0.037
34.23	17475	VV	0.104	0.033
34.59	20273	VV	0.111	0.039
34.90	18217	VV	0.085	0.035
35.30	16410	VV	0.111	0.031
35.49	16297	VV	0.132	0.031
35.81	12324	VV	0.081	0.024
35.92	13442	VV	0.082	0.026
36.14	48367	VV	0.139	0.092
36.37	46601	VV	0.085	0.089
36.47	57334	VV	0.094	0.110
36.72	145060	VV	0.133	0.277
checkpoint: the next peak is D3; add 0.02 minutes				
36.99	1221500	VV	0.094	2.333

37.40	131530	VV	0.143	0.251
37.61	51266	VV	0.116	0.098
37.85	22370	VV	0.124	0.043
38.07	14068	VV	0.097	0.027
38.22	41228	VV	0.094	0.079
38.40	64783	VV	0.150	0.124
38.85	17266	PV	0.090	0.033
39.09	824000	VV	0.096	1.574
39.31	125760	VV	0.097	0.240
39.42	132060	VV	0.163	0.252
39.83	273010	VV	0.192	0.521
40.04	172610	VV	0.216	0.330
40.38	109360	VV	0.156	0.209
40.54	61044	VV	0.109	0.117
40.83	74929	VV	0.185	0.143
41.10	35504	VV	0.106	0.068
41.16	38720	VV	0.094	0.074
41.35	1971500	VV	0.169	3.765
41.86	157080	VV	0.185	0.300
42.43	18694	VV	0.107	0.036
42.81	64684	VV	0.121	0.124
42.88	61564	VV	0.081	0.118
42.97	190710	VV	0.155	0.364
43.40	53018	VV	0.092	0.101
43.47	123290	VV	0.144	0.235
43.77	35177	VV	0.130	0.067
43.95	50242	VV	0.114	0.096
44.35	27571	PV	0.148	0.053
44.93	14068	VV	0.081	0.027
45.19	81490	PV	0.123	0.156
45.36	14601	VV	0.105	0.028
45.58	10657	VP	0.097	0.020
45.83	11615	PV	0.126	0.022
45.95	27374	VV	0.113	0.052
46.20	32247	VV	0.139	0.062
46.37	57862	VV	0.145	0.111
46.50	37157	VV	0.124	0.071
46.67	28165	VV	0.128	0.054
46.81	23102	VV	0.104	0.044
47.02	30923	VV	0.124	0.059
47.18	48371	VV	0.137	0.092
47.65	234990	VV	0.216	0.449
47.78	104740	VV	0.139	0.200
48.01	57220	VV	0.123	0.109
48.32	134230	VV	0.178	0.256
48.71	149140	VV	0.252	0.285
49.02	155780	VV	0.222	0.298
49.59	96850	VV	0.146	0.185
49.70	87047	VV	0.120	0.166
50.07	204580	VV	0.242	0.391
50.35	130860	VV	0.170	0.250
50.51	53535	VV	0.075	0.102
50.75	68099	VV	0.095	0.130
50.91	195140	VV	0.220	0.373
51.11	149740	VV	0.163	0.286
51.21	96064	VV	0.105	0.183
51.62	800090	VV	0.326	1.528
52.04	100990 D	VV	0.100	0.193
52.21	122500	VV	0.120	0.234
52.56	581630	VV	0.417	1.111
53.53	95891	VV	0.168	0.183
53.78	143060	VV	0.182	0.273
54.25	72568	VV	0.160	0.139
54.60	31755	VV	0.111	0.061
54.84	90557	VV	0.236	0.173
55.07	29057	VV	0.121	0.056
55.56	79959	VV	0.206	0.153
56.27	93044	VV	0.128	0.178
56.76	54787	VV	0.162	0.105
57.70	31196	PP	0.139	0.060
59.10	432620	VV	0.250	0.826
60.20	568020	VV	0.239	1.085
61.00	90702	VV	0.193	0.173
62.61	66582	VV	0.195	0.127
64.13	13061	VP	0.149	0.025
64.80	26255	VV	0.163	0.050
65.58	74236	PP	0.179	0.142
66.88	36107	PV	0.226	0.069
68.24	14550	BV	0.191	0.028
68.62	40015	VV	0.133	0.076
69.47	21799	VV	0.096	0.042
69.88	22991	VV	0.233	0.044
70.43	63247	VV	0.232	0.121
71.48	35764	BV	0.220	0.068
74.12	941690	VV	0.407	1.798
77.32	50558	PV	0.109	0.097
77.36	29873	VV	0.057	0.057
79.47	25200	PV	0.178	0.048
85.22	29354	VV	0.233	0.056
88.76	11778	VV	0.089	0.023
88.86	37530	VV	0.205	0.072

TOTAL AREA= 5.2367E+07
MUL FACTOR= 1.0000E+00

Table A17

pH 5

RUN # 791, MAY/01/86 ,16:30:36
WORKFILE ID: C ,WORKFILE NAME:
ID: 000
AREA%

RT	AREA	TYPE	AR/HT	AREA%
checkpoint: the next peak is A1; subtract 5.48				
5.51	5064000	BB	0.174	7.643
6.62	1740600	BV	0.169	2.627
7.25	165160	VP	0.183	0.249
7.88	2.0569E+07	PV	0.195	31.045
8.06	1.1564E+07	D VV	0.161	17.454
8.31	7744000	VB	0.240	11.688
9.46	15204	BP	0.110	0.023
9.84	71219	PV	0.169	0.108
10.18	289840	VV	0.175	0.438
10.37	130080	VV	0.159	0.196
10.69	424650	VV	0.114	0.641
10.84	371770	VV	0.132	0.561
11.09	162290	VV	0.148	0.245
11.35	48019	VP	0.126	0.073
11.96	16915	PV	0.091	0.026
12.05	27115	VV	0.112	0.041
12.58	64142	PV	0.178	0.097
12.94	36674	PP	0.097	0.055
checkpoint: the next peak is A14; add 0.01 minutes				
13.36	3687900	PB	0.113	5.566
14.18	19618	VV	0.081	0.030
14.59	357130	VV	0.218	0.539
14.86	198270	VV	0.179	0.299
15.20	185450	VV	0.139	0.280
15.32	333380	VV	0.216	0.503
15.70	327510	VV	0.189	0.494
15.85	246990	VV	0.153	0.373
16.07	766770	VB	0.151	1.157
checkpoint: the next peak is A18; add 0.02 minutes				
16.91	1898700	BB	0.117	2.866
17.69	26288	VV	0.103	0.040
17.93	54365	VV	0.103	0.082
18.70	18924	VP	0.132	0.029
19.11	27543	VV	0.182	0.042
19.36	54009	VV	0.100	0.082
19.65	27288	VP	0.133	0.041
21.76	23499	VV	0.190	0.036
22.06	33509	VV	0.149	0.051
22.61	59226	VV	0.100	0.089
23.38	10355	PV	0.177	0.016
23.69	15553	VV	0.083	0.024
23.79	48627	VV	0.181	0.073
24.03	15513	VV	0.080	0.023
24.13	40160	VV	0.094	0.061
24.46	14932	VV	0.109	0.023
24.68	81021	VP	0.109	0.122
25.16	111160	PV	0.135	0.168
25.40	480680	VV	0.153	0.726
26.02	86193	VV	0.176	0.130
26.22	28644	VV	0.114	0.043
26.48	33972	VV	0.149	0.051
26.78	37186	VV	0.252	0.056
26.97	44860	VV	0.177	0.068
27.19	13446	VV	0.067	0.020
27.27	27489	VV	0.113	0.042
27.53	53804	VV	0.243	0.081
27.88	42054	VV	0.120	0.064
28.04	28205	VV	0.118	0.043
28.17	38369	VV	0.152	0.058
28.40	57914	VV	0.143	0.087
28.85	33205	VV	0.178	0.050
29.11	26400	VV	0.175	0.040
29.55	17866	VV	0.159	0.027
29.82	23205	VV	0.119	0.035
29.93	25710	VV	0.128	0.039
30.13	20675	VV	0.125	0.031
30.57	46978	VV	0.141	0.071
30.84	10562	VV	0.107	0.016
31.22	33051	VV	0.108	0.050
31.39	28000	VV	0.100	0.042
31.72	12030	VV	0.083	0.018
31.85	16225	VV	0.084	0.025
31.98	11186	VV	0.093	0.017
32.14	26929	VV	0.149	0.041
32.59	50880	VV	0.135	0.077
32.87	20419	VV	0.102	0.031
33.06	20532	VV	0.117	0.031
33.24	24412	VV	0.069	0.037
33.42	16008	VV	0.095	0.024
34.27	60014	PV	0.126	0.091
34.42	39572	VV	0.109	0.060
34.89	12317	VV	0.087	0.019
35.26	28214	PP	0.103	0.043
35.89	15283	VV	0.084	0.023
36.03	55801	VV	0.169	0.084
36.36	24709	VV	0.087	0.037
36.45	67330	VV	0.099	0.102
36.70	129640	VV	0.131	0.196
checkpoint: the next peak is D3; add 0.04 minutes				
36.97	815220	VV	0.101	1.231
37.21	24614	VV	0.085	0.037
37.37	111610	VV	0.140	0.169
37.60	85646	VV	0.124	0.129
38.20	40130	VV	0.094	0.061
38.39	55190	VP	0.165	0.083
39.07	685630	VV	0.094	1.035
39.30	145610	VV	0.191	0.220

