Alternative Processes for Removal of Organohalogens and Organohalogen Precursors from Reverse Osmosis Treated Secondary Effluents

by

Michael K. Stenstrom, Ph.D., P.E. Professor

Lew C. Bauman, Ph.D. Postgraduate Research Engineer

J.B. Neethling, Ph.D. Assistant Professor

Civil Engineering Department University of California, Los Angeles, CA 90024-1600

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LIST OF SYMBOLS

Symbol	Meaning	
BOD	Biological oxygen demand	
EBCT	Empty bed contact time	
EPA	Environmental Protection Agency	
GAC	Granular activated carbon	
ITHM	Instantaneous trihalomethanes	
ITOX	Instantaneous total organic halogen	
MCL	Maximum contaminant level	
NVTOC	Non-volatile total organic carbon	
QC/QA	Quality control/Quality assurance	
RDF	Rotary disk filter	
RO	Reverse osmosis	
THM	Trihalomethanes	
THMFP	Trihalomethane forming potential	
TOC	Total organic carbon	
TOX	Total organic halogen	
TOXFP	Total organic halogen forming potential	
TTHM	Terminal trihalomethanes	
TTOX	Terminal total organic halogen	
UV	Ultra violet	
XAD-8	Synthetic resin (Rohm and Haas Co.)	

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ABSTRACT

This report describes research, funded by the California Department of Water Resources, conducted at the City of San Diego's Aqua II advanced wastewater reclamation facility.

An earlier report described removal of halogenated disinfection by-products and byproduct precursors from the reverse osmosis effluents of the Aqua I pilot water reclamation facility. The research extends the previous work on both characterization and unit operation removal of the non-volatile gas chromatographable fraction (NVCO) of disinfection by-products. The NVCO are an unknown fraction of the total organic halogen (TOX) formed upon chlorination.

The earlier research indicated that chlorine disinfection negated the positive effects of carbon adsorption/reverse osmosis treatment of secondary effluent by producing the high molecular weight non-volatile chlorinated organics (NVCO). After process evaluation, recommendations were made for modifications to treatment and disinfection protocols to reduce levels of the observed disinfection by-products.

This research expanded upon these initial findings to encompass characterization and unit operation removal of total organic halogen (TOX), trihalomethanes (THM), and THM/TOX precursors from Aqua II effluents that are to be disinfected with chlorine. The TOX analysis accurately quantitates all halogenated compounds in water including synthetic organic chemicals and disinfection by-products.

In the past decade, considerable research has been directed to the removal of halogenated organics in natural raw water sources. The objective of this research is to evaluate efficiency of developing technologies for contaminant and precursor removal from the reclaimed municipal wastewaters at Aqua II. Effluent from Aqua II has been proposed as a potential raw drinking water source.

In an attempt to fully evaluate efficacy of treatment processes, this work focused upon removal of surrogate parameters: total organic carbon, total organic halogen, total trihalomethanes, and halogen forming potentials, rather than on a specifically defined class of contaminants. Fractionation of secondary effluent, based upon acidity, solubility, and absorbability of dissolved organic material, using synthetic resins indicated a strong correlation between organohalogen forming potential and organic carbon. In addition to humic substances, the classic trihalomethane precursors, hydrophilic substances that comprised the largest fraction of the dissolved material were implicated for their tendency to form organic halogens upon chlorination.

Evaluation of existing comprehensive advanced treatment process at Aqua II indicated that it provides a high level of treatment with respect to removal of surrogate parameters. Several unit operations, for removal of the selected surrogate parameters, were evaluated and modeled to identify alternative or supplemental cost-effective methods of treatment: chloramination, sulfite dehalogenation of organics, carbon and activated alumina adsorption, and advanced oxidation processes.

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INTRODUCTION

The U.S. Water Resources Council (WRC) conducted studies estimating the potential for wastewater reuse and recycling in the country in 1985 and 2000. In the Second National Water Assessment, the WRC found that there are major water supply problems in most regions and severe local problems in certain subregions. Shortages resulted from inadequate distribution systems, ground water overdrafts, quality degradation of both surface and groundwater supplies, institutional constraints, and competition between various users (Culp et al., 1980).

The use of reclaimed wastewater may provide a solution to these shortage problems; however, unknown health risks remain a major barrier to the use of reclaimed water for potable and municipal purposes.

The quality of treated municipal wastewater is determined by 1) the type of treatment system, 2) quality of the water supply, 3) industrial discharge to the system, and 4) infiltration into the collection system (Culp et al., 1980). Major contaminants of secondary municipal effluents include metals, priority pollutants, BOD, coliform bacteria, and viruses. Although there are no standards for reuse of wastewater for potable purposes, a comparison of average municipal secondary effluents with drinking water standards (USEPA, 1978) indicates that minimum contaminant levels (MCL's) are exceeded for relatively few substances: turbidity, coliform bacteria, viruses, color, foaming agents, and odor. Generally, non-volatile total organic carbon (NVTOC) and biological oxygen demand (BOD) levels in sewage far exceed drinking water levels. Therefore, in addition to presence of

microbes, one of the primary concerns in reuse of municipal wastewater is the effect of organic material on the specific application (Culp et al., 1980).

Because wastewater generally contains levels of bacteria and viruses far above levels found in natural drinking water sources, a safe and particularly effective method of disinfection must be employed in treatment processes designed for the reclamation of wastewater for potable purposes. Chlorination is ideal for this purpose and has been successfully and widely used as a disinfectant for water sources since its introduction in 1896 at the Louisville, Kentucky, Experiment Station (Fuller, 1898).

In recent years, the use of free chlorine as a disinfectant has come under scrutiny following Rook's initial discovery of THM's in drinking water (Rook, 1974) and findings, in 1975, by the EPA's National Organic Reconnaissance Survey (NORS) of widespread occurrence of THM's is U.S. drinking supplies (Symons, et al., 1975). Since that time, a plethora of research has ensued concerning alternate disinfectants, modified methods for water treatment, and health effects of disinfectants and disinfectant byproducts.

A great deal of this research has focused on the use of alternative disinfectants including ozone, chlorine dioxide, and chloramines. However, there remains a great deal of uncertainty concerning the efficacy of these agents; particularly with respect to disinfectant ability, by-product formation, and health effects (Bull, 1982; Wolfe et al, 1984; Cooper et al., 1985; Symons et al., 1977; Boardman and Hoehn, 1979; Robeck, 1981; Hoff and Geldreich, 1981; Bull, 1980; Bull, 1982).

In addition to disinfecting oxidants a variety of chemicals are utilized in water treatment processes: alum, iron salts, lime, acids and bases, and polymeric coagulants and filter aids. All of these may leave residuals or byproducts in the finished water. Nevertheless, the principle risk factors in drinking water (except for radioactivity) are biological in origin (Cotruvo, 1984). The fact that biological contaminants are of prime concern and that free chlorine provides a cheap reproducible method of ensuring the bacteriological quality of water (National Academy of Sciences, 1977) points to the need for identification and optimization of treatment methods that minimize chlorination by-product formation. The focus of this dissertation, toward this goal, is the assessment of current and developing technologies for removal of organohalogens and organohalogen precursors in reclaimed wastewater prior to disinfection with chlorine.

Currently, the City of San Diego, as an integral part of the Total Resource Recovery Program, has been experimenting with an aquatic based wastewater treatment system coupled with an advanced treatment scheme since 1981. The goal of the project is to provide an alternate source of safe drinking water to help reduce projected shortages (Miller and Willets, 1987).

Fam (1987) conducted extensive studies concerning precursors, by-product formation and characterization, and treatment methodologies of gas chromatographable non-volatile chlorinated organics (NVCO) in the disinfected reclaimed wastewater at San Diego (see also Fam and Stenstrom 1987; Fam and Stenstrom, 1988). The NVCO are a fraction of the total dissolved organic halogens (TOX). A summary of significant findings indicated that 1) the physical and chemical properties of the precursors to these chlorinated hydrocarbons were

significantly different than that of humic and fulvic acids (commonly implicated as precursors in water sources); 2) dechlorination with sulfites reduced levels of chlorination byproducts; and 3) that carbon adsorption after chlorination appeared to be the most effective method for minimizing levels of the observed chlorinated organics.

The major goals of this research are to expand upon these initial finding's to include the characterization and treatment of precursors to the total, rather than just nonvolatile gas chromatographable portion, organic halogen content of chlorinated reclaimed water. A brief discussion is included on reduction of trihalomethanes (THM's) and TOX by the use of chloramines. The experimental work will focus on quantitative characterization of the TOX precursors, removal of TOX by sulfite dechlorination, removal of TOX and TOX precursors by carbon and activated alumina adsorption, and advanced oxidation processes.

LITERATURE REVIEW

Chlorine Chemistry

Chlorine is used in several forms in water treatment processes. Chlorine may be added as chlorine gas (Cl_2) , hypochlorites, or as a combined residual. Chlorine gas dissolves in water to form hydrolysis or disproportionation products:

$$Cl_{2(g)} \longrightarrow Cl_{2(ag)} \tag{1}$$

$$Cl_2 + H_2O --- > HOCl + HCl$$
 (2)

or in the presence of alkalinity:

$$Cl_2 + HCO_3^{-} --> HOCI + CO_2 + Cl^{-}$$
(3)

Hydrolysis is rapid an occurs in a few tenths of a second at 18°C (Shilov and Soludushenkov, 1936, 1945).

The Effect of pH and Temperature. Hypochlorous acid (HOCl) is a weak acid and dissociates as follows:

$$HOCI < ---> H^+ + OCI^-$$
(4)

The equilibrium constant is a function of temperature (Morris, 1966) and is defined as follows:

$$K = [H^+][OCl^-]/[HOCl]; pK = 7.5 (25^{\circ}C)$$

(5)

Morris (1966) developed a best fit formula for the hypochlorous acid ionization constant (k) as a function of temperature:

$$pK = 3000/T - 10.0686 + 0.0253T$$
(6)

where T is absolute temperature (°K). This equilibrium is also affected by ionic strength. The higher the TDS (and therefore the ionic strength) the greater the degree of dissociation. However, in dilute solutions (TDS = 10mg/l) effect of ionic strength can be neglected (White,1986).

Free residual chlorine is defined as the sum of $[Cl_{2(aq)}]$, $[OCI^{-}]$ and [HOCI] species. Generally, a specified free residual chlorine value of 0.5 to 1 mg/l is a process objective in water supply treatment systems. Speciation of free chlorine residuals is pH dependent and may be calculated using dissociation constants for monoprotic acids. [HOCI] is by far a more effective disinfectant than hypochlorite (or monochloramine) which makes pH an important parameter in the chlorination process (Fair et al., 1947; Williams, 1951).

Inorganic Chloramine Formation. The reaction of chlorine with ammonia is complex and the mechanism is poorly understood and varies with pH, reaction time, and chlorine to ammonia nitrogen ratios. In dilute solution aqueous chlorine reacts with ammonia nitrogen in a series of competing reactions. The reactions are complex and involve catalytic intermediates (Saunier, 1976). The reactions, taken

together as the breakpoint reaction, can be summarized as follows (Tchobanoglous and Schroeder, 1985):

$$HOCl + NH_2 ---> NH_2Cl(monochloramine) + H_2O$$
 (7)

$$HOCl + NH_2Cl ---> NHCl_2(dichloramine) + H_2O$$
 (8)

$$HOCl + NHCl_{2} --- > NCl_{3}(trichloramine)^{*} + H_{2}O$$
(9)

$$NH_2CI + NHCL_2 + HOCI ---> N_2O + 4HCI$$
(10)

$$2NH_2Cl + HOCl --- > N_{2(g)} + H_2O + 3HCl$$
 (11)

*undesirable breakpoint residual.

As chlorine is added to a pure solution of ammonia monochloramines are primarily produced up to a chlorine: ammonia molar ratio of 1:1 or 5:1 weight ratio. Further addition of chlorine results in the conversion of monochloramine to dichloramine and trichloramine and finally to nitrogen gas at breakpoint. The overall reaction of chlorine with ammonia in pure solution can be summarized as follows:

$$3HOCI + 2NH_3 ---> 3H^+ + 3CI^- + 3H_2O + N_{2(g)}$$
 (12)

This breakpoint reaction occurs at a chlorine to ammonia dose of approximate 1.5:1 on a molar basis or 7.6:1 on a weight basis. The formation of monochloramine has been shown to be an elementary second order reaction with a rate constant of 5.1 x

 10^6 liter/mole-sec. Solution pH exerts a profound influence on the speciation of the reactants and the rate exhibits a maximum at pH 8.4 (Morris, 1967).

Dechlorination and Sulfite Chemistry

Dechlorinating Agents. Dechlorination is the process of removing combined and free chlorine residuals. Dechlorination has been employed in potable water treatment to reduce residuals to a desired level and to improve taste and in wastewater treatment to reduce effluent toxicity (White, 1986). Sulfur dioxide is one of the most commonly employed dechlorinating agents. Other methods of dechlorination in water treatment include addition of sodium metabisulfite, sodium sulfite, hydrogen peroxide, or adsorption onto granular activated carbon.

Reactions of Sulfur Dioxide (Sulfite) with Chlorine. Sulfur dioxide reacts with water to form sulfurous acid:

$$SO_2 + H_2O --> H_2SO_3$$
 (13)

with the following ionic equilibria and dissociation constants (Brasted, 1961):

$$H_2SO_3 < --> H^+ + HSO_3^ K_{A1} = 1.6x10^{-2}$$
 (14)

$$HSO_3^- < --> H^+ + SO_3^{-2-}$$
 $K_{A2} = 1.0 \times 10^{-7}$ (15)

From these equilibria the distribution of ions in solution as a function of pH can be determined (see Figure 9).

The reaction sulfites with aqueous chlorine residuals is given (White, 1986):

$$HOCI + HSO_3^{-} -> HCI + H_2SO_4$$
(16)

$$NH_2Cl + H_2SO_3 + H_2O -> NH_4Cl + H_2SO_4$$
 (17)

$$NHCl_2 + 2H_2SO_3 + 2H_2O --> NH_4Cl + HCl + 2H_2SO_4$$
 (18)

$$NCl_3 + 3H_2SO_3 + 3H_2O --> NH_4Cl + 2HCl + 3H_2SO_4$$
 (19)

For complete dechlorination the stoichiometric weight ratio of sulfur dioxide to chlorine is 0.9 to 1 and consumes 2.8 mg/l alkalinity (as $CaCO_3$) for each mg/l chlorine removed (White, 1986 and Metcalf and Eddy, 1979).

The Effect of pH on Oxidation/Reduction Potentials. Acid solutions of SO_2 are commonly referred to as *sulfurous acid*, H_2SO_3 . However, no evidence exists for this species and it can be denoted as hydrated sulfur dioxide, SO_2xH_2O . The species is weakly reducing:

$$SO_4^{2-} + 4H^+ + (x-2)H_2O + 2e^- -> SO_2xH_2O = E^\circ = 0.17 V$$
 (20)

Aqueous sulfite salts are significantly stronger reducing agents, with a higher half cell potential:

$$SO_4^{2-} + H_2O + 2e^{-} - > SO_3^{2-} + 2OH^{-} E^{\circ} = 0.93 V$$
 (21)

It appears that all sulfite reductions should be carried out at high pH; however, the free energy of each redox reaction should be calculated as the oxidant half cell may be reversely pH dependent (Eilbeck and Mattock, 1987).

Formation and Analysis of Aqueous Halogenated Organics

The practice of water chlorination, the most commonly employed method for the destruction of pathogens in wastewater treatment, produces residuals that have been shown to be toxic to aquatic life (Esvelt et al., 1971; Mich. Dept. of Nat. Res., 1971) and halogenated organics that are potentially mutagenic, carcinogenic, or toxic (Meier and Bull, 1985; Kool et al. 1985).

Extensive research has been conducted on the characterization of the halogenated compounds formed during the chlorination of water and wastewater following Rook's (1974) initial demonstration that chlorination of naturally colored waters results in the formation of chloroform. Soon thereafter the U.S. EPA promulgated an amendment the National Interim Primary Drinking Water Regulations on November 29, 1979. The amendment established a maximum contaminant level (MCL) of trihalomethane in water at a concentration of 100 μ g/l (Cotruvo, 1983; Culp, 1984).

Other studies have indicated that a large portion chlorination products are nonvolatile (Oliver, 1978, Glaze et. al., 1979, Rook, 1980). McCreary and Snoeyink (1980, 1981) have determined that less than 0.1% of the total organic halide from the chlorination humic acid, extracted from peat, is gas chromatographable.

A complete review of the literature concerning the chemistry and analysis of chlorination byproducts is beyond the scope of this study and the interested reader is referred to Fam (1987) for a thorough discussion. However, as TOX and THM measurements are employed here as surrogate measures of organic precursors (TOXFP/THMFP), a brief summary will be given of the factors affecting THM/TOX formation as well as a description of the selected analytical methods.