39.81	296620	VV	0.139	0.448
40.04	383640	VV	0.137	0.579
40.55	58081	VV	0.123	0.088
40.78	190420	VV	0.147	0.287
41.12	56537	VV	0.166	0.085
41.35	1114300	VV	0.162	1.682
41.73	77646	VV	0.115	0.117
41.84	70200	VV	0.157	0.106
42.82	82364	PV	0.180	0.124
42.96	60216	VP	0.154	0.091
43.35	19298	PV	0.087	0.029
43.47	43507	VV	0.138	0.066
43.74	68726	VV	0.114	0.104
43.93	17394	VV	0.124	0.026
44.20	130740	VV	0.097	0.197
44.33	65388	VV	0.133	0.099
44.71	134340	VV	0.121	0.203
45.19	42373	VV	0.146	0.064
45.34	13123	VV	0.097	0.020
45.93	28427	VV	0.119	0.043
46.11	28738	VV	0.128	0.043
46.28	21510	VV	0.093	0.033
46.84	13970	PV	0.098	0.021
47.17	12872	PV	0.080	0.019
47.58	91625	VV	0.204	0.138
47.75	118870	VV	0.106	0.179
48.09	189510	VV	0.108	0.286
48.31	71726	VV	0.113	0.108
48.52	10767	VV	0.104	0.016
48.69	51264	VV	0.169	0.077
48.98	68936	VV	0.139	0.104
50.02	24259	PV	0.121	0.037
50.49	10590	VV	0.079	0.016
50.74	15302	VV	0.098	0.023
50.89	32699	VV	0.120	0.049
51.46	52244	VV	0.140	0.079
52.03	13859	VV	0.083	0.021
52.50	88839	VV	0.198	0.134
53.12	55529	VV	0.233	0.084
53.73	43807	VV	0.147	0.066
54.20	50389	VV	0.208	0.076
54.78	29356	VV	0.161	0.044
55.15	16786	VV	0.127	0.025
55.51	41993	VV	0.207	0.063
56.21	15417	PV	0.056	0.023
56.23	22165 D	VV	0.074	0.034
56.71	29222	BV	0.131	0.044
57.65	32110	PP	0.151	0.049
60.19	82454	VP	0.189	0.125
60.98	61936	PV	0.159	0.094
62.24	10055	BV	0.158	0.015
64.10	16324	PP	0.167	0.025
65.13	17688	VP	0.179	0.027
65.50	82021	PP	0.179	0.124
67.06	15603	VV	0.136	0.024
69.17	14985	VV	0.160	0.023
69.42	26653	VV	0.103	0.040
70.01	14973	VV	0.079	0.023
70.09	11273	VV	0.058	0.017
70.15	14955	VV	0.062	0.023
70.36	134310	VV	0.282	0.203
71.40	13444	VV	0.230	0.020
71.92	59006	VV	0.398	0.089
73.98	36547	VV	0.178	0.055
74.77	25909	VV	0.239	0.039
76.40	22116	VP	0.283	0.033
77.24	76310	VV	0.111	0.115
77.29	36812	VV	0.049	0.056
77.32	86074 D	VV	0.112	0.130
82.99	60624	BV	0.163	0.092
83.05	42719	VV	0.102	0.065
84.95	10529	VV	0.096	0.016
85.04	12568	VV	0.070	0.019
88.79	39555	PV	0.272	0.060

TOTAL AREA= 6.6254E+07
MUL FACTOR= 1.0000E+00

Table A18

pH 9

RUN # 793, MAY/01/86 ,20:11:17
WORKFILE ID: C ,WORKFILE NAME:
ID: 000
AREA%

RT	AREA	TYPE	AR/HT	AREA%
checkpoint: the next peak is A1; subtract 0.03 minutes				
5.51	107370	BP	0.212	0.147
6.62	2482500	BV	0.201	3.394
7.25	188160	VP	0.190	0.257
7.64	34755	PV	0.095	0.048
7.87	4.6082E+07	VV	0.349	62.999
9.23	229790	VV	0.209	0.314
9.52	226690	VV	0.259	0.310
9.84	188510	VV	0.267	0.258
10.39	405280	VV	0.159	0.554
10.70	466940	VV	0.126	0.638
10.85	288160	VV	0.135	0.394
11.11	200600	VV	0.165	0.274
12.03	49492	VV	0.213	0.068
12.29	10522	VP	0.094	0.014
12.94	37155	PV	0.108	0.051
checkpoint: the next peak is A14; RT exact				
13.37	1678300	VB	0.117	2.294
14.23	13118	PV	0.092	0.018
14.43	16972	VV	0.073	0.023
14.62	203540	VV	0.181	0.278
14.90	121000	VV	0.165	0.165
15.21	144930	VV	0.118	0.198
15.32	112670	VV	0.135	0.154
15.70	45983	BV	0.116	0.063
15.85	57493	VV	0.133	0.079
16.10	117160	VB	0.158	0.160
checkpoint: the next peak is A18; add 0.02 minutes				
16.91	1683200	BB	0.118	2.301
17.69	15528	BV	0.141	0.021
17.94	28169	VP	0.081	0.039
19.38	27187	BV	0.096	0.037
19.64	13652	VV	0.203	0.019
20.55	11371	VP	0.172	0.016
20.98	13666	PV	0.090	0.019
21.77	22981	VV	0.154	0.031
22.07	11144	VP	0.132	0.015
22.62	19684	PV	0.134	0.027
23.68	17907	VV	0.098	0.025
23.81	31833	VV	0.181	0.044
24.02	12525	VV	0.086	0.017
24.13	29405	VV	0.084	0.040
24.68	48951	VP	0.110	0.067
25.14	640480	PV	0.107	0.876
checkpoint: the next peak is A25; add 0.04 minutes				
25.37	5806200	VV	0.147	7.938
25.75	187290 D	VV	0.081	0.256
25.85	92728 D	VV	0.056	0.127
26.01	149490	VV	0.110	0.204
26.11	103130	VV	0.095	0.141
26.21	67687 D	VV	0.065	0.093
26.29	93721	VV	0.097	0.128
26.38	54604	VV	0.058	0.075
26.47	39991 D	VV	0.045	0.055
26.72	40641 D	VV	0.053	0.056
26.95	51605	VV	0.064	0.071
27.14	32606	VV	0.046	0.045
27.23	162900	VV	0.185	0.223
27.40	45240	VV	0.067	0.062
27.53	79594	VV	0.111	0.109
27.89	93031	VV	0.148	0.127
28.05	50339	VV	0.113	0.069
28.21	74818	VV	0.176	0.102
28.53	46546	VV	0.138	0.064
28.83	31437	VV	0.148	0.043
29.11	11348	VV	0.076	0.016
29.93	66309	VP	0.163	0.091
30.30	14868	PP	0.116	0.020
30.56	53392	PP	0.186	0.073
31.23	502320	PB	0.118	0.687
31.72	12486	BP	0.082	0.017
32.05	40732	PV	0.125	0.056
32.42	18714	VV	0.124	0.026
32.59	51621	VV	0.192	0.071
32.87	27292	VV	0.123	0.037
33.07	54414	VV	0.095	0.074
33.25	18513	VV	0.076	0.025
33.42	26237	VV	0.104	0.036
34.09	115010	VV	0.084	0.157
34.28	52585	VV	0.128	0.072
34.42	28468	VV	0.097	0.039
34.89	17699	VV	0.092	0.024
35.27	25185	PV	0.125	0.034
36.04	728380	VV	0.107	0.996
36.34	89844	VV	0.096	0.123
36.45	163630	VV	0.103	0.224
36.70	137780	VV	0.139	0.188
checkpoint: the next peak is D3; add 0.04 minutes				
36.97	671160	VV	0.091	0.918
37.22	27602	VV	0.092	0.038
37.39	144520	VV	0.134	0.198
37.60	104580	VV	0.108	0.143
37.83	16206	VV	0.101	0.022
38.00	20405	VV	0.102	0.028
38.21	20650	VV	0.109	0.028
38.63	12968	VP	0.097	0.018
39.08	214410	VV	0.101	0.293
39.30	74537	VP	0.134	0.102
39.80	1984600	PB	0.100	2.713

40.56	20874	PV	0.096	0.029
40.78	39244	VP	0.102	0.054
41.12	10980	PV	0.117	0.015
41.41	601120	VV	0.165	0.822
42.82	82270	PV	0.182	0.113
43.07	41962	VV	0.166	0.057
43.35	46558	VV	0.143	0.064
43.50	22920	VV	0.102	0.031
43.72	36178	VV	0.095	0.050
44.42	28380	VV	0.100	0.039
44.54	24973	VV	0.092	0.034
44.70	48780	VV	0.122	0.067
44.92	10300	VP	0.087	0.014
46.29	16610	VV	0.098	0.023
46.70	11837	PV	0.087	0.016
46.82	13673	VV	0.102	0.019
47.03	10990	VV	0.096	0.015
47.16	40728	VV	0.111	0.056
47.44	80318	VV	0.205	0.110
47.66	50734	VV	0.137	0.069
47.77	55059	VV	0.132	0.075
47.98	34965	VV	0.125	0.048
48.08	22486	VV	0.101	0.031
48.29	32210	VV	0.150	0.044
48.69	33032	VV	0.150	0.045
49.09	60028	VV	0.217	0.082
49.55	15699	BV	0.087	0.022
49.98	35696	VV	0.096	0.049
50.32	59584	VV	0.131	0.082
50.50	65778	VV	0.142	0.090
50.63	15197	VV	0.046	0.021
50.74	48429	VV	0.128	0.066
50.87	75729	VV	0.153	0.104
51.04	91979	VV	0.196	0.126
51.49	147600	VV	0.205	0.202
51.70	38513	VV	0.076	0.053
51.89	144900	VV	0.225	0.198
52.48	147050	VV	0.192	0.201
52.72	103190	VV	0.171	0.141
52.94	102100	VV	0.179	0.140
53.31	29522	VV	0.061	0.040
53.72	123150	VV	0.253	0.168
54.21	44952	VV	0.108	0.062
55.51	129400	VV	0.263	0.177
56.44	34855	VV	0.105	0.048
56.71	100730	VV	0.209	0.138
57.25	20192	VV	0.162	0.028
57.63	32493	VP	0.146	0.044
58.68	10080	VV	0.092	0.014
59.87	12864	VV	0.186	0.018
60.18	37575	VP	0.139	0.051
60.61	53789	PV	0.239	0.074
60.93	72693	VP	0.186	0.099
64.08	15419	PP	0.162	0.021
65.48	71230	VP	0.166	0.097
67.06	30887	VV	0.260	0.042
69.40	47928	VV	0.196	0.066
70.33	33185	VV	0.117	0.045
72.66	409630	PV	0.232	0.560
77.17	41282	VV	0.089	0.056
77.20	13514	VV	0.027	0.019
77.23	20558	VV	0.039	0.028
77.26	72384	VB	0.129	0.099
78.49	12101	VP	0.224	0.017
82.84	22083	BV	0.118	0.030
82.89	10032	VV	0.043	0.014
82.96	12147 D	VV	0.041	0.017
84.94	12507	VV	0.122	0.017
88.73	62700	BV	0.362	0.086

TOTAL AREA= 7.3146E+07
MUL FACTOR= 1.0000E+00

Table A19

pH 11

RUN # 786, APR/30/86 ,14:52:07
WORKFILE ID: C ,WORKFILE NAME:
ID: 000
AREA%

RT	AREA	TYPE	AR/HT	AREA%
5.12	49971	D BB	0.140	0.055
6.65	623830	BV	0.167	0.692
6.95	64744	VV	0.109	0.072
7.05	93940	VV	0.157	0.104
7.28	152030	VP	0.177	0.169
7.66	60074	PV	0.098	0.067
checkpoint: A5 is next; RT is off becaus peak is broad				
7.91	4.7555E+07	VB	0.334	52.757
9.27	73480	BP	0.111	0.082
9.52	21829	PP	0.141	0.024
9.87	63485	PP	0.131	0.070
10.41	479000	PV	0.131	0.531
10.72	705220	VV	0.117	0.782
10.87	371440	VV	0.128	0.412
11.12	161020	VV	0.151	0.179
11.38	20457	VP	0.130	0.023
12.08	58414	BV	0.217	0.065
12.51	55388	PV	0.128	0.062
12.79	44774	VV	0.135	0.050
12.96	101850	VV	0.176	0.113
13.26	324620	VV	0.091	0.360
checkpoint: the next peak is A14; subtract 0.01 minute				
13.38	690880	VV	0.142	0.767
13.87	178840	VV	0.211	0.198
14.24	236700	VV	0.269	0.263
14.37	75978	VV	0.084	0.084
14.44	99555	VV	0.102	0.110
14.62	484970	VV	0.228	0.538
14.89	387750	VV	0.277	0.430
15.22	270920	VV	0.163	0.301
15.34	318220	VV	0.229	0.353
15.72	495220	VV	0.222	0.549
16.13	224100	VP	0.245	0.249
checkpoint: the next peak is A18; RT exact				
16.93	1667400	PB	0.114	1.850
17.70	19816	BV	0.148	0.022
17.95	29896	VV	0.080	0.033
18.14	11360	VP	0.103	0.013
19.38	24409	VV	0.094	0.027
20.55	14289	VP	0.144	0.016
21.79	15656	VV	0.171	0.017
23.32	11273	PV	0.117	0.013
23.69	19841	VV	0.111	0.022
23.88	17973	VV	0.135	0.020
24.04	12872	VV	0.092	0.014
24.15	24234	VV	0.078	0.027
24.27	14996	VV	0.095	0.017
24.70	48044	VP	0.122	0.053
25.14	602410	PV	0.098	0.668
checkpoint: the next peak is A25; add 0.03 minutes				
25.38	4997500	VB	0.126	5.544
27.06	23158	VV	0.120	0.026
27.25	46161	VV	0.157	0.051
27.50	10060	VV	0.064	0.011
27.93	20224	VV	0.110	0.022
28.23	12000	PP	0.098	0.013
28.55	13707	BV	0.107	0.015
29.16	12113	VV	0.117	0.013
29.86	24841	BV	0.090	0.028
30.32	17834	PP	0.125	0.020
30.58	32599	PV	0.104	0.036
31.25	930880	PB	0.120	1.033
32.07	66028	PV	0.211	0.073
32.44	19301	VV	0.119	0.021
32.60	28372	VV	0.136	0.032
32.71	36727	VV	0.133	0.041
32.90	21494	VV	0.103	0.024
33.09	28233	VV	0.096	0.031
33.44	18386	PP	0.090	0.020
34.11	177110	PB	0.088	0.197
34.92	19783	PP	0.096	0.022
35.31	55688	PV	0.151	0.062
35.80	15554	VV	0.196	0.017
36.06	1396100	VV	0.107	1.549
36.36	83899	VV	0.101	0.093
36.47	143040	VV	0.111	0.159
36.72	93482	VV	0.126	0.104
checkpoint: the next peak is D3; add 0.02 minutes				
36.99	534280	VV	0.086	0.593
37.24	23383	VV	0.098	0.026
37.38	47146	VV	0.140	0.052
37.63	112190	VV	0.097	0.125
38.02	21225	VV	0.108	0.024
38.25	38156	VV	0.086	0.042
38.34	58532	VV	0.132	0.065
39.10	200530	VB	0.108	0.223
39.82	2609100	PB	0.096	2.895
40.80	22586	VP	0.109	0.025
41.33	8174700	PB	0.152	9.069
42.76	43094	PV	0.083	0.048
42.84	76788	VV	0.136	0.085
42.98	96664	VV	0.171	0.107
43.45	102530	VV	0.181	0.114
43.75	15016	VV	0.099	0.017
43.96	12558	VP	0.086	0.014
44.36	444570	VV	0.151	0.493
44.73	86717	VV	0.252	0.096
45.19	379770	VV	0.154	0.421
45.79	52108	VV	0.252	0.058

46.04	42473	VV	0.158	0.047
46.30	61333	VV	0.205	0.068
46.51	187470	VV	0.112	0.208
46.69	57485	VV	0.138	0.064
46.89	85440	VV	0.160	0.095
47.05	52882	VV	0.130	0.059
47.19	48456	VV	0.102	0.054
47.30	61919	VV	0.100	0.069
47.57	1937700	VV	0.221	2.150
48.30	181110	VV	0.237	0.201
48.71	418780	VV	0.173	0.465
49.14	100410	VV	0.119	0.111
49.58	115110	VV	0.157	0.128
49.80	153450	VV	0.171	0.170
49.95	201760	VV	0.208	0.224
50.36	95940	VV	0.115	0.106
50.63	866130	VV	0.373	0.961
51.07	205780	VV	0.199	0.228
51.32	202050	VV	0.170	0.224
51.61	520480	VV	0.352	0.577
52.22	302170	VV	0.251	0.335
52.52	81278	VV	0.089	0.090
52.69	88611	VV	0.108	0.098
52.91	451340	VV	0.349	0.501
53.77	133480	VV	0.185	0.148
53.91	154430	VV	0.199	0.171
54.27	1139900	VV	0.427	1.265
55.55	112900	VV	0.198	0.125
55.82	238700	VV	0.323	0.265
56.48	41458	VV	0.141	0.046
56.76	63217	VV	0.213	0.070
57.68	14551	PP	0.163	0.016
59.06	21632	VP	0.202	0.024
60.02	545450	VV	0.346	0.605
60.58	131890	VV	0.311	0.146
60.99	87537	VP	0.200	0.097
62.20	32697	PV	0.263	0.036
64.16	12366	PV	0.142	0.014
65.13	19886	VV	0.207	0.022
65.55	83878	VP	0.172	0.093
67.09	11917	BP	0.159	0.013
69.27	11606	VV	0.139	0.013
69.50	58348	VV	0.218	0.065
70.39	41894	PV	0.129	0.047
71.07	1051800	PV	0.277	1.167
71.16	223860	VV	0.062	0.248
71.22	242220	VV	0.071	0.269
73.92	12433	PV	0.089	0.014
73.98	14195	VV	0.084	0.016
74.08	15414	VV	0.062	0.017
74.86	17245	VV	0.221	0.019
76.44	16315	BP	0.245	0.018
77.25	24209	PV	0.075	0.027
77.36	56099	VV	0.089	0.062
77.39	79368 D	VP	0.121	0.088
79.51	16441	VV	0.253	0.018
82.99	19129	VV	0.100	0.021
83.10	26408	VV	0.094	0.029
85.12	14883	VV	0.119	0.017
88.77	30208	PV	0.161	0.034
88.84	87291	VV	0.406	0.097
91.83	15319	VV	0.324	0.017
94.99	12600	VV	0.128	0.014
95.23	42845	VV	0.199	0.048
95.87	31876	VV	0.126	0.035
95.91	11366	VV	0.038	0.013
95.99	28089	VV	0.073	0.031