In general, the reaction of chlorine or chloramines with organic precursors can be simply described:

Free Chlorine + Precursors --> THM's + (Volatile and Non-Volatile Organic Halogens) 22)

Chlorination products can be classified as volatile or purgable organic halogen (POX) and non-volatile or non-purgable organic halogen (NPOX). Trihalomethanes often constitute a significant portion of the POX, while the NPOX is diverse and poorly defined. THM's are measured utilizing gas chromatography. The total organic halogen content of water, [TOX = (NPOX + POX)], can be measured by carbon adsorption, oxidative combustion, with measurement of the liberated halide by microcoulometry (TOX analysis).

Trihalomethanes

Formation. The most common trihalomethane species encountered in chlorinated waters are, in decreasing order of abundance, chloroform, bromodichloromethane, dibromochloromethane, and bromoform. The rate of THM formation is influenced by a number of factors as summarized by Culp (1984):

* pH

* Temperature

* Form and Concentration of Chlorine

* Type and Concentration of Organic Precursor

* Bromide Concentration

In general, THM levels increase with temperature, pH, free chlorine concentration, and bromide concentration. The effect of precursor type is variable and is the subject of current research, including this dissertation. However, it is commonly observed that, for a given water source, increases in precursor levels result in higher levels of THM (or non-volatile organohalogens).

Analysis. The analysis of the THM's in water can be accomplished by several concentration methods followed by GC analysis : purge and trap/desorption, liquid-liquid extraction, head-space sampling, direct aqueous injection, or resin adsorption/elution (Glaze, et. al, 1981). The U.S. EPA has specified purge and trap as a specific method for the analysis of THM's in water (Method 501.1- Purge and Trap GC). The method was developed by the Environmental Monitoring and Support Laboratory (EMSL) and is published in the *Federal Register* as part of an amendment to the Interim Primary Drinking Water Regulations (Lichtenberg, et. al., 1984).

Total Organic Halogen

Formation. The factors affecting the formation of TOX is the subject of current research. Preliminary results indicate that NPOX formation is affected by the same

parameters as THM's although trends are different. Stevens (1983) measured THM's and TOX from humic acids chlorinated at several pH values, reaction periods, and chlorine concentrations. THM's increased with increasing pH while NPOX decreased dramatically. Temperature caused a significant increase in NPOX only at low pH. THM's increased with increasing pH and temperature. Reaction rates for NPOX formation appeared higher at high pH. Chlorine concentrations caused greater increases in NPOX than in THM's. Johnson and Jensen (1986) found similar trends. Decreasing pH values cause an increase in NPOX and a decrease in THM's. At low chlorine doses, substitution products dominate. Higher doses results in more oxidation products and eventually higher levels of THM's and NPOX (Fleischhacker and Randtke 1983; Rechow and Singer, 1984; Chow and Roberts, 1981).

Becher and Carlberg (1985) showed that low molecular weight compounds account for only a minor part of the chlorination byproducts of polymeric aquatic humus by separating the heavier fraction using high performance size exclusion chromatography. Johnson and Jensen (1986) state that THM's are the tip of the TOX iceberg and show that chlorination of diverse naturally occurring compounds produces 1.5 to 11 times as much NPTOX as chloroform and that the importance of TOX cannot be overemphasized. They conclude that the analysis of the effect of pH, contact time, and chlorine dose indicate that a trade off between THM's and TOX.

Analysis. Stevens et al. (1985) has recently reviewed the current methods utilized for the analysis of halogenated compounds in water. Most of the organic

compounds causing chlorine demand are oxidized and can be accounted for by the presence of chloride ion. However, approximately 10% of these compounds may react by addition or substitution to form halogenated nuisance residuals. Many of these compounds are amenable to GC and GC-MS analysis and include THM's, chloroacetic acids, chloroacetonitriles, trichloroacetone, chlorinated phenols, and others. However, compounds detected by these techniques do not account for all the halogenated residuals. Stevens indicates the usefulness of the TOX (and particularly the NPOX) parameter as a measure of the degree of formation of halogenated compounds, thereby useful as a tool in unit process design and control.

Carlberg and Kringstad (1983) compared three methods for the determination of organic halogen in industrial effluents: the extraction method, the carbon adsorption method, and the ultrafiltration/XAD-4 method. The extraction method consists of a sulfuric acid/butylacetate extraction followed by neutron activation analysis. A Dohrmann DX-20 TOX analyzer was used for the carbon adsorption method. The ultrafiltration/XAD-4 method involves separation into low and high molecular weight fractions and adsorption of adjusted samples on XAD-4 columns. The retained substances were eluted with acetone, combusted and analyzed by potentiometric titration. The carbon adsorption method was the easiest to perform and gave the highest concentrations for the three methods tested.

The TOX method involves sample concentration by carbon adsorption followed by oxidative combustion with measurement of the released inorganic halide by microcoulometry. The method is currently the basis of USEPA Method 450.1. A complete discussion of the method is given by Takahashi et. al. (1981).

Precursors to TOX and THM's in Water and Wastewater

Natural Waters. In the United States, over 1300 organics have been identified in water and wastewater. Even in treated drinking water, approximately 300 synthetic compound have been identified occurring in two or more systems. Undoubtedly, with advances in analytical technology, many more compounds will be identified. The unpolluted surface and ground waters of North America contain, on the average, about 8 mg/l of organic material. A survey of water supplies for 80 cities showed the median concentration for water supplies from groundwater sources to be about 1.0 mg/l with surface sources at 6.0 mg/l (Koenig, 1987).

The organics in natural unpolluted water are derived primarily from decay of plant material, leachates from soils, and bacterial and algal origin. The major classes of these natural organics are humic substances, tannins, lignins, phenolics, hydrocarbons, amino acids, and fatty acids (Koenig, 1987).

Humic substances are responsible for imparting color to natural water and have been implicated as precursors to THM's and other chlorinated organics (Rook, 1976; Stevens et al., 1978; Oliver and Visser, 1980). Humic acids are complex macromolecules, with molecular weights ranging from 200 to 10,000, that are predominantly aromatic and hydrophilic. At pH's encountered in natural waters, humic substances are stabilized by negatively charged functional groups (Edzwald, 1987).

Classification of humic substances is based upon solubility and is divided into three main fractions:

- 1) Humic Acid.....alkali soluble, insoluble in acid.
- 2) Fulvic Acid soluble in both alkali and acid.

3) Humin.....insoluble in both alkali and acid.

Although humic substances are structurally similar, they differ in structural group content, elemental analysis, and molecular weight. They contain a variety of structural groups: alcoholic, phenolic, carboxyl, methoxyl, carbonyl, ether, and ester. Fulvic acids have a larger proportion of oxygen containing functional groups per unit mass (Edzwald, 1987).

In addition to humic substances, many other compounds have been implicated as potential precursors to THM's and other chlorinated organics including chlorophyll (Morris and Baum, 1978), extracellular algal products (Briley et al., 1979; Hoehn et al., 1979), phenols and ketones (Onodera, 1984; Boyce et al., 1983; Boyce and Honig, 1979), and free, proteinaceous, and humic bound amino acids (Trehy et al., 1986).

Wastewaters. Industrial and municipal use of treated waters results in aqueous wastes with high levels of dissolved organic substances. Wastewater effluents from standard secondary treatment plants have organic levels ranging from 20 to 100 mg/l. Much of this organic material is proteinaceous, fatty or carbohydrate like - byproducts of microbial metabolism. However, a large proportion of this material is recalcitrant and is indicated by high COD/BOD effluent ratios. The source of these compounds are largely industrial; however, small businesses and households contribute a variety of synthetic materials to domestic wastes including organic solvents, deodorants such as dichlorobenzene, pesticides, cresols, and terpenoid

wastes (Morris and Donovan, 1987). Many of these compounds are toxic, mutagenic, or carcinogenic and have been classified by the USEPA for regulatory purposes as priority pollutants (see Table 1.).

Fam (1987) and Fam and Stenstrom (1987) have shown that chlorination of treated municipal wastes results in the formation additional chlorinated products: a variety of experiments were conducted to elucidate the nature of the precursors to non-volatile chlorinated organics (NVCO) in the effluent of the San Diego water hyacinth based treatment facility. Because of the direct applicability of this work to the work presented here these experiments will be reviewed in detail.

Acidic (pH 2) secondary effluent was extracted onto polymeric XAD8 resins . Resins were eluted with 0.1N NaOH and diluted to 1 mg/l NVTOC, typical of effluents at the plant, and chlorinated with a dose of 2.5 mg/l. GC-ECD chromatograms were compared to chromatograms of extracts of chlorinated plant effluents with good reproducibility indicating that NVCO precursors are acidic compounds (adsorbable in acid and desorbable in alkaline solution).

Table 1. Organic Priority Pollutant categories. *

Pollutant	Comments
Polychlorinated Biphenyls	Industrial uses include paints, plastics, insecticides, electrical capacitors, and transformers. Bioaccumulated in nature.
Pesticides	Includes many chlorinated hydrocarbons. Some bioaccumulated in food chain.
Halogenated aliphatics	Industrial uses include fire extinguishers, refrigerants, pesticides, solvents, dry cleaning solvents and propellants. Implicated in liver and central nervous system (CNS) damage.
Phthalate esters	Used in the production of PVC and other thermoplastics as plasticizers. Teratogenic and mutagenic.
Ethers	Uses include solvents for polymer plastics. Some carcinogenic.
Phenois	Industrial uses include intermediates for synthetic polymers, dyestuffs, pesticides and herbicides, and pigments. Toxicity increases with chlorine substitution.
Polycyclic Aromatic Hydrocarbons (PAH's)	Found in pesticides, motor fuels and oils, and dyestuffs. Also used as chemical intermediates. Some found in nature. Suspected Carcinogens.
Other Monocyclics	Used in the manufacture of explosives, dyes, solvents, fungicides, herbicides, and other chemicals CNS depressants. Can cause liver and kidney damage.

*Modified after Council on Environmental Quality (1978).

To determine the efficacy of XAD-8 extraction as a method of precursor collection acidified reverse osmosis effluents from the treatment plant were pretreated using XAD-8 resin and by extraction with methylene chloride. Upon chlorination, the XAD-8 samples showed an average drop of 70% in total ECD area compared to an average of 30% for the methylene chloride extracted samples. This indicated the higher affinity of the precursor compounds for the XAD-8 resin at low pH.

The polarity and solubility of the precursors was determined using column chromatography with silica gel and XAD-8 resin. Methylene chloride extracts of the aquaculture effluent were redissolved in purified water and chlorinated (pH 7, 2.5 mg/l, 2 hrs), re-extracted, and total GC-ECD area determined. This result was compared to ECD areas obtained from chlorination of solvent fractions eluted from a silica gel column that had been used to collect the precursors. Percentages of total ECD area obtained from chlorination of each fraction is reported below (Table 2). Solubility of the XAD-8 adsorbed components was determined by chlorinating increasing polar eluates of a XAD-8 resins which had been used to adsorb 16 liters of aquaculture effluent at pH 2. GC-ECD areas were determined before and after chlorination. Chlorination of the ether fraction resulted in the largest increase in ECD area indicating that the majority of the precursors are ether soluble (Table 3).

Table 2. Percentage of Total ECD area obtained from chlorination of silica gel extracts (After Fam, 1987).

Solvent	<pre>% Total ECD Area</pre>	
Hexane	<5	
Benzene	<5	
CH2Cl2:WeOH	~65	
Difference (NEP)*	~30	

* non-elutable polars.

Table 3. Chlorination of XAD-8 eluants (After Fam, 1987).

Solvent	Net increase in GC-ECD area after chlorination	<pre>% of Total ECD Area</pre>
Ether	2.88 x 10^8	62.58
CH ₂ CL ₂	9.75 x 10^7	21.18
MeOH	7.3×10^7	15.86
0.1N NaOH	1.73×10^6	0.38

Fam and Stenstrom interpreted these results to indicate that NVCO precursors were polar, yet solvent extractable. Because humic and fulvic acids were not solvent extractable, the NVCO precursors were unique and did not fit the classic definition of humic or fulvic compounds.

A humic/fulvic split (after Thurman and Malcolm, 1981) of the XAD-8 extract was chlorinated to compare results with other workers. Samples were centrifuged at pH 1 to precipitate the insoluble humic fraction. Both fractions were subsequently chlorinated (10 mg/l NaOCL, pH 7, 2 hrs). GC-ECD responses were compared to unfractionated samples. The soluble, "fulvic", fraction accounted for over 95% of the total ECD response. Fam and Stenstrom felt that labeling the NVCO precursors, in the San Diego effluent, as fulvics was too broad a classification since these precursors are organic soluble and classically fulvics are only water soluble.

The MW range of the precursors was determined by chlorination of five molecular weight ranges of aquaculture effluent separated by ultrafiltration. Fractions were analyzed by GC-ECD before and after chlorination (10 mg/l NaOCl, pH 7, 2 hrs). The largest fraction of total ECD area (~85%) was found in the less than 1000 MW fraction.

XAD-8 extracts from two other wastewater treatment facilities were collected and chlorinated to compare results to the San Diego plant. Samples were taken from Whittier Narrows Treatment Plant (Whittier, CA), a conventional tertiary activated sludge plant and from a water hyacinth treatment plant located in central Florida. Both samples resulted in GC-ECD profiles similar to samples collected at

San Diego indicating that the NVCO precursors were neither unique to San Diego or to water hyacinth based treatment systems.

To determine the NVCO forming potential of naturally occurring compounds that may be encountered in sewage effluents Fam (1987) chlorinated (2:1 Cl_2 :TOC ratios, pH 7, 2 hrs) a variety of commercially available compounds representing naturally occurring organics: carbohydrates, lipids, aminoacids, metabolic acids, and plant pigments. GC-ECD results of the extracted samples were compared to XAD-8 samples from the San Diego treatment facility. Retention time matches with the XAD-8 sample are summarized in Table 4.

		······································
Compound	#RT matches with XAD-8	Other halocarbons produced
Fatty Acids:		
Lactic Pyruvic Malic Oleic	0 0 0 0	High High High High
Flavone Type	Plant Pigments:	
Catechin Flavone Kaempherol Morin	7 10 13 15	High High High High
Carbohydrates	•	
Cellulose Tannic Acid	0 1	Low Low
Amino acids/F	Proteins:	
Pepsin Proline Tryptophan	1 1 2	Low Low Low
Lipids/Choles	terol:	
Cholesterol Psychosine Sphingosine	0 0 1	Low Low Low
Unsaturated H	ydrocarbon:	
Squalene	3	Low

Table 4. Positive GC-ECD results of chlorination of pure compounds (After Fam, 1987).

In summary, Fam and Stenstrom (1987) suggested that flavones and flavonols were ideal model compounds for NVCO precursors because their chemistry agrees well with the experimental results from compounds extracted from the San Diego treatment facility: their MW range is less than 1000, they are soluble both in water and in organic solvents (depending upon degree of hydroxylation), they are moderately polar as well as acidic, and finally their pale yellow color was reminiscent of XAD-8 aquaculture extracts.

The source of precursors of the total fraction of chlorinated organics (TOXFP) in wastewater may be partially from natural substances in unpolluted source waters; undoubtedly a portion is from anthropogenic sources or derived from the treatment process itself, e.g. bacterial or hyacinth extracellular products.

Measurement and Characterization of TOX Precursors

Measurement and characterization of organic halogen precursors ranges from sophisticated methods such as GC/MS analysis of degradation products and X ray crystallography to surrogate parameters such as color, TOC, UV, THMFP, and TOXFP. Operational characterization of precursors can be realized by combining fractionation procedures, such as column adsorption-elution, extraction, and size exclusion chromatography, with surrogate or analytical methods.

Advanced methods yield a great deal of information concerning precursor structural identity. For example, Laio et al. (1982) identified fractionated methylated oxidation fragments of aquatic humic and fulvic acids by GC/MS. This procedure

allowed for both structural assignment and semi quantitative analysis of the polymeric precursors. Identified products accounted for approximately 25 wt. % of starting materials.

The use of surrogate parameters, although providing little or no structural information, provide a relatively easy, rapid, and inexpensive method for measuring precursor concentration. For water and wastewater treatment, these characteristics are especially important from an operational point of view. Precursor characteristics and concentrations are highly source dependent and surrogates provide a method for rapidly and accurately quantifying and characterizing them; data which allows for rapid assessment of unit operations and optimization of treatment protocol.

Color provides an aesthetic measure of (humic) color causing compounds. There is no standard instrumental method (Standard Methods, 1980).

UV absorption measures organic compounds that have aromatic structures or conjugated double bonds absorb light in UV regions. Humic substances have a variety of aromatic moieties and adsorb light in the UV region; absorbance generally decreases with increasing wavelength (Schnitzer and Khan, 1972). Edzwald et al. (1985) examined the use of UV absorbance as a measure for TOC and THMFP. Surrogate least linear square equations developed from a single water source were effective in predicting levels in other waters and performance of pilot plants. THM levels of finished waters could be predicted from multiple correlations of raw water UV, finished water pH, chlorine consumption, and temperature.