TOTAL AREA= 9.0140E+07
MUL FACTOR= 1.0000E+00

Table A20

5 mg Bromide, 10 mg chlorine dose

RUN # 769, APR/27/86 ,18:24:52
WORKFILE ID: C ,WORKFILE NAME:
ID: 000
AREA%

RT	AREA	TYPE	AR/HT	AREA%
6.10	436570	BP	0.218	0.197
6.62	4.4640E+07	SPB	0.279	20.158
7.92	2280800	TBV	0.166	1.030
8.11	2621500	TVV	0.193	1.184
8.42	1500700	TVV	0.153	0.678
8.49	2609700	DTVB	0.272	1.178
9.35	383410	BV	0.117	0.173
9.62	185640	VV	0.165	0.084
9.91	15513	VV	0.074	0.007
10.61	2372000	PH	0.133	1.071
10.86	5.1527E+07	SHB	0.258	23.267
11.40	250070	TBP	0.084	0.113
11.60	285700	TPB	0.078	0.129
11.99	365190	TBP	0.143	0.165
12.50	10513	VV	0.061	0.005
12.61	53548	VP	0.147	0.024
13.22	192770	VV	0.109	0.087
13.39	484440	VV	0.131	0.219
13.54	44063	D VV	0.043	0.020
13.73	2861000	VV	0.119	1.292
13.87	3380000	VV	0.235	1.526
14.29	94799	VV	0.026	0.043
14.32	373570	D VV	0.100	0.169
14.46	75303	VV	0.024	0.034
14.50	168970	D VV	0.053	0.076
14.64	424710	VV	0.114	0.192
14.67	163820	D VV	0.044	0.074
14.72	154620	VV	0.042	0.070
14.88	3075500	VV	0.158	1.389
15.10	386230	VV	0.070	0.174
15.22	477810	VV	0.083	0.216
checkpoint: the next peak is bromoform				
15.37	1552000	VH	0.204	0.701
15.69	5.1591E+07	SHB	0.252	23.296
15.99	1011000	TBB	0.082	0.457
16.34	50623	TBB	0.072	0.023
16.94	2757000	TVV	0.160	1.245
17.23	229420	DTVV	0.102	0.104
17.38	88108	DTVB	0.108	0.040
17.63	133910	BV	0.087	0.061
17.86	353380	VV	0.136	0.160
18.11	93988	VP	0.102	0.042
18.54	22916	PP	0.125	0.010
19.11	330450	VV	0.093	0.149
19.29	103150	VP	0.149	0.047
19.68	140700	PV	0.080	0.064
19.86	1117800	VV	0.111	0.505
19.99	279400	VV	0.123	0.126
20.31	79112	VV	0.159	0.036
20.52	20828	VV	0.098	0.009
20.92	76260	PV	0.195	0.034
21.29	37930	VV	0.146	0.017
21.80	61346	PV	0.143	0.028
22.04	129380	VV	0.108	0.058
22.52	21159	PV	0.085	0.010
22.63	18412	VP	0.078	0.008
22.86	205530	PV	0.108	0.093
23.22	245980	VV	0.083	0.111
23.39	430070	VV	0.119	0.194
23.77	335490	VV	0.119	0.152
24.14	88291	VV	0.111	0.040
24.30	112210	VV	0.167	0.051
24.61	38360	VV	0.070	0.017
24.71	203540	VV	0.128	0.092
24.99	34609	VV	0.094	0.016
25.18	56185	VV	0.115	0.025
25.49	247080	VV	0.142	0.112
25.63	12399	VV	0.043	0.006
25.81	1380100	VV	0.084	0.623
26.00	1140300	VV	0.113	0.515
26.26	215330	VP	0.096	0.097
26.57	14220	PV	0.088	0.006
26.69	39017	VV	0.078	0.018
26.80	103190	VV	0.093	0.047
27.09	33085	VV	0.129	0.015
27.21	105030	VV	0.121	0.047
27.47	1798300	VV	0.092	0.812
27.88	99939	VV	0.137	0.045
28.07	190520	VV	0.113	0.086
28.22	120870	VV	0.112	0.055
28.41	124710	VV	0.169	0.056
28.67	46798	VV	0.084	0.021
28.84	131150	VV	0.118	0.059
29.12	99938	VV	0.099	0.045
29.31	24653	VV	0.080	0.011
29.46	25084	VV	0.080	0.011
29.62	209200	VV	0.139	0.095
29.80	54068	VV	0.096	0.024
29.96	79009	VV	0.113	0.036
30.13	28624	VV	0.077	0.013
30.29	35432	VV	0.112	0.016
30.60	357950	VV	0.099	0.162
30.98	62899	VV	0.114	0.028
31.28	179980	VV	0.107	0.081
31.40	90999	VV	0.100	0.041
31.72	247540	VV	0.086	0.112
31.92	37461	VV	0.080	0.017
32.17	48590	VP	0.094	0.022
32.53	33516	PH	0.073	0.015

32.59	26197	HH	0.077	0.012
32.77	1721500	HH	0.094	0.777
33.04	13198	HP	0.058	0.006
33.19	26322	PP	0.072	0.012
33.37	66460	PH	0.081	0.030
33.54	103950	HH	0.088	0.047
33.89	166640	PH	0.127	0.075
34.23	34000	PH	0.083	0.015
34.65	106210	HH	0.114	0.048
34.86	252890	HH	0.144	0.114
35.09	46194	HH	0.078	0.021
35.29	22966	HH	0.073	0.010
35.50	56971	HH	0.083	0.026
35.62	308090	HH	0.109	0.139
35.79	86179	HH	0.092	0.039
35.92	30245	HH	0.063	0.014
36.04	241610	HH	0.140	0.109
36.21	30342	HH	0.044	0.014
36.54	724290	HH	0.244	0.327
36.70	381550	HH	0.142	0.172
36.90	649040	HH	0.128	0.293
37.24	51126	HH	0.065	0.023
37.37	324940	HH	0.177	0.147
37.63	164220	HH	0.175	0.074
37.84	97069	HH	0.086	0.044
37.94	139380	HH	0.099	0.063
38.04	137870	HH	0.108	0.062
38.22	109710	HH	0.113	0.050
38.44	130850	HH	0.182	0.059
38.67	27390	HH	0.096	0.012
38.92	53632	HH	0.101	0.024
39.09	599600	HH	0.134	0.271
39.27	120980	HH	0.067	0.055
39.36	313120	HH	0.138	0.141
39.54	223610	HH	0.108	0.101
39.69	128600	HH	0.111	0.058
39.90	355150	HH	0.158	0.160
40.03	196550	HH	0.099	0.089
40.37	297950	HH	0.183	0.135
40.78	513080	HH	0.120	0.232
41.09	190710	HH	0.135	0.086
41.34	258310	HH	0.140	0.117
41.53	560440	HH	0.095	0.253
41.69	537490	HH	0.171	0.243
41.90	198270	HH	0.098	0.090
42.00	248280	HH	0.120	0.112
42.25	625750	HH	0.141	0.283
42.39	149520	HH	0.105	0.068
42.58	104970 D	HH	0.112	0.047
42.78	77947	HH	0.100	0.035
42.88	165020	HH	0.181	0.075
43.12	160500	HH	0.133	0.073
43.29	258410	HH	0.112	0.117
43.35	151400 D	HH	0.073	0.068
43.47	143600	BV	0.059	0.065
43.65	1270000	VV	0.123	0.574
43.74	904560	VV	0.110	0.409
43.94	683380	VV	0.128	0.309
44.20	538090	VV	0.130	0.243
44.41	125790	VV	0.127	0.057
44.59	113630	VV	0.093	0.051
44.71	880770	VV	0.126	0.398
44.94	266930	VV	0.160	0.121
45.21	275280	VV	0.150	0.124
45.29	182190	VV	0.103	0.082
45.63	747390	VV	0.189	0.338
45.86	72110	VV	0.088	0.033
45.99	92531	VV	0.119	0.042
46.13	86536	VV	0.106	0.039
46.40	270790	VV	0.233	0.122
46.61	98144	VV	0.127	0.044
46.84	98550	VV	0.153	0.045
47.15	216940	VV	0.235	0.098
47.47	2035500	VV	0.123	0.919
47.72	431780	VV	0.149	0.195
47.93	38324 D	VV	0.051	0.017
48.09	932590	VV	0.122	0.421
48.36	38013	VV	0.050	0.017
48.43	70568	VV	0.080	0.032
48.56	172870	VV	0.109	0.078
48.66	205300	VV	0.118	0.093
48.83	261990	VV	0.160	0.118
49.02	84478	VV	0.097	0.038
49.17	54057	VV	0.085	0.024
49.23	33793 D	VV	0.058	0.015
49.29	13003	VV	0.028	0.006
49.40	248410	VV	0.136	0.112
49.61	116130	VV	0.118	0.052
49.70	79816	VV	0.102	0.036
49.81	29897	VV	0.041	0.014
49.84	42646 D	VV	0.058	0.019
49.99	118740	VV	0.119	0.054
50.10	39173 D	VV	0.087	0.018
50.20	13756 D	VV	0.042	0.006
50.30	37664	VV	0.112	0.017
50.46	19934	VV	0.084	0.009
50.69	141530	VV	0.145	0.064
50.82	34942 D	VV	0.047	0.016
50.90	71533	VV	0.112	0.032
51.02	42872	VP	0.104	0.019
51.34	17444	PV	0.071	0.008
51.41	14616	VV	0.053	0.007
51.46	25757	VV	0.088	0.012
51.80	618360	VV	0.138	0.279
52.22	14659	PV	0.062	0.007
52.47	48412	VV	0.125	0.022
52.73	54750	VV	0.118	0.025
52.92	15713	VV	0.068	0.007
53.02	15542	VV	0.052	0.007
53.11	37169	VV	0.079	0.017
53.23	548700	VV	0.107	0.248
53.45	210070	VV	0.186	0.095
53.67	52410	VV	0.079	0.024
53.72	116700	VV	0.166	0.053
54.21	17035	VV	0.123	0.008
54.49	46456	PV	0.127	0.021
54.68	23704	VV	0.089	0.011
55.28	36469	VV	0.132	0.017
55.54	45804	VV	0.135	0.021
55.73	23752	VV	0.117	0.011
55.85	22150	VV	0.097	0.010
56.05	31078	VV	0.103	0.014
56.25	510870	VV	0.165	0.231
56.48	54076	VV	0.099	0.024
56.58	21485	VV	0.047	0.010
56.74	16941	VV	0.060	0.008
56.80	37365	VV	0.130	0.017
57.49	137730	BV	0.129	0.062
58.23	11675	VV	0.060	0.005
58.41	10549	VV	0.063	0.005
58.51	26882	VV	0.101	0.012
58.69	16835	VV	0.077	0.008
58.77	20650	VV	0.061	0.009
58.82	24123	VV	0.062	0.011
59.44	65001	VV	0.106	0.029
60.78	66013	VV	0.160	0.030
60.93	100670	VV	0.198	0.046
61.30	499210	VV	0.167	0.225
61.78	107400	VV	0.216	0.049
62.24	65192	VV	0.102	0.029
62.27	62885 D	VV	0.100	0.028
65.22	44195	VV	0.120	0.020
65.40	43358	VV	0.150	0.020
65.68	78532	VV	0.223	0.036
66.82	35105	VV	0.132	0.016
67.43	10311	VV	0.098	0.005
67.94	20652	VV	0.182	0.009
69.37	16487	VV	0.123	0.008
70.22	132770	PV	0.249	0.060
72.17	14839	PV	0.219	0.007
73.31	476770	BV	0.266	0.215
77.11	17072	PV	0.098	0.008
81.33	21304	VV	0.105	0.010
81.44	39530	VV	0.171	0.018
82.88	11374	VV	0.103	0.005

TOTAL AREA= 2.2146E+08
MUL FACTOR= 1.0000E+00

APPENDIX 4

This appendix includes the data used to calculate the coefficient $K_L A$ in the aeration experiment (Table A21).

Table A21 Aeration Data

Time (minutes)	Dissolved Oxygen (mg/L)
0:00	0.2
0:33	1.0
1:00	1.8
1:15	2.2
1:30	2.6
1:45	3.9
2:00	4.8
2:15	5.0
2:30	5.6
2:45	5.7
3:00	6.2
3:30	6.5
4:00	6.5
4:30	6.5
5:00	6.6
6:00	6.7

APPENDIX 5

In an effort to compare the San Diego effluent with other plants, two other plants were selected for investigation, the Whittier Narrows treatment plant in Los Angeles County, and an aquaculture treatment system in central Florida.

Methylene chloride extractable organics were analyzed for the Whittier Narrows and a Florida plant's gravimetrically, by GC, and by GC/MS. This survey was done to compare the profiles of the solvent extractable organics from these two plants with the identified compounds at the San Diego Wastewater Treatment Plant. The Florida plant provides a water hyacinth based secondary treatment plant for the comparison, whereas the Whittier Narrows plant allows for comparison to activated sludge treatment.

The Whittier Narrows Plant is an activated sludge facility, with primary clarification operating at an F/M ratio of approximately 0.50/days. This plant is one of the LA County Sanitation Districts inland plants. It receives largely domestic wastewater, with most industrial waters being routed around the Whittier Narrows Plant to the Joint Plant at Carson. The Florida plant is a water hyacinth facility. It uses a single stage basin, approximately 0.5 meters deep, with a hydraulic retention time of approximately one day.

Tables B1 through B3 summarize the gravimetric data and the lump GC data on the three treatment plants. The data used for the San Diego plant represent an average of all the collected samples (Tables 9 and 10) whereas the data on the Whittier Narrows and Florida plants represent a single sampling (4/86). The data shown in Table B1 shows several similarities and differences between the samples. The non-polar fractions (1 and 2) roughly represent one quarter to one third of the total extract (gravimetrically). The Florida plant extract seems to be primarily composed of gas chromatographable polar compounds since 75% of the extract is polar by weight and the non-polar fractions represent a small fraction (7%) of the total FID area. The GC analysis of the Florida wastewater treatment plant sample shows the presence of many straight chain fatty acids. In contrast, the San Diego and Whittier Narrows samples show large amounts of non-polar compounds in their chromatographs (69 and 72%, respectively).

The Whittier Narrows plant extract gives a much larger ECD response than either of the other two plants. Most of this ECD response is due to chlorination by-products which were previously discussed. These compounds were in low concentrations however (less than 1 μg/l) and were consequently not identifiable by GC/MS for the Whittier Narrows extract. These compounds were detectable by the more sensitive ECD and showed retention time matches with the halogenated chlorination by-products (Table 14). It is plausible that the influent to the Whittier Narrows plant contained larger amounts of these halogenated compounds, causing high effluent concentrations were higher.

The GC and GC/MS for the San Diego Wastewater Treatment Plant effluent extract were previously shown (Figures 12 and 13). Fig-

Table B1 General Makeup of Treatment Plant Extracts

Treatment Plant	Weight (mg/L)	Total Weight Represented in Fractions 1,2	% Gravimetric Area Represented by Fractions 1,2	% of the FID Ratio of Total ECD/FID Areas
San Diego	5.04	32	69	0.81
Disney World	14.91	25	7	0.20
Whittier Narrows	2.61	27	72	6.11

Table B2. Compounds Identified in the Whittier Narrows Wastewater Treatment Plant Secondary Effluent (4/86) by GC/MS

Scan No.	RT (minutes)	ID Compound Name or Formula	Conc. (µg/L)	% Confidence in ID	Method of ID
269	--	chloroform	ND	>95	1,2,3
294	--	bromochloromethane	ND	>95	1,2,3
448	8.18	chloroiodomethane	0.4	90	1
474	8.26	benzene, 1-ethyl, 4-methyl	0.4	70	1,2
483	8.50	2-pentyl furan	0.4	80	1,2
595	12.60	benzene 1,2,3, trimethyl	0.5	70	1,2
659	14.50	tetradecane (is)	11.0	>95	1,2,3
709	15.51	1,4 dichlorobenzene	0.3	>95	1,2,3
752	17.51	1,3 dichlorobenzene	7.1	>95	1,2,3
759	17.80	C_{17} aliphatic hydrocarbon	2.9	90	1
843	20.40	2-furancarboxaldehyde, 5-methyl	3.7	90	1,2
907	22.54	1-hexanone-1-phenyl	10.5	70	1,2
949	24.01	C_{19} aliphatic	2.3	90	1
1146	30.53	tetradecanal	3.9	60	1
1203	32.45	hexadecanal	4.8	80	1
1213	32.76	phenol	5.3	>95	1,2,3
1265	34.45	1-decanoic acid	3.5	>95	1,2,3
1283	34.75	p-cresol	3.1	>95	1,2,3
1308	35.90	phosphoric acid-tributyl ester	10.0	90	1,2
1410	39.39	lh-pyrole-2,5 dione-3-ethyl-4-methyl	2.9	60	1,2

Table B2. Compounds Identified in the Whittier Narrows Wastewater Treatment Plant Secondary Effluent (4/86) by GC/MS (Continued)

Scan No.	RT (minutes)	ID Compound Name or Formula	Conc. (µg/L)	% Confidence in ID	Method of ID
1419	39.64	1-undecanoic acid	2.0	>95	1,2,3
1421	39.81	phenol 2-(1,1-dimethylethyl)	4.0	85	1,2
1463	40.90	1-hexadecanol	1.3	90	1,2,3
1503	42.58	1-propanone,1-(methoxyphenyl)	4.6	80	1,2
1560	44.43	1-dodecanoic acid	6.5	>95	1,2,3
1573	44.91	2(5H)-furanone, 5-methyl-5phenyl	1.6	70	1,2
1616	46.38	1-octadecanol	4.1	90	1,2,3
1631	46.91	phenol, 4-(2,2,3,3-tetramethylbutyl)	6.8	70	1,2
1660	47.83	branched C_{13} acid	1.1	90	1,2
1671	48.16	4-nonyl-phenol	0.3	90	1,2
1682	48.32	nonyl-phenol	0.8	90	1,2
--	48.55	long chain alkylphenol	0.2	--	F2
--	48.6	long chain alkylphenol	1.3	--	F2
1690	48.82	1-tetradecanoic acid	9.4	>95	1,2,3
1722	49.93	benzenemethanol, alpha-phenyl	4.8	60	1,2
1724	50.02	1-pentadecanoic acid	7.3	>95	1,2,3
1812	53.35	1-hexadecanoic acid	72.6	>95	1,2,3
1913	57.72	C_{31} n-alkane	4.9	>95	1,2,3
1958	59.56	1-octadecanoic acid	53.1	>95	1,2,3
1987	60.75	pthalate compound	22.3	90	1,2
2003	61.53	$(C_{20}H_{30}O_4)$	32.5	90	1,2

Table B2. Compounds Identified in the Whittier Narrows Wastewater Treatment Plant Secondary Effluent (4/86) by GC/MS (Continued)

Scan No.	RT (minutes)	ID Compound Name or Formula	Conc. (µg/L)	% Confidence in ID	Method of ID
2109	62.51	pthalate compound	15.0	90	1,2
2380	78.14	pthalate compound	8.6	90	1,2
-	-	$C_{15} - C_{33}$ n-alkanes	-	>95	3

Key:

1. manual interpretation of MS data
2. computerized matching of MS data
3. GC retention time matched with known standards

ND not determined because peaks are too broad
% confidence in ID is a personal judgement
\- concentrations evaluated based on area response of similar classes of compounds.
(is) internal standard

Table B3 Compounds Identified in the Florida Waste Water Treatment Treatment Plant Secondary Effluent (4/86) by GC/MS

Scan Number	RT (minutes)	ID Compound Name or Formula	Conc. (μg/L)	% Confidence in ID	Method of ID
244	--	decane (is)	ND	>95	1,2,3
267	--	chloroform	ND	>95	1,2,3
282	--	methyl benzene	ND	95	1,2
293	--	bromochloromethane	ND	>95	1,2,3
383	--	1,4 dimethyl benzene	ND	90	1,2
522	10.33	benzene, 1-methyl-3-(1-methylethyl)	2.1	90	1,2
658	14.56	tetradecane (is)	10.0	>95	1,2,3
780	17.77	$C_{10}H_{16}O$	5.2	60	1
899	22.23	cyclohexanol,5-methyl -2-(1 methylethyl)	31.3	85	1,2
932	23.21	1-octanoic acid	165.0	>95	1,2,3
952	23.98	C_{10} alcohol	10.1	90	1
997	25.32	branched $C_9 acid$	108.9	90	1,2
1089	28.39	1-nonanoic acid	179.4	>95	1,2,3
1138	30.18	aromatic alcohol	22.9	80	1,2
1169	30.84	branched C_{10} acid	14.8	90	1,2
1179	31.08	branched $C10$ acid	3.1	90	1,2
1203	32.39	hexadecanal	4.9	70	1,2
1212	32.67	phenol	17.8	>95	1,2,3
1230	33.34	branched C_{10} acid	1.9	90	1,2
1260	34.17	1-decanoic acid	148.0	>95	1,2,3
1271	34.64	p-cresol	207.7	>95	1,2,3
1277	34.87	m-cresol (is)	8.6	>95	1,2,3
1416	39.45	1-undecanoic acid	89.1	>95	1,2,3
1463	40.85	1-hexadecanol	1.3	90	1,2,3
1531	43.44	1-H-indole	14.3	90	1,2
1558	44.27	1-dodecanoic acid	78.3	>95	1,2,3
1615	46.32	1-octadecanol	6.2	90	1,2,3
1630	46.83	phenol 4-(1,1,3,3-tetramethyl-butyl	56.5	90	1,2
1651	47.38	benzene acetic acid	13.8	60	1,2
1671	48.23	alkyl phenol	31.4	80	1,2
1680	48.59	nonyl-phenol	91.2	90	1,2
1690	48.79	1-tetradecanoic acid	109.1	>95	1,2,3
1700	49.05	4-dodecyl phenol	39.2	90	1,2
1789	52.21	1H-indole,2,3-dihydro 4-methyl	4.3	80	1,2

Table B3 Continued

Scan Number	RT (minutes)	ID Compound Name or Formula	Conc. (µg/L)	% Confidence in ID	Method of ID
1812	53.45	1-hexadecanoic acid	1052.4	>95	1,2,3
1837	54.33	branched C_{16} or C_{17} acid	127.1	90	1,2
1870	54.70	branched C_{16} or C_{17} acid	68.7	90	1,2
1913	57.68	C_{31} n-alkane	18.0	90	1,2,3
1959	59.58	1-octadecanoic acid	248.0	>95	1,2,3
1987	60.74	1-nonadecanoic acid	281.1	>95	1,2,3
2380	77.95	pthalate compound	10.6	90	1,2
3342	120.10	cholesterol isomer	18.0	90	1,2
-	-	$C_{15} - C_{33}$ n-alkanes	-	>95	3

Key:

1. manual interpretation of MS data
2. computerized matching of MS data
3. GC retention time matched with known standards

ND not determined because peaks are too broad

% confidence in ID is a personal judgement

\- concentrations evaluated based on area response of similar classes of compounds.