TOC is a effective and accurate method for analyzing small amounts of dissolved organic carbon. One instrumental method involves UV catalyzed persulfate oxidation of the dissolved organic matter with measurement of the released carbon dioxide with a non-dispersive infrared detector. Concentrations are reported as mass carbon. (Dohrmann Instruments, Sunnyvale, CA). Rechow and Singer (1984), examining the effect of ozonation and coagulation on precursor levels, determined that TOC and UV absorbance were reasonably good measures for organic halide precursors.

THM forming potential (THMFP) and TOX forming (TOXFP) provide an indirect measure of precursor concentration. These forming potentials are defined as the difference between levels of chlorinated organic (THM or TOX) measured prior to and after chlorination under specified conditions. Standardization of chlorination conditions is critical since a variety of parameters affect both quantity and quality of the chlorination byproducts (see discussion on formation of organic halogens). These parameters are particularly useful since they provide a direct measure of the water's suitability for treatment with chlorine based oxidants.

Humic substances content of a water source may be operationally characterized as hydrophobic or hydrophilic utilizing adsorption chromatography on XAD-8 resins (Thurman and Malcolm, 1981) coupled with a surrogate measure of the fractionated organic carbon. Giabbai et al. (1987) have evaluated a similar integrated adsorption method utilizing XAD-8, AG MP-50, and carbopack B columns to provide a finer resolution of solubilities; a method not limited to humic materials.
Dissolved organic material may further fractionated into apparent molecular weight distributions by gel permeation chromatography (GPC) or ultrafiltration (UF). Both methods give comparable trends in molecular weight distribution; however, GPC generally indicates higher molecular weights and is more sensitive to pH than UF (Amy et al., 1985). Bruchet et al. (1985) utilized GPC to characterize TOC, UV absorbance, and TOX molecular weight distributions to determine effects of chlorination, sand filtration and GAC filtration. Source related effects on precursor removal, utilizing surrogates, were examined by Collins et al. (1986). Their results indicated that molecular weight distribution in addition to carboxylic acidity and humics substances content may affect removal by commonly employed treatment processes.

The distribution of oxygen containing functional groups of humic materials can be determined using wet chemical methods and potentiometric titrations (Schnitzer and Khan, 1972). The value of these measurements, with respect to halogen forming potentials is unclear; McCreary and Snoeyink (1980) found no correlation between functional group analysis and THMFP. Collins et al. (1986) note, that for humic substances, carboxyl content is inversely related to molecular weight and that this may have implications for treatment by coagulation.

U.O. Removal of TOX and TOX Precursors

Reductions in levels of THM's (and TOX) in drinking and wastewaters may be effected by changing points of chlorination in the treatment process, changing type of disinfectants, or employing modifications or additions to the treatment process (Culp, 1984).

Reductions in levels of THM's (and TOX) have been observed using alternative disinfectant's such as ozone, chlorine dioxide, and monochloramines (Cooper et al., 1985; Chow and Roberts, 1981). However, the efficacy of the use of alternative disinfectants remains in question, primarily due to incomplete knowledge of their health effects (Wolfe et al., 1984).

Other methods of THM/TOX reduction may focus on removal of organic precursors prior to disinfection or on removal of chlorinated products after disinfection. The removal of organics and THM/TOX organic precursors in water may be accomplished by a variety of chemical and physicochemical processes. Physical processes include solvent extraction, centrifugation, foam flotation, air stripping, distillation, reverse osmosis, ultrafiltration, adsorption, electrokinetic processes, filtration, and coagulation and flocculation. Chemical processes include chemical oxidation, electrolytic oxidation, chemical precipitation, radiation, and ion exchange (Koenig, 1987). The role of biochemical processes in removal of dissolved organics is well documented and recently microbes have been associated with organic removal in physicochemical processes such as fixed bed carbon adsorption (see review by Faust and Aly, 1987).

The current discussion focuses upon reduction in levels of TOX (includes THM's) in water by 1) use of chloramines as a disinfectant; 2) removal/reduction of chlorinated disinfection products by dechlorination; 3) precursor and TOX removal by adsorptive processes; and 4) advanced oxidation processes.

Use of Chloramines as a Disinfectant

As a result of the National Organics Reconnaissance Survey (NORS) the Environmental Protection Agency (EPA) amended the National Interim Primary Drinking Water Regulations (43 Fed. Reg 5755) (specifying a maximum contaminant level (MCL) of 0.1 mg/l of THM's in drinking water) to suggest that chloramines be used as a secondary disinfectant to maintain a chlorine residual in water already meeting primary standards. EPA has allowed, since 1983, the use of chloramines with the requirement of maintaining a free chlorine residual for ten minutes prior to the addition of ammonia.

Chloramines are formed upon addition of free chlorine to ammoniated water. Typical levels of free ammonia in untreated domestic wastewaters range from 10 to 50 mg/l. With respect to disinfection of reclaimed wastewaters, the presence of ammonia may be advantageous to limit TOX/THM formation upon disinfection. Excess ammonia could be removed after chlorination. Conventional methods for ammonia removal include biological nitrification-denitrification, breakpoint chlorination, ion exchange, and air stripping (Metcalf and Eddy, 1979).

Much controversy exists about the disinfecting capabilities of chloramines. From the work by Butterfield and Wattie, and later by Kabler it was concluded that for the same conditions, contact time, temperature, and pH range of 6-8 that it will take at least 25 times more combined chlorine that free available chlorine for the same disinfectant ability (see White G.C., 1986). However, the work conducted between 1980-1982 at the San Jose/Santa Clara Water Pollution Control Plant shows that monochloramine residuals can achieve coliform kills equivalent to free chlorine of

the same concentration and contact time (50 min) (see White G.C., 1986). The city of Denver, Colorado has been successfully disinfecting with chloramines for nearly 70 years; although this has been partially attributed to high quality raw water and a well maintained distribution system (Dice, 1985).

Hack (1985) presented the results of AWWA's Disinfection Committee's survey of the practice of chloramination in the United States and territories. Results of the survey indicated that 46% of the respondents did not use chloramines in their water supply. Of these, only Hawaii and West Virginia indicated that chloramination would be used as a result of the THM regulation. Other states reported between 1 and 50% of their states population was served by water supplies disinfected by chloramines. Recently, the Metropolitan Water District (MWD), one of the nations largest water utilities, has changed to the use of chloramines in it's disinfection process. Metropolitan determined this to be the most effective and economical method of after bench scale studies using reducing THM's preoxidation methods and plant scale coagulation/flocculation/sedimentation failed to produce significant reductions of precursors. Other disinfectants were dismissed due to economic and health effect considerations (Kreft et al., 1985). Metropolitan is currently operating its plants at a 3:1 chlorine to ammonia weight ratio. The current procedure involves prechlorination of influent to approximately a 1.5 mg/l residual prior to filtration to insure disinfection. Ammonia is subsequently added to the process stream in a region of turbulence to obtain the 3:1 weight ratio. The pH is subsequently adjusted to a Langelier Saturation Index (LI) of 0.1 with caustic soda before distribution. The 3:1 ratio allows for variability in chlorine demand and the excess ammonia allows for subsequent chlorination by sister agencies (Barrett et al., 1985 and Davis, personal communication, 1987). To prevent the formation of

dichloramine and trichloramine, which leave an unpleasant taste or the possibility of over chlorinating to breakpoint (and loss of residual) MWD has developed a computational model to provide sister agencies information for desirable blends of chlorinated and chloraminated waters (Barrett et al., 1985).

Monochloramine/Organic Precursor Chemistry. Jensen et al. (1985) has characterized the reaction between monochloramine and isolated aquatic fulvic acid. Three types of experiments were preformed: demand on chloramine by fulvic material was determined by oxidant loss studies; second, attempts were made to identify products of the reaction; and finally monochloramine produced TOX and its characteristics were investigated. Characterization of the organic halide was determined by column chromatographic techniques using XAD-8 resins and TOX and GC analysis. Oxidant loss studies indicated that the ultimate demand of fulvic acid was the same for chlorine and monochloramine. They also note that monochloramine decomposition is significant at higher monochloramine concentrations.

Their work indicated that no compounds, from the reaction of monochloramine and fulvic acid at pH 9, were detected in ether extracts using GC-FID techniques. Other researchers using similar techniques were able to detect up to one hundred compounds from the chlorination of fulvic acid. They interpreted these results to indicate that monochloramine is relatively unreactive to these type of compounds. Characterization studies indicated that overall quantities of TOX produced by monochloramine were significantly lower than that produced by chlorine. Batch extraction of the chloraminated solution showed that 20% or less of the monochloramine produced TOX was ether extractable as compared with 43% from

chlorinated solutions. Finally, a larger portion of the monochloramine produced TOX appeared in the first eluant peaks from the XAD-8 columns. Results indicated that monochloramine produced TOX is more hydrophilic and of higher molecular weight than that produced from samples treated with free chlorine.

Fam (1987) chlorinated ammoniated XAD-8 extractable organics from San Diego aquaculture sewage effluent at pH's 3, 7, and 11. Ammonia doses were 14, 35 and 70 mg to represent different portions of the breakpoint curve. At low pH the dominant species is dichloramine and at higher pH the dominant species is monochloramine. Non-volatile chlorinated organics, NVCO (a portion of NPOX), were determined as total ECD area (GC analysis). Results indicated that total ECD area decreased with increasing concentrations of ammonia and was lowest at high pH and high (>3) ammonia to chlorine ratios. Overall, NVCO levels were reduced by 32-62%.

Fleishacker and Randtke (1983) conducted a comprehensive study of the formation of purgable and nonpurgable organic chlorine as a function of the type and concentration of precursor material, the type and dosage of chlorine, pH, temperature, and ammonia concentration. This work will be reviewed here only as it pertains to chloramination. Results indicated that increasing dosages of monochloramine (and chlorine) increased concentrations of both NPOX and CHCl₃ but sometimes reached a plateau. Combined chlorine produced much less TOX than free chlorine and more that 75% of the TOX was nonvolatile and was detected as NPOX. Results of precursor studies indicated that higher chlorine concentrations result in more oxidation rather than substitution products. The effect of pH on TOX formation was found to exert a profound effect. For both chlorine and

combined chlorine increasing pH resulted a sharp decrease in NPOX formation (CHCl₃ increased with pH for chlorinated samples). The authors hypothesize that monochloramine may convert to more reactive dichloramine at low pH or partially hydrolyze to HOCl which is also influenced by pH. The effect of temperature was indicated with NPOX formation decreasing with temperature.

The use of combined chlorine as a disinfectant for reclaimed water is attractive to limit TOX formation. However, this advantage will have to be carefully weighed against it's limited disinfectant ability (subject to debate), and the possible difficulties associated with storage of chloraminated effluents in surface reservoirs (ammonia levels can cause algal blooms and monochloramine is highly toxic to fish).

Removal of TOX by Dechlorination

Dechlorination of effluents released to the environment is necessary to reduce toxicity of chlorine residuals (Stone et al., 1973). Recent evidence suggests that sulfites, used for dechlorination, may also react directly with chlorinated organics produced during disinfection to reduce mutagenicity (Cheh et al., 1979; Cheh et al., 1980).

Wilcox and Horth (1984) conducted microbial assays on concentrated extracts of various surface waters subjected to both chlorination and to industrial pollution. The mutagenicity test system selected was a modification of the Ames test in which bacteria are exposed to a test substance in the liquid phase rather than an agar overlay. Water assays against Salmonella typhimurium TA98 and TA100 were conducted to detect frameshift and basepair substitution mutagens respectively.

Water samples were concentrated by two methods: freeze-drying followed by methanol extraction and XAD adsorption followed by solvent elution. Overall, a positive correlation between TA100 activity and water chlorination was found and an association between TA 98 activity and reuse. Mutagenic fractions were fractionated by reverse and normal phase HPLC and further assayed to simplify isolation and identification of compounds of biological significance.

Samples from a water treatment facility, taken both from a chlorine contact chamber and final effluent stream, that had been partially dechlorinated with sulfur dioxide (0.5 mg/l residual), were processed and assayed for mutagenic activity in parallel. The result confirmed that dechlorination attenuated, but did not eliminate mutagenic activity. Furthermore, water that had been completely dechlorinated proved slightly less mutagenic than the partially dechlorinated sample.

Reactions of Sulfites with Chlorinated Organics. The chemistry of dehalogenations has been well documented in the organic chemistry literature. Reaction categories include 1,2-dehalogenations, substitutions, and eliminations (Baciocchi, 1983; Norris, 1983). Dehalogenations can also be promoted by electrochemical means, heating, and radiation. The range of reactivity and reported mechanisms is enormous and mostly reported for solvents other than water; Although, a few generalizations can be made. The tendency for (organic) halogens to be attacked by ionic or radical reductants is I > Br > Cl > F; identical to the leaving group abilities of halogens in nucleophilic displacements (Bacciocchi, 1983; Streitwieser, 1962). Important nucleophiles, potentially present in water, include organic and inorganic selenides, organometallic compounds, halide ions, sulfur and phosphorous nucleophiles, cyanide ions, amines, and hydroxide ions (Bacciocchi, 1983).

Schroeter (1966) compiled an excellent review of literature concerning reactions of aqueous sulfur dioxide. A brief synopsis of his work summarizing some reactions of sulfites with organics will be given here. Sulfites react, under a wide variety of conditions, with many classes of organics: carbonyl compounds, alkenes, alkynes, aromatic nitro compounds, alcohols and phenols, disulfides, esters, diazo compounds, amines, sulfur containing organics, Grignard reagents, and organic halides. Any reaction of sulfites and halogenated organic molecules, whether directly with the carbon halogen bonds or with other functional groups, may have significant implications with respect to chemical behavior, analysis, and toxicity.

Nucleophilic attack the of carbonyl group of aldehydes and methyl and cyclic ketones by aqueous sulfites or bisulfites yields hydroxy sulfonic acids. Sulfonic acids are also produced by the reaction of bisulfite with olefins (unsaturated compounds). Kinetic studies of aqueous reactions of bisulfite at 25°C with nitrile and acrylate compounds indicated that reactions were second-order and increased with pH, suggesting that sulfite ion was the reactive species.

The reaction of aromatic nitro compounds with sulfite results in the formation of sulfamino and sulfonic acids. These reactions were used in the production of azo dye intermediates, described by Piria in the mid 19th century.

Sulfites react with a variety of halogenated organics including alkanes, carboxylic acids and esters, di and trihalomethanes, and aryl and alkyl halides. Kinetic studies of the reaction of aqueous bisulfite and halo substituted acetic acids at 25°C

indicated that second-order rate constants increased significantly with size of the halogen substituent (Cl, Br, I).

Sulfite has been reported to react with brominated dihaloacetonitriles (Trehy and Bieber, 1981). Stanbro and Lenkevich (1982) demonstrated that several organic chloramines are not instantaneously reduced by aqueous sulfite ion, as had been previously assumed, and may require several hours to dechlorinate. N-terminal amino groups and alkyl amines that readily react with hypochlorous acid or hypochlorite at concentrations expected to be found in effluents (10^{-5} M) dechlorinate slowly according to the reaction:

$$RNHCl + HSO_{2}^{-} + H_{2}O - RNH_{2} + SO_{4}^{2-} + Cl^{-} + 2H^{+}$$
(23)

(R is an organic substituent).

The authors determined decay of the organic chloramines using the fluorescamine fluorometric methods and reported second-order rate constants for several representative organic chloramines. Rate of appearance of reduced amine was shown to be successfully described by the equation:

$$d[Amine]/dt = k[SO_3^{2-}][Chloramine]$$
(24)

The second-order rate constant varied linearly with pH, with maximum approaching pH 6 and a minimum near pH 10, and was attributed to the difference in the reaction rate of HSO_3^{-1} and SO_3^{-2-1} . In contrast to chloramine, organic bromoamines were found to react completely with sulfite within 15 seconds. The authors

concluded that under some circumstances organic chloramine residuals could be quite long-lived (on the order of hours) in the presence of sulfite.

It is important to note that several of the classes of persistent halogenated compounds, in particular those reviewed by Schroeter (1966), that are reactive with sulfites have been identified as byproducts of the reaction of chlorine with aqueous humic substances or of chlorinated water : halomethanes (Rook, 1974; Bellar et al., 1974), haloacetic acids (Quimby et al., 1980; Miller and Uden, 1983), chloral hydrate (Miller and Uden, 1983), and alkylene and aryl halides (Coleman et al., 1984).

Fam and Stenstrom (1988) demonstrated that certain non-volatile gas chromatographable chlorinated organics produced during the chlorination of reclaimed wastewater were attenuated or eliminated from solution by the addition of sulfite prior to solvent extraction and gas chromatographic analysis. However, the fraction of total organic halogen (from the chlorination of water and humic acid preparations) amenable to direct analysis by gas chromatography may range from 0.1% (McCreary and Snoeyink, 1980 and 1981) to 50% (Glaze et al., 1979). Thus these initial observations only apply to a portion of chlorination byproducts. However, their work has important implications for the art of the detection and analysis of chlorinated organics produced during disinfection.