(is) internal standard

ures B1 and B2 are the GC and GC/MS for the Whittier Narrows sample and Figures B3 and B4 are the corresponding figures for the Florida wastewater treatment plant. The large ECD response is quite noticeable for the Whittier Narrows sample (Figure B1). The most striking feature about the Florida plant chromatograph (Figure B3) is that it is primarily composed of fatty acids.

Figures B5 and B6 represent the gas chromatographs of fractions 1 and 2 of the Florida plant. The fraction 1 chromatograph shows a biomodal series of n-alkanes. The lighter series centered at C_{18} represents diesel fuel contamination. The heavier series with C_{29}, C_{31} and C_{33} n-alkane contributions is most likely of biogenic origin. These aliphatic hydrocarbons were not identifiable by GC/MS (Figure B4) because of carryover from neighboring higher concentration compounds. The GC shown in Figure B5 however eliminates (by silica gel fractionation) many of these interfering compounds (fatty acids) and allows for GC analysis at higher sensitivities. Figure B6 (fraction w) clearly shows the surfactant series of compounds present in the extract. These surfactants are long chain alkyl phenolics. Again this chromatograph was run at higher sensitivities than Figures B3 and B4 after silica get fractionation.

The compounds which were identified by GC/MS for the Whittier Narrows and Florida plants are presented in Tables B2 and B3, respectively. Table 12 is a similar listing for the San Diego Wastewater Treatment Plant. There are several similarities and differences between the treatment plants. First, the San Diego and Whittier Nar-

Table B4 Gravimetric Data from other Activated Sludge Plants

Date	EBMUD Treatment Plant (mg/L)	MVSD Treatment Plant (mg/L)
4/84	5.15	11.21
7/84	6.98	8.23
	7.41	
10/84	6.64	11.41
11/84	3.78	6.98

Key:

EBMUD = East Bay Municipal
MVSD = Mountain View Sanitation District

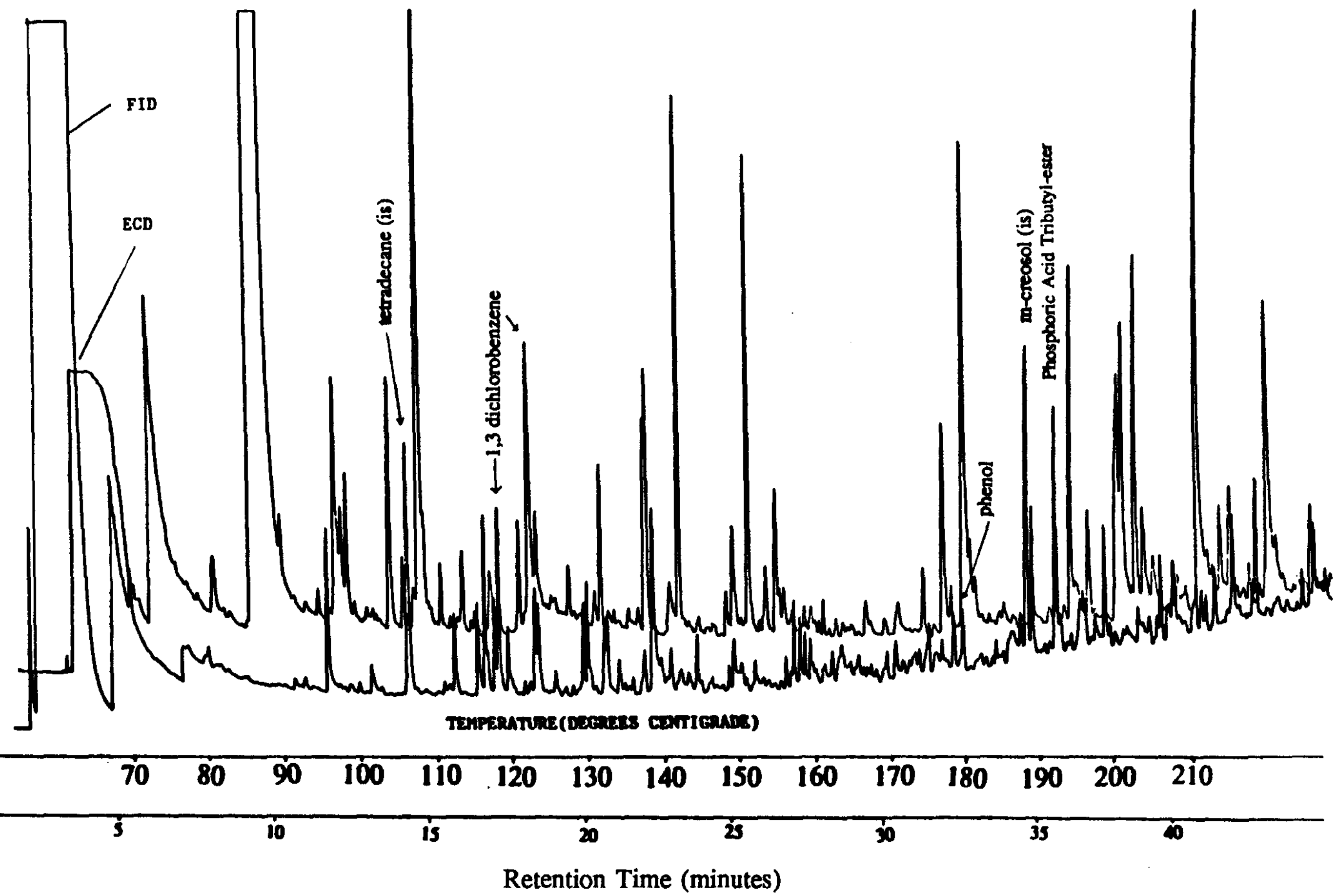


Fig. B1 GC of Whittier Narrows Wastewater Treatment Plant total extract. Axes are labeled for the FID. See Figure B2 and Table B2 for compound ID. GC conditions as previously described.

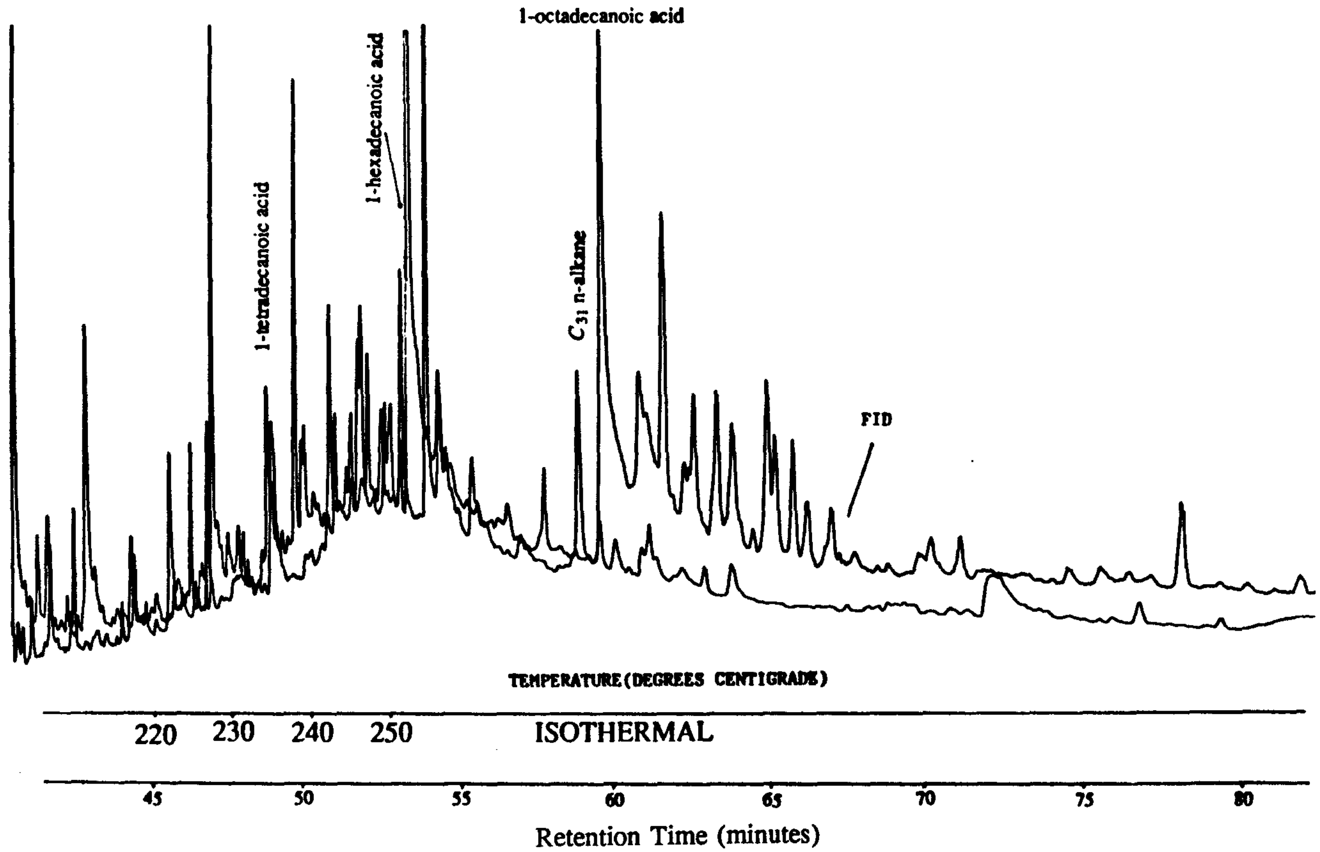


Fig. B1 GC of Whittier Narrows Wastewater Treatment Plant total extract. Axes are labeled for the FID. See Figure B2 and Table B2 for compound ID. GC conditions as previously described. (Contined)

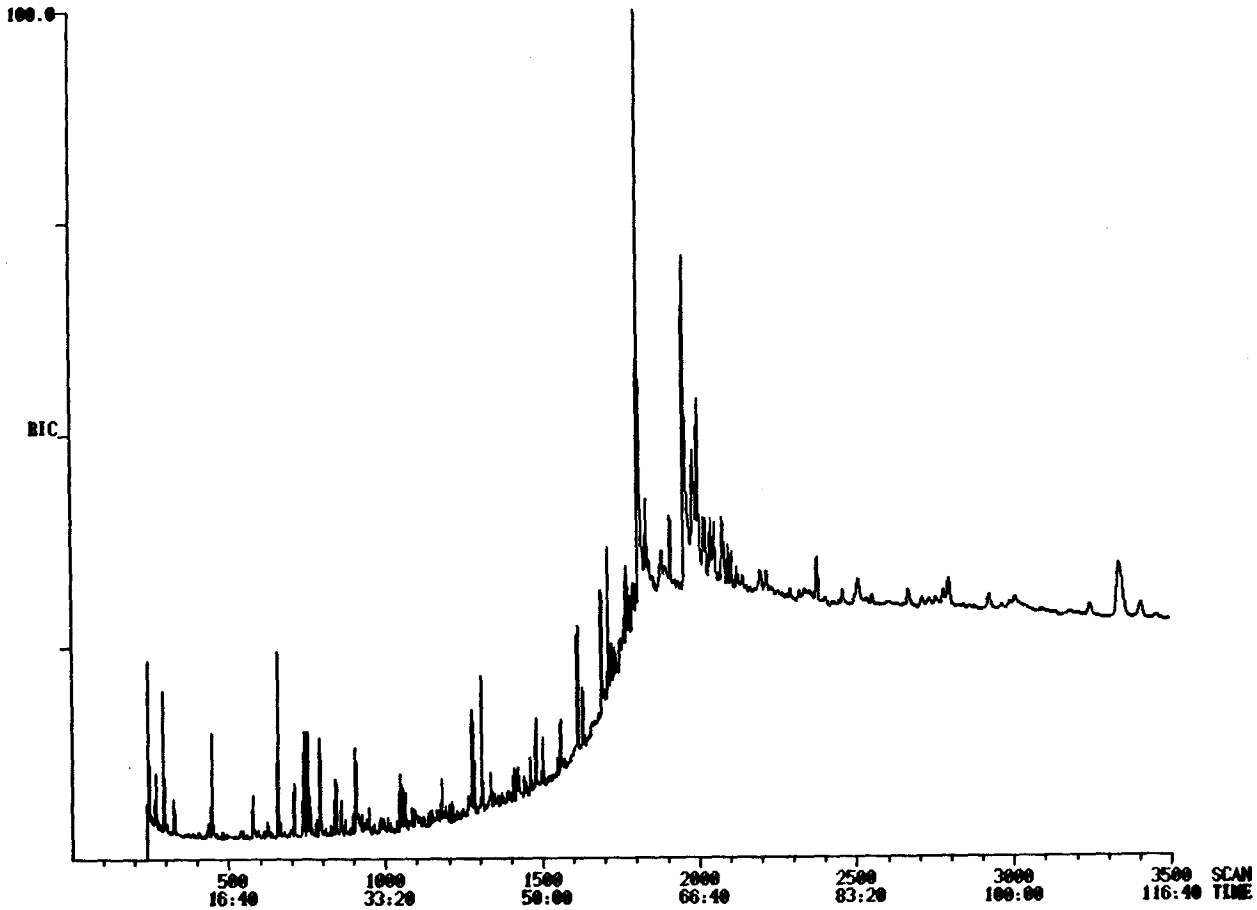


Fig. B2 GC/MS of Whitter Narrows Wastewater Treatment Plant Total extract. See Table B2 for compound ID.

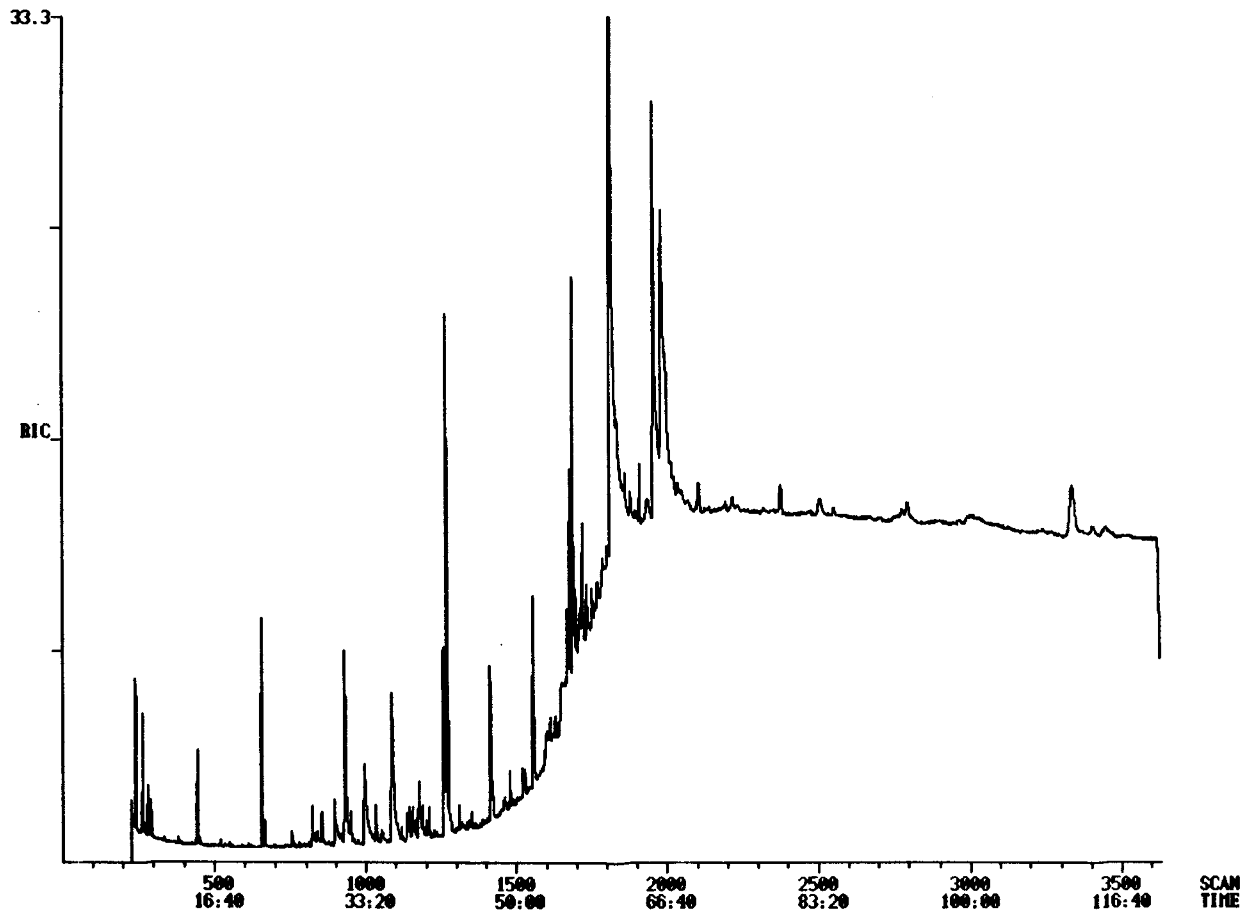


Fig. B4 GC/MS of Florida Wastewater Treatment Plant total extract. See Table B3 for Compound ID.