Removal of TOX Precursors by Carbon Adsorption

Granular activated carbon (GAC) has been shown to be effective in removing both THM/TOX precursors and undesirable synthetic organic contaminants. Despite the many existing technologies that exist for control of organic substances in water GAC

has been considered the best available broad spectrum control technology currently available. Costs for GAC treatment (of drinking water) have been estimated at \$7 to \$26 per family per year in affected systems. In the EPA's judgement, this is a nominal price to pay for minimizing human exposure to hazardous substances (Cotruvo and Wu, 1980).

Batch Adsorption. Adsorption is classified as either physical or chemical. Physical adsorption results when weak attractive Van der Waals forces between solute and adsorbent are stronger than forces between solute and solvent. Chemical adsorption involves a chemical reaction between solute and adsorbent and is often irreversible. Adsorption of solutes onto activated carbon is a physical process (Reynolds, 1982).

At equilibrium there is a specific distribution of adsorbable solutes between the solid and liquid phases. The adsorption isotherm is a mathematical model describing the amount of solute adsorbed on the solid to the solution concentration at equilibrium at a given temperature (Weber and Van Vliet, 1980). Common isotherms include Langmuir, Freundlich, Linear (Henry's Law), and BET. The Langmuir isotherm is derived from rational considerations and is given:

$$q_e = Q_{max} b[C_e] / (1 + b[C_e])$$
 (25)

and the Freundlich isotherm:

 $q_e = k[C_e]^{1/n}$ (26)

with values at equilibrium:

q_e = mass solute/mass sorbate

 C_{e} = solute concentration

 Q_{max} , b, k, n = experimentally determined parameters

Methods of construction, properties, and linearized and multicomponent forms of the various isotherms can be found elsewhere.

In general, the adsorption isotherm gives an indication of how effectively carbon will adsorb the impurities in question, and if purification requirements can be obtained. It also provides an estimate of the quantity carbon required for a given treatment objective. Various factors influence adsorption of solutes and therefore the observed isotherms: molecular structure, solubility, degree of ionization (pH), temperature, competitive effects in mixtures (multisolute adsorption), and properties of the activated carbon (Ford, 1981).

Dynamic Adsorption. Adsorption of solutes is a time dependent process and knowledge of rate of solute uptake is critical to the design carbon adsorbers. The adsorption of aqueous organics onto porous carbon can be described by three consecutive mass transfer steps (Smith, 1968; Weber, 1972). External or film diffusion transports adsorbates from bulk solution to the surface of the particle.

Internal diffusion and pore surface diffusion carries the particle into interior sites where the final adsorptive step occurs. The rate limiting step, controlled by the slowest step, is attributed either to film or pore diffusion.

Rates are usually determined by change in concentration of solution in contact with carbon (batch) over time. A linear relationship is sometimes observed between q_e (mass sorbate/mass sorbent) and $t^{1/2}$ for the initial adsorption period. Adsorption rates (units of mg/g/hr^{1/2}) is determined from the slope of the line; these are not true rates but rather relative for comparative use. The rate limiting step can be determined from 1) concentration dependence of the adsorption rate 2) relationship between adsorption rate and particulate size of sorbent 3) activation energy as determined from rate constants at different temperatures and Arrhenius's law (Faust and Aly, 1987).

Mass Transfer Zone. As contaminated water passes through a fixed carbon bed a sorption zone or wavefront develops as solute is transferred from the aqueous to solid phase. Within this mass transfer zone (MTZ) and for substances exhibiting favorable isotherms, the concentration of the solute changes from the initial level on the inlet side to undetectable levels on the leading edge. Breakthrough is observed as the leading edge of the MTZ reaches the end of the bed (Wagner and Jula, 1981).

The length of the MTZ can be the determinant factor in the design of a adsorption system. The length and rate of progress of the MTZ can determine the design

parameters: 1) the size of the adsorption system and media contained; 2) the exhaustion rate of carbon for given flowrate and treatment objective (Waller, 1975).

Design. Carbon contactors can be designed from empirical isotherm and pilot plant data. Isotherm data establishes feasibility of the use of GAC provides preliminary estimates of mass of sorbent required. Pilot plant studies (effectively conducted using serial columns) yield breakthrough curves. The dynamic capacity of the columns can be determined from breakthrough curves from the area between column influent and effluent at breakthrough divided by the weight of carbon in the column. Subsequent scale-up is based upon use of one of two major design approaches: 1)Empty Bed Contact Time (EBCT); and 2) Bed Depth Service Time (BDST) (Faust and Aly, 1987).

The EBCT is a simple method which provides for maximal use of the carbon. The EBCT is the hydraulic retention time of process stream based upon the total adsorber, "empty bed", volume. The carbon usage per column is determined from weight of carbon divided by volume of effluent at breakthrough. A plot of carbon usage rate (calculated from serial carbon columns) vs. EBCT reveal a rapidly decreasing function which reaches an asymptote at an EBCT corresponding to an minimal carbon usage rate (Bilello and DeJohn, 1981).

Mass Transfer Models for Dynamic Systems. Mathematical models derived from fundamental principles allow for forecasting the process dynamics for a given wastestream and adsorption system. The use of numeric solution methods further eliminates restrictions imposed by expressions simplified to facilitate analytic solution.

Early models that describe chromatographic separations have been utilized to describe adsorption. One model employs a one dimensional generalized mass balance on solute partitioning between liquid and solid phases within an adsorption column. Dispersion is neglected and local equilibrium assumed between solute in both phases. The unsteady state mass balance can be expressed to give the effective velocity of a particular solute moving down the column (DiGiano and Weber, 1964):

$$V_{eff} = dz/dt |_{C} = V_{0} / [\phi + (1-\phi) f'(C)]$$
(27)

and assuming an Langmuirian isotherm, a mass balance on the adsorption front yields:

$$dz/dt|_{front} = V_0 / \left[\phi + (1-\phi) C_{ad} / C_0 \right]$$
(28)

Where:

$$V_{eff}$$
 = effective velocity of component C
 V_o = flow velocity
 ϕ = bed porosity
f = equilibrium isotherm
 C_{ad} = equilibrium solid phase concentration
 C_o = inlet concentration

This equation allows the calculation of breakthrough from inlet flow rate, bed geometry, and equilibrium data.

Later adsorption models invoked mass transfer principles commonly applied in chemical engineering. An early model developed by Keinath and Weber (1968) was quite successful in describing GAC laboratory data. Crittenden and Weber (1978) have developed a dynamic mass transfer model (MADAM) based upon numerical solution techniques that accommodates parameters such as dispersion, mixing, multisolute interactions, and biological growth. The model assumes surface diffusion the be major intraparticulate transfer mechanism. The solid and liquid phase continuity equations are solved using the Crank-Nicholson and Implicit Backward finite difference analogs, respectively. MADAM has been used successfully to predict breakthrough profiles for phenol, dodecyl benzene sulfonate (DBS), and mixtures of these substances (Crittenden and Weber, 1978). Successful predictions using MADAM were also obtained for organics in bioactive columns (Ying and Weber, 1978).

Use of these models requires determination of isotherm and mass transport coefficients (generally from correlations available in chemical engineering literature and batch studies)(Faust and Aly, 1987). Liu and Weber subsequently (1981) described a minicolumn method by which the mass transfer coefficients, k_f (external film mass transfer coefficient) and D_s (internal surface diffusion coefficient), can be simultaneously and accurately determined from the initial portion of the column breakthrough curve.

Influent Characterization. Chemical characterization of the process stream is critical to the design of an effective carbon adsorption system. There are several important parameters affecting adsorption (see section on Batch Adsorption). For a given process, TOC can be an essential parameter as it directly measures organic content of the influent including refractory or toxic components (Petura, 1981). THMFP and TOXFP can also be used as they provide an alternative measure of dissolved organics.

Other important characteristics of the waste stream include pH, dissolved and suspended solids, oil and grease, and heavy metals. The pH of the water affects ionization (and therefore adsorbability) of acidic and basic dissolved organics and solubility of inorganics. Excessive levels of suspended solids may result in excessive pressure drops across the column or may result in the development of anaerobic condition within the column; sulfates, when present, can become converted to hydrogen sulfide gases. Metallics such as mercury or lead can poison columns making regeneration unfeasible. Finally, miscible oils can coat carbon particles resulting in premature column exhaustion (Petura, 1981).

Removal of THM and TOX Precursors by Carbon Adsorption. Previous studies of adsorption of humic materials (as precursors to halogenated organics) onto activated carbon have indicated that humic source(s), inorganic and organic solution composition, carbon particle and pore size distribution, pH, and operational parameters are important factors.

McCreary and Snoeyink (1980) characterized activated carbon adsorption of humic substances from several sources by functional group analysis, molecular sizefractionation, and haloform forming potential. The extent of adsorption of humics was inversely related to the carboxyl content of the substance. Increased adsorption of low molecular weight humic and fulvic was attributed to more surface area available for the molecules. Adsorption of soil fulvic acids increased at low pH's and with increases in inorganic phosphate levels.

Pore size distribution was shown to be an important parameter relative to carbon's capacity for adsorbing humic substances by Lee, Snoeyink, and Crittenden (1981). They determined, from equilibrium and rate studies coupled with computer models, that adsorption capacity and rate of uptake was inversely related to molecular weight and that increasing pore volumes positively correlated with adsorption of increasing molecular weight fractions of humic substances. Wilson (1960), working with preoxidized fulvic acids, suggested that pore exclusion was a limiting factor in observed decreases in adsorption.

Carbon particle diameter also affects uptake of humic substances. Weber et al. (1978) reported that rates of uptake were inversely related to carbon particle size.

In general, a decrease in pH increases adsorption of humic substances (McCreary and Snoeyink, 1980; Weber, et al., 1978; Black and Christman, 1963; Schnitzer and Kodama, 1966). Black and Christman (1963) found that increasing the pH of a colored water decreased the size of organic colloids and increased the number of particles present. As ionized functional groups are neutralized at low pH particles

may aggregate in absence of interparticulate charge repulsion and/or an increase in hydrophobicity.

Dissolved metallic salts have been shown to significantly influence the carbon adsorbability of humic substances. Randtke and Jepsen (1982) found that calcium, magnesium, and sodium salts enhanced the adsorption of fulvic acids, while inorganic anions have no observable effect. Effectiveness of cations was in the order $Ca^{2+} > Mg^{2+} > Na^+$. Sensitivity to salts was greatest at high pH and low salt concentrations (<1.0 mM). Column studies indicated that while calcium greatly improved adsorption, withdrawal of calcium from a heavily loaded column resulted in partial desorption of fulvic acids. Explanations for these observations include charge reduction of negative sites or possible complexation with divalent cations.

Pretreatment of THM (TOX) precursors can have a profound effect on subsequent treatment by carbon. Commonly employed unit operations in drinking water treatment include settling, coagulation/flocculation, mono or multimedia filtration, sedimentation, and chemical oxidation with chlorine, ozone, or permanganate. Generally, municipal waters are pretreated with metal salts for turbidity removal or lime for softening; both followed by sedimentation or filtration. These processes generally remove soluble organic contaminants.

The fate of fulvic acids during various pretreatments prior to carbon adsorption was examined by van Breemen et. al (1979). Coagulation preferentially removed the fulvic acid fraction with high carboxylic group content, was highly pH dependent, and resulted in substantial TOC removals. Bench scale experiments indicated only an approximate 5% removal of TOC was achieved after coagulation and preoxidation.

Lee et al. (1981) demonstrated that alum coagulation prior to adsorption increased both rate and terminal capacity of carbon. Faust and Aly (1987) have summarized results from several pretreatment schemes successful at improving subsequent carbon adsorption: 1) UV absorbing organics from preozonated Rhine River bank filtrate was removed by coagulation with ferric chloride and alum. Use of alum, in lieu of ferric chloride, resulted in better carbon adsorption; 2) other studies using organics in raw water indicated that ozonation and alum used together prior to carbon adsorption resulted in superior removals.

Randtke and Jepsen (1981) observed significant increases in the adsorptive capacity of activated carbon following coagulation; except when little TOC removal was associated with the process. The authors suggested several possible explanations for the phenomenon: 1) organo-aluminum complexes form during coagulation which are more adsorbable and 2) hydrophilic functional groups are neutralized lowering hemimicelle formation and/or the reduction of electrostatic repulsion between the carbon surface and solute functional groups.

Glaze and Wallace (1984) compared THMFP removal by GAC treatment and ozone-GAC treatment at a pilot facility in Cross Lake, La. Physical adsorption was prevalent during the early stages of adsorber operation and declined during the study period. Microbiological growth was later observed on the carbon filter and accounted for removal of roughly 1.0 mmol THMFP/m³ GAC-hr during optimal periods. Preozonation before GAC adsorption did not have a significant effect on

removal of THM precursors; however, careful analysis indicated that ozone treated organics were slightly less adsorbable and more biodegradable. The authors suggest this phenomena makes ozonation a promising pretreatment process for biologically activated carbon adsorption.

Much of the pilot and full scale plant data concerning removal of humics or THMFP substances is highly variable. Generally, a lower influent concentration and a longer EBCT result in increased carbon bed lifetimes. GAC used in filter beds, as a sand replacement, has been shown to be effective in removing THM precursors at Little Falls, New Jersey since 1981 (Culp, 1984). Symons, et al. (1981) present data describing precursor (THMFP) removal from bench-, pilot-, and full scale treatment facilities throughout the U.S. Approximate initial THMFP removals range from 10 to 98% with times to steady state ranging from 2 to 24 weeks. THMFP removals at steady state were lower; ranging from 0 to 73%.

Ozone and Advanced Oxidation Processes (AOP's). The use of oxidation processes to remove organic material and trace level contaminants in drinking and wastewaters is receiving increased attention. In water and wastewater treatment oxidation processes potentially provide the combined benefits of contaminant mineralization, conversion of recalcitrant materials to more biodegradable substrates, and concurrent destruction of viral, bacterial, and protozoal organisms.

Ozone is used widely in drinking water treatment practices in Europe. Its earliest use was in Oudshoorn, Netherlands, in 1983, to treat filtered Rhine River water.

Today well over one thousand treatment facilities throughout the world utilize ozone (Reynolds, 1982).

Ozone, an allotrope of oxygen, is a powerful oxidant and has a half-life of 20 - 30 minutes in distilled water at $20 \,^{\circ}C$ (Reynolds, 1982). It is 10-20 times more soluble in water than oxygen. Ozone can be generated, in quantities necessary for water treatment, by high frequency or voltage corona discharges through oxygen or oxygen containing gases. Ozone is often generated at 1-2% in air to 2-4% in pure oxygen (Rice, 1985).

Oxidation reactions initiated by ozone, in water, are complex and involve decomposition that is catalyzed by hydroxyl ions and other solutes. Highly reactive products, such as the hydroxyl radical (OH), are formed which can in turn accelerate the decomposition of ozone or react with other dissolved substances (Hoigne and Bader, 1976; Stumm, 1954; Taube and Bray, 1940; Staehelin and Hoigne, 1981; Taube, 1941). The hydroxyl radical(OH), an extremely powerful oxidant, has recently been found to be an effective agent for the mineralization of a variety of synthetic and naturally occurring organic substances (Wallace et al., 1988; Aieta et al., 1988; Glaze and Kang, 1988; Brunet et al., 1985; Duguet et al., 1985; Nakayama et al., 1979). Processes utilizing hydroxyl radical(OH) as the principle oxidant are referred to as advanced oxidation processes (AOP's). The relative oxidation power of ozone and the hydroxyl radical in reference to other species is given in Table 5.

Oxi Species	dation Potential (Volts)	Relative Oxidation Power [*]
Fluorine	3.06	2.25
Hydroxyl radical	2.80	2.05
Atomic oxygen	2.42	1.78
Ozone	2.07	1.52
Hydrogen peroxide	1.77	1.30
Perhydroxyl radical	1.70	1.25
Hypochlorous acid	1.49	1.10
Chlorine	1.36	1.00

Table 5. Relative oxidation power of ozone and other species (After Rice, 1985).

* Chlorine = 1, as reference

Formation of the hydroxyl radical may be effected by the use of 1) ozone at high pH, 2) ozone and UV irradiation; 3) ozone and hydrogen peroxide; and 4) ozone, hydrogen peroxide, and UV. The ozone hydrogen peroxide (O_3/H_2O_2) method of hydrogen generation may be the easiest method to implement at a full scale level (Brunet et al., 1984). Ozone in combination with hydrogen peroxide was shown to increase greatly the concentration of hydroxy radicals formed during ozonation (Staehelein and Hoigne, 1982) giving an approximate stoichiometry:

$$2O_3 + H_2O_2 -> 2(OH) + 3O_2$$
 (29)

Although complex, the reaction of ozone and hydroxyl radicals with an organic contaminant(s) may be represented:

$$C_0 + O_3 -> C_{oxid} + C_{oxid} + \dots$$
 (30)

$$C_0 + OH -> C_{orid} + C_{orid} + \dots$$
 (31)

where C_0 is the substrate and C_{oxid} , and C_{oxid} , are the oxidation products.

The corresponding rate expression for decay of the organic(s) is:

$$-d(\ln C)/dt = K_0 [O_3] + K_1[OH]$$
(32)

where K_0 is the rate constant for the oxidation of C_0 by ozone and K_1 the rate constant for oxidation by hydroxyl radical. If excess ozone and peroxide is supplied throughout the reaction, and assumed to result in constant ozone and hydroxyl radical concentrations, the right hand of the expression can be given as a pseudo first-order rate constant:

$$K_{ps} = K_0 [O_3]_{average} + K_1 [OH]_{average}$$
(33)

In an completely mixed batch reactor, sparged with ozone containing gas, the flux of ozone is given by film theory (Roustan and Mallevialle, 1982):

$$N_{O3} = K_1 [C_1 - C_1]$$
(34)

where:

 $N_{O3} = \text{flux of ozone; (mass)/[(time)(area)]}$ $K_1 = \text{film mass transfer coefficient; (length/time)}$ $C_L^* = \text{equilibrium concentration of ozone with feed gas}$ $C_L = \text{liquid concentration of ozone}$

In a gas-liquid transfer system, the interfacial area is difficult to assess and mass transfer can be expressed:

$$dC/dt = K_{l}a \left[C_{L}^{*} - C_{L}\right]$$
(35)

where:

K_ia = observed mass transfer coefficient (1/time)
V = reactor volume (length ³)
a = area/volume

When ozone reacts with substances in solution the mass transfer rate expression becomes (Glaze and Kang, 1988):

$$dC/dt = K_{1}a [C_{L}^{*} - C_{L}] - \{ K_{j1} [O_{3}] [S_{j1}] - K_{j2} [O_{3}] [S_{j2}] - \dots \}$$
(36)

where:

 K_{jn} = rate constants for species that consume ozone S_{in} = substrates that consume ozone. The reaction of ozone with hydroperoxide anion HO_2^- , derived from hydrogen peroxide $[H_2O_2 -> HO_2^- + H^+]$, is extremely rapid with a rate constant of $(5.5 \pm 1.0) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ (Hoigne et al., 1984 (III)). Hydroxyl radicals, subsequently formed through a series of complex reactions, are scavenged by many natural water components particularly carbonate species and dissolved organic material. Evidently, due to ozone consumption in ozone peroxide systems, mass transfer is highly efficient. Aieta et al. (1988) have reported transfer efficiencies, in O_3/H_2O_2 systems, as high as 96 to 100 % in completely mixed reactors with G values of 165 s⁻¹ (max.).

Removal of NVTOC and organohalogens by AOP's. A substantial amount of literature exists concerning the effect of ozonation on synthetic and naturally occurring materials. The hydroxyl radical is produced, particularly at higher pH's, during a normal ozonation process and is likely responsible for many of the observed oxidized products. The review of literature here, however, will focus on recent studies involving the use of the O_3/H_2O_2 method to generate hydroxyl radicals as the principle oxidant.

Ozonation of natural water containing carbon often result in the production of lower molecular weight products, with little loss of NVTOC. Many of the oxidation products are carbonyl and peroxidic compounds and which are resistant to further oxidation by ozone (Laplance and Martin, 1982; Brunet et al., 1984). The use of H_2O_2/O_3 , to foster hydroxyl radical production, may provide a mechanism to fully mineralize dissolved organic material. Brunet et al. (1984) conducting studies concerning the mineralization of aromatic and aliphatic compounds in water, using the H_2O_2/O_3 process, found that the oxidation reactions were pH dependent. The concentration of hydroperoxide ion, which reacts with ozone to form hydroxyl radicals, increases with pH. However, at pH values around 10 and a $O_3:H_2O_2$ ratio of 1.0 that hydroxyl radicals were quenched by excess peroxide according to the scheme:

$$OH + H_2O_2 -> H_2O + HO_2$$
 (37)

$$OH + HO_{2} -> O_{2} + H_{2}O$$
 (38)

The authors concluded that optimal pH and $O_3:H_2O_2$ ratios should be determined to maximize substrate mineralization.

Duguet et al. (1985) observed a substantial increase, over ozone alone, in both reaction and ozone mass transfer rates during the O_3/H_2O_2 oxidation of glycine. Treatment of natural waters by the O_3/H_2O_2 process resulted in substantial removal of UV absorbing substances, trihalomethane precursors, and adsorbability on activated alumina. Treatment with both O_3 and O_3/H_2O_2 resulted increases in assimilable organic carbon with the O_3/H_2O_2 process giving slightly higher values.

Nakayama et al., 1979 used the O_3/H_2O_2 process to treat COD in effluents from an industrial electrodeposition process. Reaction rates were observed to be dependent on pH, $O_3:H_2O_2$ ratios, and initial NVTOC levels. The catalytic ozonation process reduced the COD in the effluent for 70 mg/l to 10 mg/l with a dosing of 200 mg/l O_3 and 45 mg/l H_2O_2 . The authors estimated operating costs to be about half the cost required for carbon regeneration for the same degree of treatment.

Wallace et al. (1988) treated Shreveport, LA lake water with both ozone and O_3/H_2O_2 at applied ozone dosages of 20, 25 and 30 mg/l. No significant reduction was observed in THMFP by ozone alone. However, addition of 20 mg/l of hydrogen peroxide (or 0.67 W/L UV radiation @ 254 nm) resulting in 60% reductions of THMFP in 60 minutes. Between 10 and 50 minutes of contact increases over initial in THMFP levels were observed for ozone, O_3/H_2O_2 and other treatments. Ozone mass transfer was increased 5 fold by the addition H_2O_2 .

Glaze and Kang (1988) examined the effectiveness of the O_3/H_2O_2 process at removing TCE and PCE from distilled and natural groundwaters in the laboratory. At $H_2O_2:O_3$ dosage ratios of >0.7 (w/w) the process appeared to be mass transfer limited. Mineralization of the organohalogen substrates, in distilled water, was verified by the increase in chloride ions as determined by ion chromatography. Although the rate constants for the reaction of hydroxyl radicals with organohalogens is greater than the constants for hydroxyl radicals and bicarbonate species, it was shown that the large relative molarity of latter resulted in quenching of hydroxyl radicals. The authors estimate that in natural groundwaters, with high alkalinity values (300 mg/l as CaCO₃), that TCE and PCE (at ppb concentrations) were oxidized by no more that a few percent of the available hydroxyl radicals. Encouraged by Glaze and Kang's laboratory studies Aieta et al. (1988) conducted pilot scale studies on the removal of TCE and PCE from the high alkalinity well water. The authors determined that dosage ratio of $H_2O_2:O_3$ (w/w) of 0.5 was optimum. They note the stoichiometric dose of 0.35 (w/w). They suggest that the optimum dosage is likely dependent on both reactor configuration and water quality. Finally, a cost evaluation of the H_2O_2/O_3 process indicated that it is very competitive with more conventional technologies such as GAC adsorption and air stripping.

MATERIALS AND METHODS

San Diego Treatment Facility (Aqua II)

The existing Aqua II facility treats wastewater of primarily domestic origin with limited industrial flow from small businesses. Primary treatment is effected with course screening and suspended solids removal by a rotary disk filter (RDF). The secondary treatment system is water hyacinth-based and treats approximately 1.0 mgd. Advanced treatment consists of coagulation/flocculation/sand filtration followed by ultraviolet (UV) disinfection, reverse osmosis (RO), air stripping, and activated carbon adsorption (GAC). See Figure 1.

Water hyacinths, *Eichhornia crassipes*, are free floating aquatic plants that provide an extensive root system that serves as a mechanical filter and support structure for bacteria. Water hyacinth systems are capable of removing high levels of BOD, SS, metals, nitrogen, and significant removal of refractory organics. Removal of phosphorus can range up to 50 to 70% of loading, and is primarily due to uptake by plants (U.S.E.P.A., 1979). Each hyacinth pond, constructed with earthen berms, clay, and plastic lining, is designed to treat 300,000 gpd in a step feed mode. Ponds are supplied with a small aeration system to supply oxygen to fish, *Gambusia* spp.(provided for mosquito control), and to prevent anoxic conditions due to high sulfate levels in the influent (Tchobanoglous et al., 1987).



Figure 1. Aqua II treatment facility schematic.

The existing advanced treatment facility is designed to treat 50,000 gpd of secondary effluent and began operation in July, 1987. Coagulation/flocculation/filtration is effected in a package unit with a ferric chloride as a coagulant (dosages 10-50 mg/l). The water is then UV disinfected, stored, acidified to pH 5-7 with H_2SO_4 , and treated in a reverse osmosis system with polyamide thin film composite membranes in a spiral wound construction (Fluid Systems, Inc.). RO permeate is then air stripped and carbon filtered. The activated carbon is 12X40 sieve with an average particulate diameter of 1.1 mm and specific gravity of 1.35 (Ceca, Inc.). Process design specifies a bed loading of 0.9 gal/ft²-min. Breakthrough of contaminants or dissolved carbon is not monitored and GAC replacement is based upon pressure drop only (Chadwick, personal communication, 1987).

Data provided by the City of San Diego for February, 1988 indicate that, with respect to the RDF effluent, approximately 95% of BOD, 85% of COD, and 75% of the NVTOC are removed in the secondary treatment process. Addition of the advanced treatment process results in removal of roughly 97% of total solids, 95% of COD, and a 97% removal of NVTOC. The resultant effluent is of high clarity and quality. See Figures 2, 3, 4, and 5.





TOC (mg/l)











Analytical and Sampling Methods

General. Samples to be used for analyses of sulfite reactivity with TOX, upon return to the laboratory, were dosed with additional chlorine (from calcium hypochlorite stocks) to a final residual between 1 and 2 mg/l (if no residual was detected in the raw sample) to simulate conventional water treatment protocol and to prevent bacterial contamination. Samples for other analyses were untreated and stored, if required, at 5°C. Raw sewage, primary and secondary effluents were vacuum filtered in a glass and ceramic device. Both glass fiber filters and apparatus were washed in acid dichromate and rinsed with reagent water prior to use. Reagent water for blanks and standards consisted of commercially available distilled water or laboratory industrial water treated by carbon adsorption, reverse osmosis, ion exchange, and filtration. This water was filtered through a second activated carbon bed and stored in glass prior to use. All chemicals and solvents used were reagent or GC-capillary grade.

Quality Assurance and Control. Quality assurance/control (QC/QA) techniques and statistical quality control (SQC) measures ensure reliability and validity of analytical data gathered in the laboratory and field.

There are several important components to the implementation of a successful QC/QA program: 1) Effort must be taken to ensure proper collection, preservation, transportation, and storage of samples 2) Laboratory analyses must be conducted according to recognized methods 3) Accuracy and precision of analytical data must verified in a systematic fashion.

QC/QA measures for field samples consists of using purified sample bottles (by washing with acidic dichromate and purified water) and travel blanks for each analytical procedure. Travel blanks consist of bottles filled with ultrapure water (and appropriate preservatives, if any) at the laboratory and are transported to the field site where they are exposed to the atmosphere and sealed air tight without entrapped air.

Laboratory analytical procedures are conducted according to manufacturers, Standard Methods (APHA), or Environmental Protection Agency (E.P.A.) protocol (see Material and Methods section). Laboratory blanks and standards are included for each set of analyses.

The precision and accuracy of the collected data (SQC) is verified through the use of quality control charts. The control chart method for variables is a means of visualizing the variations that occur in the central tendency and dispersion of a set of observations. It is a graphical record of the quality of a particular characteristic (Besterfield, 1986). The fundamentals of statistical control are contained in two types of control charts: The X and R charts. The X chart is used to monitor the accuracy of analytical results, while the R chart is used to verify that observed dispersion of sample replicates is within the range to be expected for the method in question (Berger and Hart, 1986). Deviation from limit control ranges on either chart indicates that the system is out of control (due to instrument malfunction, sample contamination, or analyst error) and that the sample data is suspect.
Control charts are easily constructed and maintained using a computer based spreadsheet (Cheresmisnoff, 1988). The central lines and control limits for the X and R charts are defined as follows:

Central lines:

$X = X_{average}$	((39)
$R = R_{average}$	((40)

Control limits:

$$X_{upper}: UCL_{x} = X_{average} + 3 s_{x}$$
(41)

$$X_{\text{lower}}: LCL_{x} = X_{\text{average}} - 3 s_{x}$$
(42)

$$R_{upper}: UCL_{R} = R_{average} + 3 s_{R}$$
(43)

$$R_{lower}: LCL_{R} = R_{average} - 3 s_{R}$$
(44)

Where:

 $X_{average}$ = mean of replicate samples. $R_{average}$ = mean of replicate ranges. $S_{x,r}$ = standard dev. of the mean.

Control charts developed in this study, to date, can be found in the Appendix 3.

General Water Quality Analyses. General water quality parameters were determined according to accepted methods (Standard Methods, 1985). Colorimetric methods were used to determine ammonia nitrogen (Nesslerization)

and free and total chlorine (DPD). A Spectronic 20 Colorimeter (Bausch and Lomb) was used for these analyses. An Orion model 811 microprocessor temperature compensating pH meter was used to determine pH levels. Conductivity was measured with a YSI model 35 conductivity meter. Turbidity levels were measured with a HACH Ratio/XR turbidimeter (Loveland, CO).

TOX Analysis. TOX analyses were conducted using a Dohrmann AD-3 Adsorption Unit equipped with four dual carbon adsorption modules and a MC-3 Total Organic Halide Analyzer (Dohrmann-Xertex Corp., Santa Clara, CA). The method is described in detail elsewhere (Takahashi et al., 1981). Blanks consisted of 100ml of acidified distilled water. Reagent blanks included dechlorinating reagents and nitric acid. Calibration of the titration cell was conducted by direct injection of 5 μ l of 200 mg/l (as Cl) sodium chloride stock solution (Dohrmann-Xertex, Sunnyvale, CA) prior each set of analyses. Cell calibrations were within 5% accuracy. Replicate water samples were analyzed to verify that standard deviations were in the range associated with the method. Replicate analysis of stock trichlorophenol solutions verified system accuracy and precision (see Appendix 3.)

Purge and Trap Gas Chromatography. A Hewlett Packard 5890A gas chromatograph equipped with electron capture (ECD) and flame ionization (FID) detectors and a DB 624 (J&W scientific) capillary column ($30m \times 0.53mm$ I.D.) was used for sulfite reactivity experiments and for THM analysis. THM and other samples were diluted with reagent water to the linear range of the ECD detector. An FID detector was subsequently used , without dilution, for THM analyses at higher concentrations (> 5 µg/l). The instrument was coupled with a Tekmar LSC-

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2 Purge and Trap device (Tekmar, Cincinnati, Ohio). Conditions for the analyses were as follows: samples were purged with purified helium (40ml/min) for 11 minutes at 30°C with a subsequent desorption/bake step at 180°C for 11 minutes. The GC was automatically started by the LSC-2 Purge and Trap after desorption. For sulfite reactivity experiments the GC was programmed at 35°C for 5 minutes and 5°C/minute to 120°C for 5 minutes. For THM analyses the GC was programmed at 35°C for 4 minutes and 8°C/minute to 140°C for 1 minute. Standard curves were prepared from methanolic stocks spiked into reagent water. Quantifications were based upon linear least square equations relating sample peak area to standards (see Appendices 1 and 2). Replicate analysis of stock THM solutions verified system accuracy and precision.

TOC Analysis. TOC analyses were conducted using a Dohrmann DC-80 TOC analyzer (Dohrmann-Xertex, Sunnyvale, CA). The system is based upon persulfate oxidation of dissolved organic matter with quantification of released carbon dioxide with a non-dispersive infrared detector. Samples were acidified and purged with purified oxygen prior to analysis to remove inorganic carbon. The instrument was internally calibrated with stock solutions of aqueous organic acid. For low level analyses, (<1 mg/l), a system blank was determined, organic stocks diluted accordingly, and the system was recalibrated. Replicate analyses of stock solutions verified system accuracy and precision (see Appendix 3.)

TOX and THM Forming Potentials. TOX forming potentials (TOXFP) and THM forming potentials (THMFP) are defined as the difference between initial or

instantaneous measured TOX or THM levels (ITOX and ITHM) and terminal levels measured after chlorination under specified conditions (TTOX and TTHM).

Forming potentials were prepared by chlorinating phosphate buffered (pH 7) water samples (with calcium hypochlorite stocks) at chlorine to carbon ratios (Cl₂: NVTOC) of 3.0 on a mass basis. Additional chlorine was added stoichiometrically to samples containing ammonia to exceed breakpoint. This prevented the formation of chloramines which are known to modify the chemistry and quantity of chlorination products. Samples were then incubated in head space free BOD bottles (310 ml) at 20 \pm 0.01°C in a temperature controlled water bath (Lauda K-2/R Circulator, Brinkman, N.Y.) for seven days. Incubated samples were then dechlorinated, acidified, and analyzed for TTOX and TTHM's.