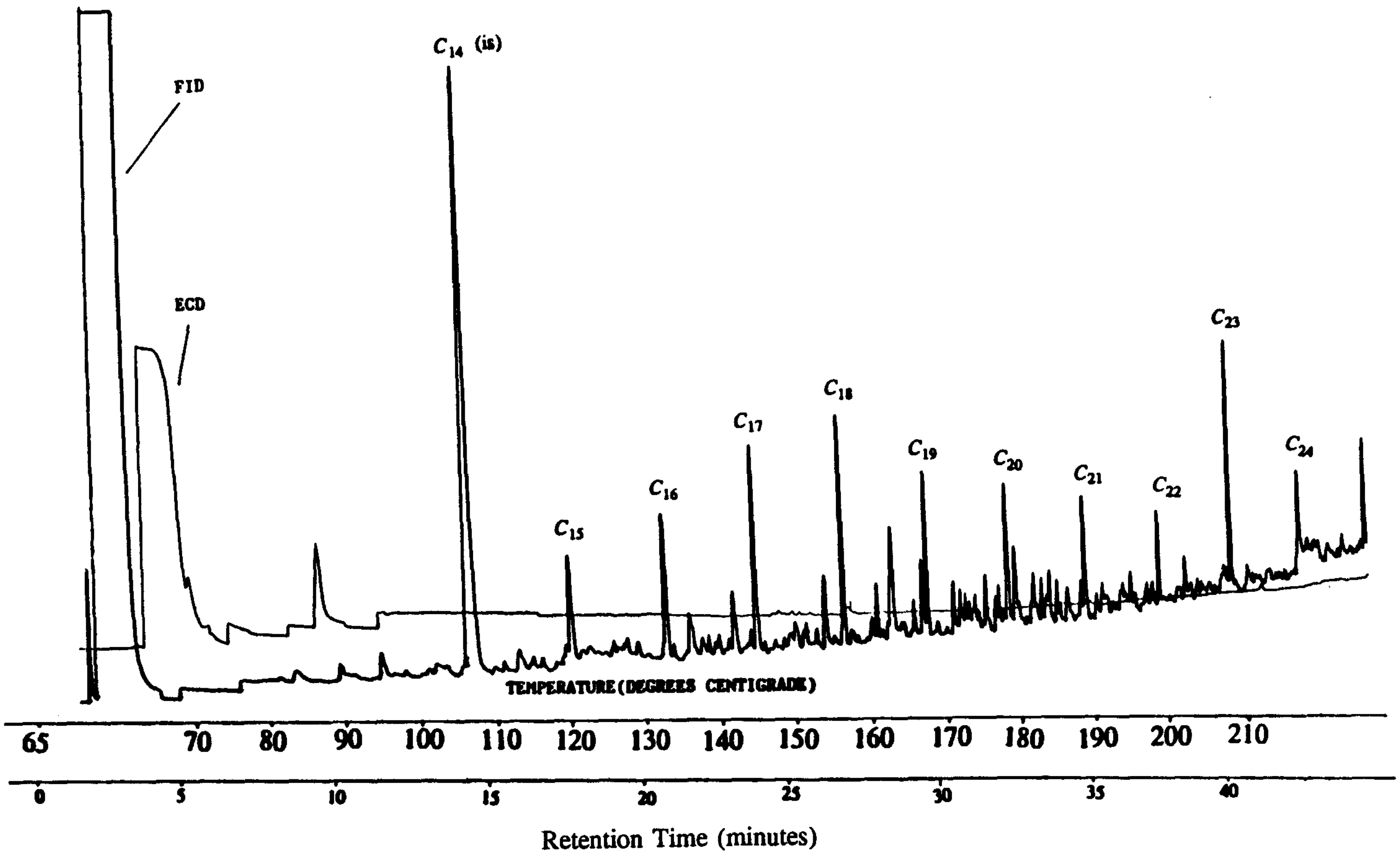


Fig. B5 GC of Fraction 1 of the Florida Wastewater Treatment Plant extract. Aliphatic n-alkanes are labeled by the number of carbon atoms. Axes are labeled for the FID. GC conditions as previously described.

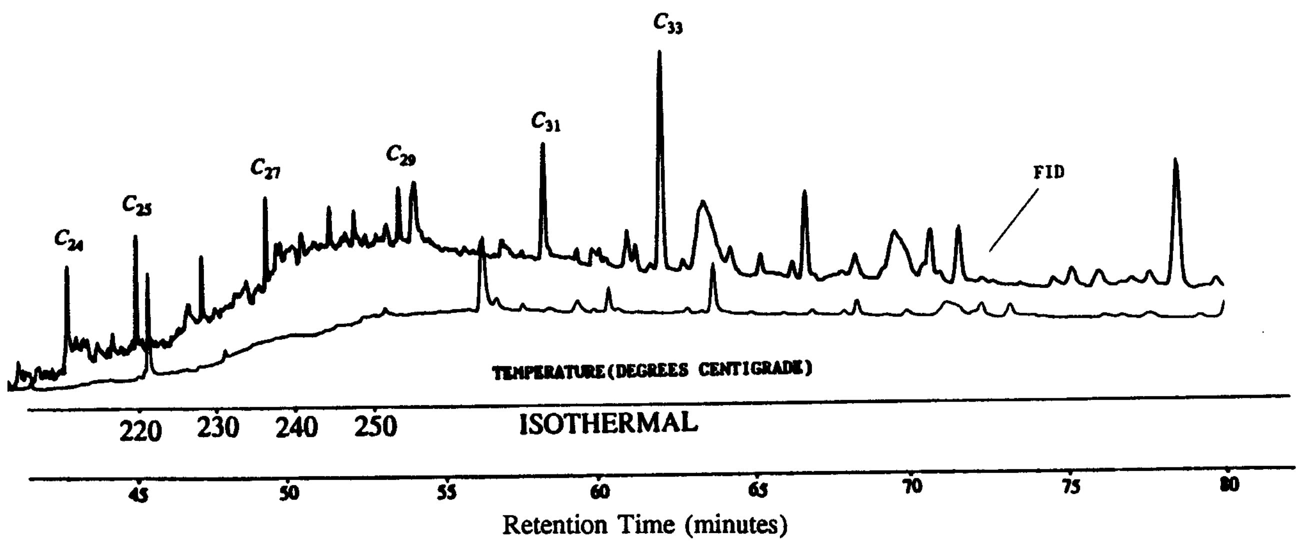


Fig. B5 GC of Fraction 1 of the Florida Wastewater Treatment Plant extract. Aliphatic n-alkanes are labeled by the number of carbon atoms. Axes are labeled for the FID. GC conditions as previously described. (Continued)

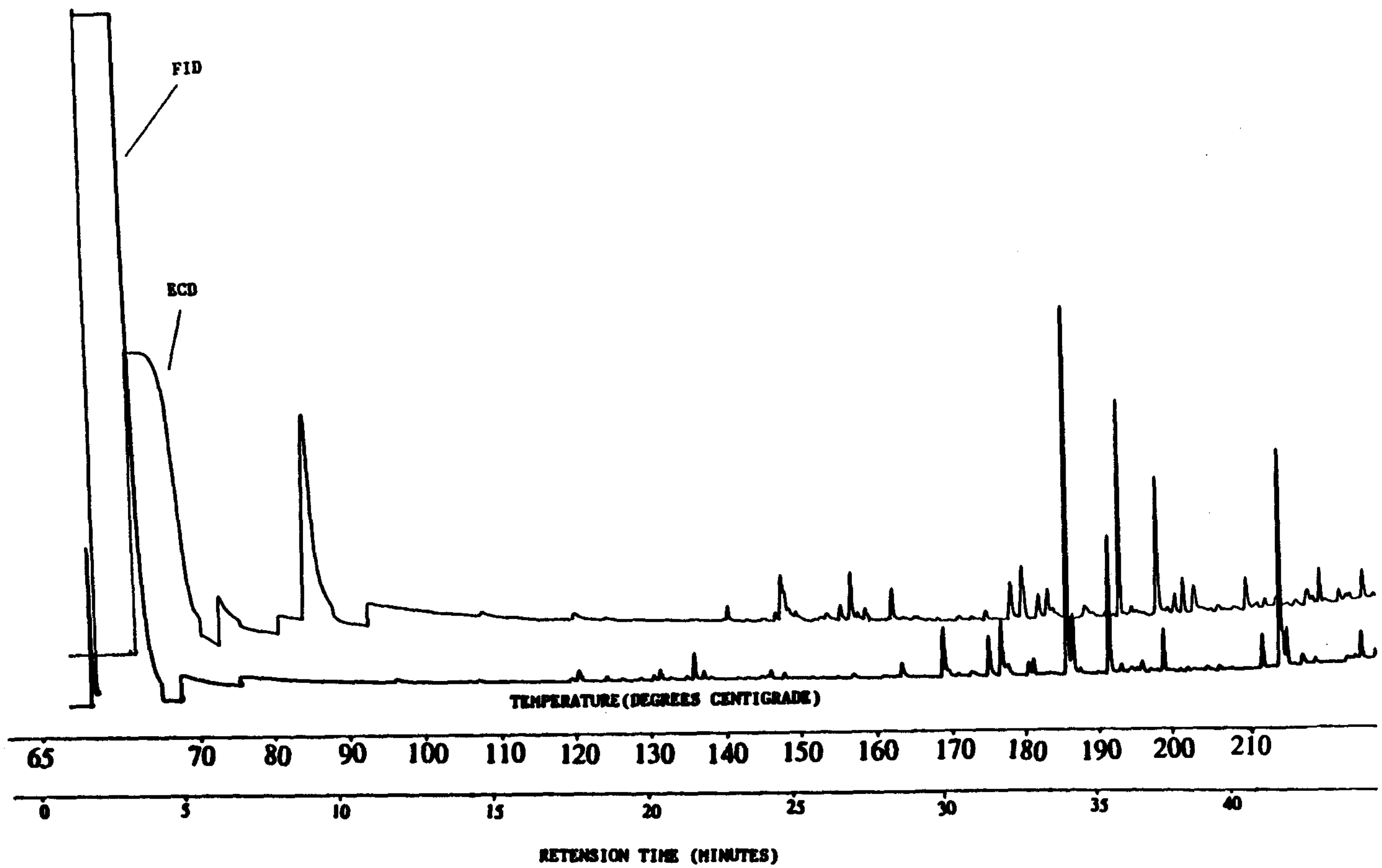


Fig. B6 GC of Fraction 2 of the Florida Wastewater Treatment Plant extract. Axes are labeled for the FID. GC Condition as previously described.

rows plants have comparable concentrations of fatty acids, whereas the Florida plant has much larger values. Although this observation is probably dependent on the treatment methodologies of the three plants, it must be partly attributable to the differing influents to the plants. The Florida influent is nearly 100% domestic, whereas the other two plants receive some industrial input (the fatty acids are of domestic origin).

Second, the Florida plant contains no dichlorobenzenes (DCB's) which at the other two plants probably result from industrial effluents. Third, all three wastewater treatment plants contain long chain alkyl phenolic surfactants. A phosphoric acid based surfactant was also found in the Whittier Narrows extract (phosphoric acid-tributyl-ester). Fourth, both water hyacinth based plants showed large concentrations (35.5 μg/l in San Diego and 18.0 μg/l in Florida) of the C_{31} n-alkane which most likely leaches off the plant leaf waxes.

Fifth, the Florida plant extract showed large concentrations of p-cresol (208 μg/l), and phenol (19 μg/l) which is somewhat surprising. It is possible that these compounds arise from solvents or paints used on the premises of the amusement park.

In summary, the effluents from the three plants show more similarities than differences. The differences are more likely due to influent variations than to the efficiencies of activated sludge treatment versus aquaculture treatment. Although the lower gravimetric value for the Whittier Narrows sample (2.61 mg/L) indicates high efficiency for activated sludge treatment, this may only be coincidental. In previously analyzed samples from other activated sludge based treatment plants, the gravimetric extracts showed much variability (Table B4).