UV Absorbance. UV absorbance measurements and scans were conducted using a HP 8452A Diode Array UV/Visible Spectrophotometer coupled to a HP Vectra CS computer with supporting software. Samples were adjusted to pH neutrality. Solvent blanks were automatically subtracted by the software. Data generated from scans were transferred to spreadsheets for plotting.

Methods for Sulfite Experiments

Analysis of Pure Compounds by TOX. Solutions of pure halogenated organics, from methanolic stocks, were prepared in distilled water at concentrations of approximately 100 μ g/l as chlorine; within the linear range of the TOX analyzer. Sodium sulfite was added (resulting in > 0.3mM solutions) to one of two 300 ml aliquots at 22-25°C. Both solutions were analyzed for TOX after several minutes.

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Analysis of Pure Compounds by Gas Chromatography. Solutions of pure halogenated organics, from methanolic stocks, were prepared in distilled water at concentrations within the linear range of the ECD detector and were transferred to 100ml serum bottles (Supelco 144). Sodium sulfite (1.6mM) was added to one, Ferrous sulfate (2mM) to another, and no addition to the third bottle as a control. Bottles were capped with teflon/rubber gas tight septa to prevent loss of volatiles. Samples were stored at room temperature (18-20°C) between replicate analyses.

Kinetic Studies. The kinetics of the reaction between bromopropene and sulfite was examined at three pH's. The reaction of hexachlorobutadiene, at a single pH, was also monitored. Solutions of 3-Bromopropene, from methanolic stocks, were prepared in phosphate buffered distilled water at concentrations of 80-100 μ g/l. Sodium sulfite was added (resulting in approx. 1mM solutions). No sulfite was added to control samples. All samples were stored in headspace free 4 dram vials at room temperatures (19.5°C ± 0.5°C for bromopropene; 21°C ± 0.1°C for hexchlorobutadiene) until analysis by GC. Reactions were monitored up to 5 hours. A control sample was analyzed at the end of each experiment.

Drinking and Reclaimed Water Samples. The water sources investigated during this study are summarized as follows:

description source well #4 drinking water Santa Monica Treatment Plant Santa Monica Treatment Plant wellfield composite Metropolitan Water District Central Project Whittier Narrows Treatment Plant reclaimed wastewater U.C.L.A. Water Quality Lab industrial tap water Miramar Reservoir natural water natural water Castaic Lake

To compare dechlorinating agents aliquots (300ml) of each sample were dechlorinated in excess with either sodium sulfite (~0.1mM), sodium thiosulfate (~0.2mM), or granular ferrous sulfate (~0.9mM). Duplicates were analyzed for TOX after several minutes. To verify dechlorinating agent effectiveness aliquots of a monochloramine blank, prepared by addition of hypochlorite to a bicarbonate buffered (pH 8) ammonia solution, were dechlorinated with each chemical. TOX analyses indicated that no dechlorinating agent left a "carbon adsorbable" residual greater that 2.3 $\mu g/l$; within the error range associated with the method (see chloramine sample, Table 9). A MWD sample was adjusted to pH 8.2 with sodium hydroxide, dosed with sodium sulfite (0.14mM), capped, and allowed to react overnight (20 hrs). A control sample was dechlorinated, prior to analysis, with sodium thiosulfate (0.21mM) as a control. Replicates of both samples were analyzed for TOX. As pH appeared to be an important factor, additional samples from various sources were analyzed after dechlorination with sulfite at high and low

pH. A sample aliquot was adjusted to pH<2 with nitric acid, and another to alkaline pH with several drops of ammonium hydroxide (if necessary). Both samples were dechlorinated with sodium sulfite (0.1 mM). After a reaction period up to several hours, the alkaline sample was adjusted to pH<2 with nitric acid and replicates of both samples analyzed by TOX. To verify efficiency of dechlorination at extreme pH a (1.5 mg/l as Cl) monochloramine blank was dechlorinated with sodium sulfite at both pH 8.7 and pH 1.5. No chlorine residual was detected in either sample by DPD analyses. TOX levels differed by 0.8 μ g/l; within experimental error.

Temporal Stability. The short-term temporal effects of sulfite addition to chlorinated water samples at various pH's was examined using Whittier Narrows chlorinated effluent (Total Chlorine 0.48 mg/l,pH 6.9). Sodium sulfite (0.2mM) was added to phosphate buffered samples at pH 2, pH 6.9, and pH 10. A sample at pH 6.9 was used as a control and sulfite added only at the time of analysis. Samples were stored at $22^{\circ}C \pm 1^{\circ}C$ and acidified aliquots analyzed at 0, 4, 24, and 72 hours by TOX.

Methods for XAD-8 Fractionations

Dissolved organics, in the filtration effluent (AQUA II) and in raw water from Miramar Reservoir, were fractionated according to a modification of the procedure developed and verified by Gabbia et al. (1983; see Figure 6). TOX, NVTOC, THMFP, TOXFP, and UV absorbance data were collected for each fraction. The data is useful in determining process conditions required to maximize adsorption (i.e. optimal pH, acidity, solubilities, and relative adsorbability) of both background organics (i.e. chlorinated priority pollutants) and organic fractions producing high levels of TOX and THM's upon chlorination. Comparison of the fractionation data from Miramar Reservoir source water to the wastewater data will provide information about the sources (and possible minimization) of TOX and THM precursors that are added to the water by municipal use.

Preparation. XAD-8 resins (Rohm and Hass) were thoroughly cleaned using a method similar to that described by Thurman and Malcolm (1984). Resin was washed for several days in 0.1 N NaOH. This was followed by successive 24 hr. soxhlet extractions with methanol, acetonitrile, and methanol. Ether was not used for safety reasons. The resin was stored in methanol prior to use. Glass columns (100 ml capacity), with 300 ml reservoirs and teflon stopcocks, were used for fractionation experiments. XAD-8 was added to each column as a methanol/water slurry. Each end of the columns was plugged with glass wool. Column were then washed repeatedly with 0.1 N NaOH and 0.1N H_2SO_4 until effluent NVTOC's were below 0.5 mg/l. 500 ml aliquots of these acids and bases, eluted from each column, were taken as blanks for all subsequent analyses.

Fractionation. Four liters of each water sample were adjusted to pH 2, with H_2SO_4 , and eluted through parallel XAD-8 columns. Flow rates were approximately 5 ml/min. The eluant consisted of hydrophilic acids and bases. The adsorbed organics were eluted from the resin with 300 ml aliquots of 0.1 NaOH and consisted of hydrophobic acids. The hydrophilic acid and bases fractions were then adjusted to pH 10, with NaOH, and re-eluted through the columns. The adsorbed organics, hydrophobic bases, were eluted with 300 ml fractions of 0.1 N H_2SO_4 (see Figure 6). Each fraction was analyzed for TOX, THM's, TOXFP, THMFP, and UV

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absorbance. The methodology for each of these analyses has been described previously.



Figure 6. Fractionation acheme. After (in part) Glabble et al. 1983.

Methods for Isotherms and Rate Studies. Both Granular activated carbon (GAC) and Activated Alumina (AA) were used for equilibrium isotherm or rate studies. The GAC (Calgon, F-400) is derived from bituminous coal with a pore volume of 1.07 cm³/g and a BET surface area of 1000-1200 m²/g (Calgon, Pittsburg, PA). The AA (F-1, Alcoa), derived alumina scale of bauxite, has a pore volume of 0.4 cm³/g and a BET surface area of 250 m²/g (Alcoa, Pittsburg, PA). Both GAC and AA were prepared for isotherm and rate studies by pulverizing and sieving through 100 mesh screen to increase surface area thereby minimizing time required to reach equilibrium. Powdered carbon was successively washed in distilled reagent water and dried at 150 °C to constant weight. The pulverized AA was allowed to equilibrate, on a shaker table, in a solution of 2 mM Ca²⁺, 1.6mM Mg²⁺, and 7.2 mEq/L alkalinity for two days, filtered, and dried to constant weight at 120°C prior to use.

UV disinfected, coagulated. and sand filtered secondary effluent samples, obtained from the Aqua II treatment facility, were adjusted to several acidic, neutral, and basic pH with phosphate buffers and combined with accurately weighed portion of powdered carbon or AA in 50ml and 100ml glass bottles. For each group of samples a pH buffered sample, with no added carbon or AA, was included as a control. Samples were allowed to equilibrate, for 6-7 days, on a shaker table at room temperature (~20-25 °C). Equilibrated samples were then filtered through prewashed glass microfiber filters, with a particle retention of 0.7 μ m (Whatman GF/F,) to remove particulates and analyzed for NVTOC or TOX. Rate studies were conducted, using pH adjusted effluent samples, in a completely mixed batch reactor. Powdered activated carbon (250 mg) was wetted with 10 ml distilled reagent water overnight to saturate the pores prior to mixing with 0.9 l of filtered effluent. After mixing, sample aliquots were removed by syringe at various time intervals, filtered, and analyzed for NVTOC.

Methods for Ion Exchange Breakthrough Curves. Ion exchange column breakthrough curves of total organic carbon were generated using microcolumns. A strong base anion exchange resin (Amberlite IRA 400 OH, Rohm and Hass), in the hydroxide form, was used to remove and quantitate the fraction of NVTOC consisting of organic acids. Microcolumns were constructed of glass 5 3/4" pasteur pipettes (5.5 mm I.D.) packed with resin using cleaned glass wool as plugs. The pipette was attached to a 100 ml glass and teflon graduated buret with teflon tubing. Prior to use resin was washed with distilled reagent water until the NVTOC was at background level. Samples of filtered Aqua II effluent were adjusted to high pH with NaOH or low pH with phosphoric acid and loaded onto columns at flow rates of approximately 0.6 to 1.0 ml/min. Three to four milliliter composite effluent samples were analyzed directly for NVTOC.

Methods for Advanced Oxidation Processes. Ozonation and ozone/peroxide experiments were conducted using UV disinfected filtered secondary effluent obtained from the Aqua II treatment facility. Untreated samples were returned to the laboratory and ozonated in batch mode. The filtered effluent had a pH range of 6.6-7.0 and an alkalinity, as determined by duplicate titration, of 102.6 mg/l as $CaCO_3$. No pH adjustment done prior to ozonation of the samples.

The ozone reactor consisted of a covered and vented 20 liter glass reactor with internal baffles to prevent vortexing. Mixing was effected with a Ruston stainless steel six bladed impeller powered by a variable speed motor resulting velocity

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gradients (G) of 257 s⁻¹ and 545 s⁻¹ for 9.0 and 16.0 liter samples respectively. Ozone and carrier gas was admitted to the reactor, adjacent to the impeller, through stainless tubing and ceramic sparger. Ozone was generated from compressed ambient air, dried with silica gel, using an OREC (Phoenix, Arizona) Model O3V-10-AR corona discharge ozone generator. The flow of air through the generator was 2.0 l/min corresponding to an ozone mass flow rate of 48.16 mg/min. Ozone concentration in the feed gas was determined directly by absorbance. Ozone was sampled from a small vessel, flushed with 20-30 volumes of feed gas, with a fully evacuated 1mm Supracil quartz cuvet. Absorbance was then directly determined, at 254 nm, using a HP diode array UV spectrophotometer. A extinction coefficient of 3031.11 l cm⁻¹ mol⁻¹, calculated from ozone absorption cross sections (Molina and Molina, 1986), was used to calculate concentrations by the Beer-Lambert law. Replicate determinations yielded an average absorbance of 0.1521 ± 0.0028 corresponding to a ozone concentration of 24.08 mg/l. Hydrogen peroxide solutions, prepared from 30% reagent grade H_2O_2 and distilled water, were metered into the reactor with a calibrated feed pump.

During an experiment, the reactor was filled with 9.0 to 16.0 liters filtered effluent, and air sparged through the ozone generator and reactor. At time zero, voltage was applied to the generator and the hydrogen peroxide feed pump simultaneously started. At 5 or 10 minute intervals samples were taken for NVTOC, TOX, or UV absorbance analyses. During one 70 minute run 50 ml samples were taken at 5 or 10 minute intervals, stored for several day to remove O_3 residuals, and mixed with accurately weighed portions of powdered (100 mesh) F-400 (Calgon Corp.) carbon. After two days of mixing at room temperature, samples were filtered and measured for NVTOC to determine the adsorbability of the dissolved carbon. At the end of certain runs samples were taken for TOXFP analyses. The total volume removed by sampling during a run generally represented 2-3% of the initial volume. Total hydrogen peroxide addition accounted for between 0.5 and 2.2% of the total volume for 9 liter (40 min) runs and 5% of the total volume for 16 liter (70 min) runs.

Ozone concentrations were not measured in the reactor offgas, precluding an exact ozone mass balance. However, the extensive results of Aieta et al. (1988) indicate that extremely high ozone transfer efficiencies are obtained in well mixed peroxide dosed reactors. Therefore a relatively high ozone transfer efficiency was expected in these experiments. The applied ozonation condition employed in this study are summarized in Table 6.

Volume _(liters)	Duration (min.)	<u>mg</u> Applied O ₃	mg NVTOC Applied H	^{H₂O₂/O₃ I<u>2O2 (w/w)</u>}	
16.0	70	29.5	29.5	1.0:1.0	
16.0	- 70	34.8	34.8	1.0:1.0	
9.0	40	28.2	0	0.0:1.0	
9.0	40	31.7	10.9	0.343:1.0	
9.0	40	32.1	22.0	0.685:1.0	
9.0	40	32.5	32.5	1.0:1.0	
9.0	40	35.2	49.2	1.4:1.0	

Table 6. Applied ozone and hydrogen peroxide dosages.

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RESULTS

Sulfite Experiments

Pure Compounds. Pure halogenated compounds were combined with sodium sulfite to determine potential reactivity. Nine of the eleven pure chlorinated compounds surveyed showed some degree of reactivity with aqueous sulfite (Table 7). Groups were compared using an analysis of variance or one tailed students t-test. Statistically significant differences between sulfite treated samples and controls (no pretreatment and ferrous sulfate) were detected in bromopropene (89% decrease; alpha=0.005), chlorobenzene (4.5% decrease; alpha=0.01), and bromobenzene (\sim 3% decrease; alpha=0.01). It must be stressed that some of these reactions are time and pH dependent (see section on kinetics) and the data here are presented only to demonstrate reactivity at room temperature and short durations commonly encountered during chemical analyses.

Table 7. Effect of dechlorinating agents on pure compounds.

COMPOUND	DECHLOR.	N¥	AVERAGE <u>TOX</u> *		METHOD OF ANALYSIS	
Hexachloro-					-tt-	
butadiene:	none	2	118.72	±	0.82**	TOX
	sulfite	2	99.35	±	3.61	
Dichloro-						
acetic acid:	none	2	88.20	±	0.85	TOX
	sulfite	2	87.55	±	1.63	
o-chloro-					,	
phenol:	none	2	104.75	±	0.49	TOX
_	sulfite	2	106.63	±	0.48	
2-chloro-						
napthalene:	none	2	130.35	±	1.77	TOX
· _	sulfite	2	126.25	±	10.39	
Trichloro-						
benzene:	none	2	127.15	±	0.07	TOX
	sulfite	2	115.95	±	4.60	
Dichloro-						
benzene:	none	2	100.60	±	1.13	TOX
	sulfite	2	95.80	±	0.28	
Hexachloro-						
ethane:	none	2	84.40	±	8.06	TOX
	sulfite	2	77.45	±	0.64	
3-bromo-						
propene:	none	7	63.67	±	6.84	
	sulfite	8	6.52	±	14.13	GC/P&T
	f.sulfate	7	60.41	±	7.02	
Chloro-		_				
benzene:	none	7	335.51	±	9.30	
	sulfite	8	320.37	±	8.92	GC/P&T
	f.sulfate	7	336.39	±	12.64	
		-	56 07	ъ	2 46	
Bromobenzene:	none	/	50.27	т т	2.40	
	Sullite	8	54.00	Т Т	1.02	GC/Par
Musich leve	r.sullate	1	5/./9	Ξ	1.29	
Trichioro-	2020	٨	155 20	+	1 90	
puenor:		4	151 00	- +	1 00	TOY
	SUILICE f gulfato	ч л	152.50	÷ +	3 10	TOV
	I.SUIIdte	4	122.00	<u>-</u>	3.10	

¥ number of sample replicates
* μg/l as chlorine
** one standard deviation

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Kinetics. Fam and Stenstrom (1988) observed the reaction between aqueous sulfite and 3-bromopropene at room temperatures. They proposed a reaction involving nucleophilic attack by the sulfite ion at the halogenated carbon to produce an unsaturated sulfonic acid and bromide ion:

$$C_{3}H_{5}Br + SO_{3}^{2} - > C_{3}H_{5}SO_{3}^{-} + Br^{-}$$
 (45)

The kinetics of this reaction were investigated, in this study, at various pH's. The kinetics of hexachlorobutadiene/sulfite reaction were investigated at one pH level. If the above equation is first-order with respect to the chlorinated organic and in $[SO_3^{2}]$, the rate of disappearance of organic can be described by the equation:

$$d[C]/dt = -K[SO_3^{2^-}][C]$$
(46)

where [C] is the concentration of the brominated organic. In the presence of excess sulfite, $[SO_3^{2}]$ is assumed to be constant, and the term $K[SO_3^{2}]$ defined as a pseudo first-order rate constant K^{*}. The pseudo first-order rate constant, K^{*}, can be determined by plotting ln[C] versus time and using a linear least squares method to fit the data (Table 8).

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Table 8. Kinetic Constants for Sulfite Decay.

Compound	K*(min ⁻¹)	рH	Temperature(°C)
Bromopropene	0.11720±0.0008**	8.1	19.4
Bromopropene	0.11755±0.0005	10.0	19.2
Bromopropene	0.00106±0.0006	3.0	19.5
Hexachloro- butadiene	not significant	8.8	21.0

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One standard deviation.

At alkaline pH's the reaction between bromopropene and sulfite is rapid with a half life of 5.9 minutes. In contrast, at pH 3 the half life is increased to 10.89 hours (Figure 7). At pH 3 the sulfite ion is an insignificant portion of the total sulfur concentration (0.01%), while at pH 8.1 and pH 10.0 it comprises 92.6% and 99.9% respectively (Figure 9). The reaction of sulfite with hexachlorobutadiene, at high pH, has a half life of roughly 18 minutes (Figure 8). As an estimate of the validity this rate constant, it was used to determine the time required to obtain the reduction of hexachlorobutadiene observed in the above experiment (Table 6). The estimated time, 4.6 minutes, agrees well with the experimental protocol. The large amount of scatter associated with the plot is likely due to the small concentrations used (2.2 $\mu g/l$), dictated by the extreme sensitivity of the ECD detector to polychlorinated compounds.

Drinking and Reclaimed Water. Of the seven water sources surveyed for reactivity with sulfite, several showed significant reduction in TOX levels depending on dechlorination conditions. Sample groups were compared using a one-tailed t-test. The greatest difficulty in the design of this experiment was definition of an adequate control for TOX analysis. An ideal control would be chlorine residual free sample that contains the same level of TOX as the original chlorinated sample. Chlorine residuals must be removed prior to TOX analysis to prevent interferences due the possibility of adsorption or reaction with activated carbon used in extraction. After a survey of various dechlorinating agents, it became clear that ferrous sulfate and sodium thiosulfate were adequate dechlorinating agents and could be used as controls. However, there are difficulties with the use of these reagents. Sodium thiosulfate is an extremely good carbon nucleophile (Nickless, 1968) and could possibly react with halogenated organic substrates. Ferrous sulfate is a coagulant and can cause clogging of carbon columns during the extraction step of a TOX analysis.







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TOX levels were slightly lower in sulfite treated samples than controls (using alternate dechlorinating agents) for Santa Monica Well and Metropolitan Water District samples. Little or no reduction was observed in UCLA tap water and reclaimed effluent from Whittier Narrows Treatment Plant. A statistically significant reduction in TOX (18.4%; alpha=0.005) was observed between a sulfite treated Santa Monica MWD sample (reaction time 20 hrs, pH 8.2) at room temperature and a control (sodium thiosulfate, reaction time < 15 minutes, pH 7.9). See Table 9.

The most profound differences were observed between identical samples dechlorinated at low and high pH. TOX levels were lower in all water samples dechlorinated under basic conditions than replicates dechlorinated at pH<2. Santa Monica MWD water was reduced significantly (25.4%, alpha=0.005), as well as the brominated sample (29.1%, alpha=0.005). The largest difference was observed in the Miramar Reservoir water (37.27%, alpha=0.005). Water samples that had been dechlorinated for less than an hour differed less than 15%. Both initial TOX level and duration of reaction appear to be determining factors suggesting a rate order of decay greater than zero (Table 10).

WATER	DECHLORINATING AGENT		N AVERAGE TOX*
Chloramine	sodium sulfite	2	$0.30 \pm 0.71^+$
(1.1 mg/l Cl):	sodium thiosulfate	2	2.35 ± 0.64
(,,,,,,, _	ferrous sulfate	2	1.05 ± 0.07
UCLA tap	sodium sulfite	2	42.45 ± 0.92
(0.05 mg/l Cl):	sodium thiosulfate	2	43.00 ± 0.85
	ferrous sulfate	2	42.40 ± 0.28
S.M. MWD	sodium sulfite	2	115.90 ± 0.28
(1.48 mg/l Cl):	sodium thiosulfate	2	117.95 ± 1.06
	ferrous sulfate	2	136.70 ± 2.97
S.M. Well	sodium sulfite	2	42.03 ± 0.52
composite	sodium thiosulfate	2	44.55 ± 3.46
(2.05 mg/l Cl):	ferrous sulfate	2	51.69 ± 4.25
S.M. Well #4	sodium sulfite	2	44.10 ± 1.98
(1.64 mg/l Cl):	sodium thiosulfate	2	44.85 ± 3.46
• • •	ferrous sulfate	2	52.60 ± 3.39
Whittier Effluent	sodium sulfite	2	183.40 ± 5.80
(0.5 mg/l Cl):	sodium thiosulfate	2	192.90 ± 8.77
	ferrous sulfate	2	178.65 ± 1.91
C M MWD	sodium sulfite**	7	88 00 + 3 72
$(0 \ 92 \ max) \ (1) \ (1) \ (1)$	codium thiogulfate	7	$107 \ 90 \ + \ 3 \ 95$
(0.52 mg/r Cr)	Sourum chirosurlace	'	107.30 - 3.33

Table 9. The effect of dechlorinating agents on TOX analysis of drinking water and reclaimed water.

* $_{\mu}$ g/l as chlorine ** reaction time 20 hrs, pH 8.2 + one standard deviation The temporal dependence of the reaction of sulfite and the total organic halogen content of reclaimed wastewater, at various pH's, was explored. The reclaimed water samples, treated with sulfite, show a clear trend of decreasing TOX levels with increasing pH (Figure 10). This is in good agreement with other observations made in this study. Decrease of TOX of neutral and alkaline samples, over the 72 hour period, (-9.46%, pH 6.9, 22°C; -13.4%, pH 10.0, 22°C) did not differ substantially from the neutral control (-8.4%, pH 6.9, 22°C). The acidic dechlorinated sample showed no decline over the period (+1.7%, pH 2.0, 22°C). The results suggest that the reaction of halogenated organics with sulfurous acid species is dependent upon pH.





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WATER	Total Cl ₂ (mg/l)	<u>Condi</u> pH	tions time(min)	N	A	VEI T(RAGE DX [*]
S.M. MWD	1.5	1.5	135	2	131.50	±	2.69 ⁺
S.M. MWD	1.5	8.2	135	2	98.10	±	1.27
S.M. MWD+Br	1.5	1.5	190	3	136.40	±	4.45
S.M. MWD+Br	1.5	8.7	190	3	96.67	±	1.10
Chloramine Chloramine	1.5	1.5 8.7	- -	1 1	14.80 14.00		-
Miramar Res.	0.41	1.7	100	3	315.13	±	12.37
Miramar Res.		9	100	3	197.67	±	13.23
UCLA Tap	1.66	1.5	60	2	112.70	±	3.25
UCLA Tap	1.66	8	60	2	96.84	±	9.37
Castaic Res.	1.12	1.5	42	2	105.57	±	15.50
Castaic Res.		7.6	42	2	94.60	±	0.46

Table 10. The effect of sodium sulfite on TQX analysis at various pH's and reaction times.

* μg/l as Chlorine ** room temperature (18-22°C) one standard deviation § 78 mg/l KBr added and allowed to react overnight.

Conclusions. It has been demonstrated that significant reduction in TOX levels can result from dechlorination with sodium sulfite under basic conditions. No mechanisms or products of the reaction between organohalides and sulfites were found in this study. There remains the possibility of spontaneous decay or hydrolysis of organohalides in the absence of chlorine or chloramines. However, significant decay of pure compounds at high pH was not observed in controls and suggests that the sulfite ion is the highly reactive species toward certain organohalides.

No method currently exists for dechlorination without potentially altering sample integrity. It is suggested that samples for organohalide analysis be returned to the laboratory soon after sampling and be immediately analyzed after dechlorination at pH<2. Storage of dechlorinated samples may alter integrity.

Aqua II Water Quality and Precursor Removal Profile

General Water Quality. Data from the April, 1988 sampling of Aqua II indicate that, with respect to the RDF effluent, approximately 73% of NVTOC is removed in the secondary treatment process. Secondary treatment reduces turbidity substantially (filtered samples) while conductivity (an estimate of TDS) remains unaffected. Coagulation/flocculation/filtration substantially reduces turbidity, while conductivity is removed primarily by reverse osmosis. The advanced treatment process results in removal of 97% of the *remaining* NVTOC. The percent removal of NVTOC by each unit operation for the secondary effluent is 46% for coagulation/flocculation/filtration, 49.6% for R.O., and 1.4% for aeration and carbon adsorption. Aeration and carbon adsorption only removed 0.183 mg/l or 183 parts per billion of dissolved organic carbon (Figures 11 and 12).

TOX and THM Removal. Occasional NVTOC and TOX samplings, taken in this study, from the treatment facility and from the City of San Diego's Miramar Reservoir indicate that the Aqua II effluent compares favorably, with respect to these parameters, to the City's existing water source (see Table 11).



Figure 11. TOC and ammonium at Aqua II, April, 1988.



NTU or MMHO

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Figure 12. Turbidity and conductivity at Aqua II, April 1988.

Sample		Parame	eter	
Date	Location	ITOX($\mu g/1$)	NVTOC(mg/l)	
· · · ·				
02-14-87	Aqua II Effluent	21.1	-	
11-12-87	Miramar Reservoir	35.4	3.1	
11-12-87	Aqua II Effluent	21.4	0.4	
04-07-88	Miramar Reservoir	-	3.1	
05-23-88	Miramar Reservoir	-	3.7	
06-22-88	Aqua II Effluent	-	0.5	
06-22-88	Miramar Reservoir	-	3.2	
07-18-88	Filtered Secondary	66.6	7.5	
07-18-88	Aqua II Effluent	5.8	0.2	
07-18-88	Miramar Reservoir	38.7	3.3	
08-15-88	Aqua II Effluent	20.6	0.3	
08-15-88	Miramar Reservoir	55.8	3.2	
09-88	Aqua II Effluent	-	0.3	
09-88	Miramar Reservoir	-	3.3	
10-17-88	Aqua II Effluent	27.3	0.3	
10-17-88	Miramar Reservoir	17.7	3.5	

Table 11. Aqua II and Miramar Reservoir ITOX and NVTOC data.

Samples taken in April, 1988 indicate that instantaneous, or initial, total THM levels in the secondary effluent were below 1 μ g/l and were essentially removed by the tertiary process (Figure 13). Total organic halide levels in the primary effluent were relatively high (> 100 μ g/l). The secondary treatment process removed 32.2%,

coagulation/flocculation/filtration 22.4%, R.O. 42.8%, and aeration/carbon adsorption 1.8% of influent organic halogen. Effluent TOX levels were below $1 \mu g/l$ approaching the limit of detection for the analysis (Figures 16 and 17).



Figure 13. Instantaneous THM removal at Aqua II.

THMFP and TOXFP. THMFP and TOXFP provide both an alternative measure of TOC and a practical estimate of the suitability of a potable water source for disinfection with chlorine (or chloramines). Of the THM products from RDF, secondary, and filter effluents chloroform was dominant with lesser quantities of bromodichloromethane, dibromochloromethane, and bromoform. Bromoform constituted a larger fraction in the R.O. and carbon effluents. The secondary treatment process removed 51%, coagulation/flocculation/filtration 35.1%, R.O. 13.7%, and aeration/carbon adsorption 0.08% of THM forming potential. Effluent total THM forming potentials were (TTHMFP) below 1 μ g/l, far below the E.P.A. limit for drinking water (Figures 14 and 15).

TOXFP removal parallels that of THMFP removal with the secondary treatment process removing 54.9%, coagulation/flocculation/filtration 38.2%, and R.O. 6.59% of influent levels. No removal was observed through the aeration/carbon adsorption process. Effluent levels were extremely low at 10 μ g/l (Figures 16 and 17).

Total THM values may be converted to micromoles as Cl allowing for direct comparison to TOX levels. When ratios of TTHM and TTOX are compared to NVTOC (as μ M Cl/ μ M C) a measure of degree of halogen substitution on the dissolved organic material is given. Furthermore, TTHM/TTOX ratios give an indication ease of oxidation and/or molecular size of precursor molecules. An increase in TTHM/TTOX represents a shift in the precursor matrix to more easily oxidized and/or lower molecular weight species.

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Observations of ratios throughout the treatment scheme indicate that TTHM values contribute roughly less that 1/6 of the total organically bound halogen species in the chlorinated sample. A slight increase in both TTHM and TTOX to NVTOC ratios were observed after secondary treatment. This indicates that a larger fraction of the remaining organics are susceptible to substitution reactions with chlorine. It is interesting to note that while coagulation/filtration reduces TTOX levels an increase is observed in THM/TOX levels; possibly due to a shift in precursor molecular weight. Finally, ratios in carbon and R.O. effluents indicate that organics penetrating the treatment process are approximately 1/3 as susceptible to chlorine addition in comparison to untreated precursors (Table 12).






Figure 15. THMFP at Aqua II up to finished effluent.







Concentration (ug/l as CI)

Figure 17. ITOX and TOXFP at Aqua II up to final effluent.

Table 12. Ratio of % organohalide (as μ M Cl, from forming potentials) to NVTOC (as μ M C) at sampling stations throughout treatment scheme.

	Station Effluent					
	Raw	Pond	Filter	R.O.	Carbon	
TTHM/NVTOC	0.38%	0.63%	0.28%	0.05%	0.05%	
TTOX/NVTOC	2.71%	4.45%	1.25%	0.53%	0.85%	
TTHM/TTOX	14.04%	14.06%	22.53%	8.97%	5.27%	

Linear least square regressions and correlations of surrogate data were conducted to determine the potential of utilizing an easily measured parameter such as TOC or turbidity as a measure of terminal organohalide levels. A two tailed test was used to determine significance of the correlations (see profile samples, Table 13). Results suggest that NVTOC is a good predictor of forming potentials. Turbidity also gave good, somewhat less significant, correlations.

Table 13. Regression equations.

Regression	Equation.*	R Significant						
Aqua II Profile Samples**								
TOC vs. CHCl ₃	Y = 11.60 * [TOC]	0.989 0.01						
TOC vs. CHBrCl ₂	Y = 1.77 * [TOC]	0.005 n.s.						
TOC vs. CHBr ₂ Cl	Y = 0.288 * [TOC]	0.000 n.s.						
TOC vs.CHBr ₃	Y = 0.072 * [TOC]	0.000 n.s.						
TOC vs. TTHMFP	Y = 13.73 * [TOC]	0.97 0.01						
TOC VS.TOXFP	Y = 82.67 * [TOC]	0.98 0.01						
NTU vs. TOXFP	Y = 306.8 * [NTU]	0.92 0.05						
NTU vs. THMFP	Y = 50.36 * [NTU]	0.89 0.05						
TOXFP vs. THMFP	Y = 0.166 * [TOXFP]	0.99 0.01						
Miramar and Filter Eff. Samples ***								
UV vs. TOC	Y = 41.54 * [UV]	0.983 0.01						
UV vs. TOXFP	Y = 7858.4 * [UV]	0.977 0.01						
UV vs. THMFP	Y = 3250.2 * [UV]	0.971 0.01						
TOC vs. TOXFP	Y = 203.19 * [TOC]	0.994 0.01						
TOC vs. THMFP	Y = 83.82 * [TOC]	0.986 0.01						
TOC vs. CHCl ₃	Y = 70.78 * [TOC]	0.990 0.01						
TOC vs. CHBrCl2	Y = 1.838 * [TOC]	0.326 n.s. [¥]						
TOC vs. CHBr ₂ Cl	Y = 2.846 * [TOC]	0.724 0.05						
TOC vs. CHBr ₃	Y = 8.361 * [TOC]	0.916 0.01						
TOXFP vs. THMFP	Y = 0.415 * [TOXFP]	0.997 0.01						

* Values of TOX and THM given in μ g/l, TOC in mg/l, UV as absorbance (254 nm) and turbidity in NTU (nephelometric turbidity units).** N = 5ⁱ *** N = 10 ¥n.s. not statistically significant

XAD-8 Fractionation.

Fractionation, using XAD-8 resin, of the organic content of the Miramar reservoir water and the filtered secondary effluent at AQUA II indicate a great deal of similarity between the two sources. Fractions were analyzed for TOC, THMFP, TOX, TOXFP, and UV absorbance.

The average NVTOC content of the filtered sewage is roughly 2.3 times higher than the reservoir water which has a NVTOC averaging around 3.0 mg/l. The additional organic material, in the sewage, is derived from various polluting sources and, possibly, a portion from the secondary treatment process itself. Nevertheless, the distribution of the functional groupings, based upon solubility and adsorbability, of NVTOC levels in the two sources are nearly identical (Figure 18). Hydrophilic acids and bases account for nearly 2/3 of the total organic carbon, while hydrophobic acids account for about 1/4 of the level. Hydrophobic neutrals and bases account for the remainder of the carbon.

XAD-8 fractions and untreated samples from both Miramar reservoir and filtered Aqua II effluent were analyzed for UV absorbance at 254 nm and scans were conducted over the UV to visible range. Highly significant correlations were observed between UV absorbance (pH 7, 254 nm) and NVTOC as well as TOXFP and THMFP (see Table 11). Despite significance of these correlations, values differed from earlier relationships derived from various samples taken throughout the Aqua II treatment facility. As each unit operation significantly changes the organic matrix, it points to the importance of developing and using correlations cautiously, and only for specific water samples. Scans of the XAD-8 fractions from each sample show similar patterns. Throughout the spectrum, except for the hydrophobic base fraction of the Miramar water, higher levels of absorbance were observed for samples with higher NVTOC levels (see Figures 19 and 20).









Figure 20. UV absorbance of XAD-8 fractions of Aqua II secondary.

When the light absorption of a solution of humic substances of constant concentration is measured in the visible and ultraviolet range and the logarithm of extinction (log K) is plotted against wavelength, the resulting spectrum is almost straight line monotonously rising in the direction of shorter wavelengths (Gieseking, 1975). The spectra obtained in this study, plotted in this fashion, resulted in a family of parallel, nearly straight, lines rising toward lower wavelengths. However, this by itself is not sufficient data to classify substances as humic. The multitude of molecular constituents of humic acids which absorb in the visible and UV range, such as phenolic compounds, phenolic oxidation products, amino acids, and heterocyclic components lead to the uncharacteristic spectra of mixtures. There are no distinct differences, in absorption properties, for different types of humic substances (Gieseking, 1975). However, the high degree of absorption of XAD-8 hydrophobic fraction over the spectrum, of both the Miramar and Aqua II samples, suggest that these fraction can be characterized, at least operationally, as humic substances.

The relative THMFP and TOXFP distributions between the reservoir and sewage effluent samples is also very similar, and parallels the distribution of NVTOC. This is confirmed by the significance of the observed correlation between NVTOC vs. TOXFP and NVTOC vs. THMFP (see Table 11). For the Miramar water hydrophilic acids and bases account for 66.3%, hydrophobic acids for 26.7%, and hydrophobic bases for 7% of the THMFP. For the filtered sewage hydrophilic acids and bases account for 66.3% in the filtered sewage hydrophilic acids and bases account for 29.6% of the THMFP (Figures 21 and 22). However, total THMFP levels are much higher in the wastewater effluent. The dependence of THMFP on initial NVTOC levels, independent of the source in these samples, is demonstrated by examining the

similarity of the ratio of THM to organic carbon between the two sources. (Figure 23). Note, that the hydrophobic acids have a slightly higher THMFP to carbon ratio than the hydrophilic component.





The total TOXFP for the Miramar reservoir water was $384.4 \mu g/l$ and the filtered sewage, substantially higher, $1280.0 \mu g/l$. For the Miramar water hydrophilic acids and bases accounted for 59.2%, hydrophobic acids 36.7%, hydrophobic bases 2.3%, and hydrophobic neutrals 1.8% of the TOXFP. In the filtered sewage hydrophilic acids and bases accounted for 65.8%, hydrophobic acids 28.2%, hydrophobic bases 1.2%, and hydrophobic neutrals 4.7% of the TOXFP. Similar to the THMFP, terminal TOX levels (TOXFP) are highly dependent upon NVTOC levels (Figure 24). Note, again, like THMFP, that the hydrophobic acids have a slightly higher TOXFP to carbon ratio than the hydrophilic component.

Collins, et al. (1986), conducting studies on a variety water sources, fractionated water samples using XAD-8 resins with subsequent characterization by NVTOC and THMFP. Their results for untreated Colorado river water are very similar to results obtained here for untreated Miramar reservoir water (Colorado derived). For a sample with a NVTOC of 3.02, the hydrophilic fraction comprised 65.2% of the NVTOC, with the remainder as hydrophobic (hydrophobic base and neutral fractions not determined). Furthermore, THMFP/NVTOC ratios were $69 \mu g/mg$ for hydrophobic and 48 μ g/mg for the hydrophilic fraction or, in other words, the hydrophilic fraction has about 70 percent the potential to form THM's per mg dissolved organic carbon. In this study, for Miramar reservoir the hydrophilic fraction represented 96% of the THMFP/NVTOC and 63% of the TOXFP/NVTOC ratios of the hydrophobic fraction. The hydrophilic fraction, of the filtered Aqua II effluent, represented 85% of the THMFP/NVTOC and 82% of the TOXFP/NVTOC hydrophobic fraction ratios. Collins, et al., note the significance, and implication concerning treatability, of the contribution of non-humic substances to the THMFP of the Colorado river water. Both NVTOC levels and

THMFP/NVTOC of the hydrophilic fraction was higher that other observed sources. The data gathered in this study support their observations and demonstrate the tendency of hydrophilic, non-humic like, compounds from both natural and artificial sources to form significant concentrations of both volatile and non-volatile halogenated compounds upon chlorination.



Figure 23. THMFP (as THMFP/NVTOC) in XAD-8 fractions.



TOXFP/TOC (ug Cl/ mg C)

The distribution of instantaneous TOX (ITOX), or levels of background organohalogens in the unchlorinated water, in the various fractions again parallels NVTOC distribution with the largest fractions in the hydrophilic portions of the samples (Figure 25). The total level of ITOX in the filtered sewage effluent is only about 30% higher that the Miramar water. This indicates that a tremendous reduction in background organics has occurred and points to the efficiency of the hyacinth/filtration treatment process with respect to removal of these contaminants (see section on AQUA II water quality profile).

These results indicate that the treated effluent contains organics that fractionate similarly, with respect to solubility, acidity, and adsorbablity, to unpolluted source waters. Based upon these characteristics it is expected that removal efficiency of the organics in either source by adsorptive processes would be comparable. Levels of background halogenated organics in both sources are similar and reasonably low. Although the chemical structures of the dissolved substances remains unknown, approximately 25% of the NVTOC (hydrophobic acids), based upon XAD-8 adsorbability and UV spectra, can be operationally defined as humic substances. The most significant result, with respect to disinfection of these waters with chlorine, is the dependence of THMFP and TOXFP on total NVTOC levels - regardless of broad chemical classifications. Therefore unit operations must be designed to maximize NVTOC removal to produce an effluent with acceptable TOX and THM forming potentials. The high proportion of non-humic like hydrophilic substances in the Aqua II effluent suggests that treatment by a nonpolar adsorbant, such as activated carbon, may be difficult and therefore may require careful control of the process.



Figure 25. Background organohalogen (ITOX) distribution in XAD-8 fractions

Carbon and Activated Alumina Isotherms.

Equilibrium isotherm results for powdered F-400 carbon indicate favorable adsorption of NVTOC from Aqua II filtered secondary effluent. As previous results have indicated, NVTOC is an excellent predictor of THMFP and TOXFP for this water. Therefore carbon adsorption, by itself, provides an excellent method for reducing levels of organohalogen precursors.

Cannon et al. (1982), examining the adsorption of organic carbon from secondary effluents, observed that data can be fitted to a modified linear isotherm of the form:

$$q_e = K_L [C_e - C_n] \tag{47}$$

with equilibrium values:

 $q_e = mass absorbate/mass carbon$ $K_L = mass transfer coefficient$ $C_e = observed equilibrium DOC level$ $C_n = non-adsorbable concentration of DOC$

Isotherms, observed in this study, fit both modified linear and Freundlich isotherm models. A slightly better fit was observed for the modified linear model. Observed data were fit with least square linear regression equations and one sided test used to determine significance (Table 14).

Sample <u>pH</u>	с _л (mg/l)	K _L (1/g)	Correlation <u>Coefficient</u> S	Level of ignificance
3.22	0.496	57.34	0.990	0.005
7.08	0.682	25.68	0.998	0.005
10.25	0.946	18.53	0.987	0.005

Table 14. Modified Linear Adsorption Model Coefficients for filtered secondary effluent.

Slope of the isotherms increased with decreasing pH (Figure 26). Cannon et al. observed K_I values, for Palo Alto secondary effluent at pH 7.5-8.0 and F-400 carbon, of 11.4 \pm 2.0 (l/g) and a C_n of 0.95 mg/l. Similar values were observed in this study at alkaline pH. At lower pH a three-fold increase in the slope of the isotherm and a an almost 50% reduction of the "non-adsorbable" fraction of the TOC was observed. Chen et al. (1987), using groundwater fulvic acids with F-400 and NORIT carbons, noted an increase in adsorptive capacity with decreasing pH. The importance of pH as factor influencing adsorption isotherms is well documented (Ford, 1981); however this parameter is occasionally overlooked in design of carbon adsorption systems. In a pilot plant study, concerning carbon adsorption treatment of municipal secondary effluent, conducted by the Los Angeles County Sanitation District (Nur and Horvath, 1985), breakthrough of THM precursors was observed even after a 30 minute EBCT. However, no pH adjustment was employed prior to adsorption and influent pH's were in the range of 7-8. Additionally, a decrease in influent pH may increase the adsorption of priority pollutants and other organics. The TOX analytical method, utilizing carbon adsorption as an isolation technique for a broad range of aqueous halogenated

organics, specifies a reduction in sample pH prior to adsorption (Takahashi et al., 1981).

The non-adsorbable fraction of NVTOC observed in this study, was confirmed by larger equilibrium dosages of powdered F-400 carbon. Dosages as high as 16.61 g/l failed to reduce equilibrium NVTOC levels below C_n levels observed above. A residual NVTOC of 0.496 mg/l corresponds, via a rough estimate for this water by correlation (see Table 11), to a TOXFP of 101 μ g/l and a THMFP of 41.57 μ g/l. These, presumably highly polar compounds, would have to be removed via other methods.

Rate studies, using powdered GAC, indicate initial NVTOC removal at various pH's (Figure 27). A plot of surface concentration (q_e) vs. $t^{1/2}$ for the first 50 minutes of contact yields nearly linear relationships. Slopes provide comparative removal rates. The slope was 3.0 (mg/g/t^{1/2}) for pH 3.09 and 2.5 (mg/g/t^{1/2}) for both pH's 6.97 and 10.1. Hand et al. (1983) have developed a user-oriented method using batch reactors to obtain surface diffusion coefficients for the homogeneous surface diffusion model. Results can be used for fixed bed predictions. However, liquid diffusivity of the adsorbate D₁, requiring knowledge of molecular weight, radius, or molal volume at boiling point, is needed for an accurate estimate. These parameters are unknown for the NVTOC in the Aqua II effluent.







Figure 27. Sorption of NVTOC in Aqua II filtered secondary effluent onto GAC.

Equilibrium TOX data was modeled by Freundlich isotherm and provides for estimates of background halogenated organic removal by carbon (Figure 28). Initial TOX levels were $69.22 \mu g/l$ and required dosages were, at pH 3.0, 0.176 g/l and 2.49 g/l to reduce terminal levels to $12.8 \mu g/l$ and $3.9 \mu g/l$ respectively. TOX removal must be considered multicomponent as NVTOC levels of approximately 7 mg/l in the samples. The NVTOC is adsorbed simultaneously with the TOX. It is expected that the column mode of operation would improve TOX, as well as NVTOC, removal efficiencies. Quinn and Snoeyink (1980) used to TOX parameter to monitor removal of products from chlorinated humic substances at the laboratory scale and removal of halogenated organics from Mississippi Water at full scale. For both studies it was found that TOX buildup within the adsorbers was gradual and consistent and that a TOX profile within the adsorber can be used to determine replacement or regeneration.

Equilibrium data obtained for pulverized activated alumina (AA) indicated that it exhibited extremely poor adsorption characteristics. Virtually no reduction in equilibrium NVTOC levels were observed except for the highest dose of 3 g/l for filtered secondary effluent samples with an average NVTOC of 6.4 ± 0.32 mg/l. Comparisons of the adsorptive capacity between AA and carbon, for dosages of 3 g/l, demonstrate the marked difference (Figure 29). Chen et al. (1987), using granular AA with groundwater fulvic acid, noted non-linear isotherms with comparatively poor adsorptive characteristics. They demonstrated an improvement by ozonating samples prior to adsorption. The presence of amphoteric hydroxyl groups on the surface of AA was used to explain adsorption of anionic humates at positively charged sites at low pH. They note that pulverization increases adsorptive capacities of AA capacities up to 80% or more. The use of pulverized AA, in this study, did not, however, result in significant adsorption. The high fraction of hydrophilic NVTOC (see section on XAD-8 fractionation) in the filtered Aqua II effluent may account for the poor adsorption observed.







Figure 29. Sorption of NVTOC in filtered secondary effluent onto AA and GAC.

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Anion Exchange Resins. The use of carbon adsorption or ozone peroxide as a final treatment step to fully reclaim filtered secondary effluent at Aqua II (in lieu of the existing system of reverse osmosis, air stripping, and carbon adsorption) would require the simultaneous use of ion exchange as a unit operation to remove high levels of inorganic nutrients and metals. Inorganic contaminants of particular concern in the San Diego secondary effluent include ammonium, phosphate, heavy metals, and sulfate in high concentrations (Tchobanoglous et al., 1987).

Selective ion exchange can be an attractive alternative to reverse osmosis for removal of these substances. Two large scale facilities in the U.S.A. have already demonstrated the potential benefits of removing ammonia from municipal secondary effluents. A 240 m³/d facility at West Bari, Italy, utilizing the RIM-NUT process is expected to remove both ammonia and phosphate from secondary effluent with the production of a premium quality slow-release fertilizer as a process by-product. A detailed cost-benefit analysis of the RIM-NUT process shows that costs of treatment can be largely recovered by revenue from sales of this fertilizer (Liberti, 1982). Furthermore, ion exchange resins can also be used to remove and/or recovery organic materials from waste streams. For instance, the removal of bleach plant effluent wastes, phenol, and proteins using ion exchange has already been demonstrated on an industrial scale (Bolto and Pawlowski, 1987).

Experience has shown that variety of organic substances can prevent optimum operation of deionizers. Anion exchange resins are most susceptible and are commonly fouled by humic, fulvic, hymatomelanic, and aromatic carboxylic acids (Abrams, 1982). Use of anion exchange, to remove high levels of sulfate and other anions at Aqua II, may be potentially affected by dissolved organics. The

interaction of NVTOC with a strong anion exchange resin was examined to determine both the possibility of use of anion exchange to remove anionic organics and the potential fouling capacity of these substances.

Adsorption of NVTOC, from the Aqua II filtered secondary effluent, by a strong anion exchange resin was observed with a significant portion of the influent NVTOC retained by the columns at two pH's (\sim 70%). It was speculated that organic acids, anionic at high pH, would be retained as on the resin. Breakthrough curves were generated and breakthrough observed at approximately 10 bed volumes for both pH's (Figure 30). An overshoot of NVTOC over influent levels was observed and may be due to a mass effect by inorganic anions. The area bounded by the influent NVTOC and the column effluent curve to saturation represents the capacity of the column (mg NVTOC). For the alkaline sample, the area was integrated and found to be 0.386 mg as carbon. With the resin capacity given my the manufacturer, in meq/ml, the equivalent weight (as C) of the retained material can be determined. The result, 41.47 mg/ Eq., is obviously orders of magnitude too small even for lower molecular weight organic acids. This observation could be explained by the high TDS of the water samples, particularly the high sulfate levels, which would result in competition for cationic exchange sites on the resin.

The observation of retention of NVTOC on the resin, for acidic samples can not as easily explained. At pH 2.77, given the range of pK_a 's for commonly observed organic acids, it is expected that acids would be neutral and largely unretained by the resin. It may be possible that, as resins were in hydroxide form, that a coupled acid-base reaction between the organic acids and the hydroxide counter-ion occurred followed by chemi-adsorption of the anionic acid. However, the observed retention

of NVTOC, may also be due to non-ionic adsorption or absorption into the ionexchange material.

Although the results are inconclusive, it is clear that for filtered secondary effluent with a treatment efficiency of 10.53 Volumes H_2O/V olume resin, that anion exchange is not a feasible unit operation for organic removal. Furthermore, as the dissolved organic material interacts with the resin, it is indicated that some form NVTOC removal occur prior to ion exchange to prevent resin fouling or NVTOC overshoot.



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Advanced Oxidation Processes

Substantial oxidation of NVTOC to mineral products was effected by treatment of filtered secondary effluent (Aqua II) with ozone/hydrogen peroxide (O_3/H_2O_2) at a dosage ratio of 1:1. Pseudo first-order decay of NVTOC was observed for the initial 30 minutes of contact time and resulted in a 45.4% removal of substrate. An additional 40 minutes of contact time resulted in terminal removals of 67.7% of initial NVTOC levels (Figure 31). However, the rate of decay slowed and deviated from pseudo first-order during this period. The observed decrease may have been due to recalcitrant materials initially present in the effluent, or may be due to the formation of oxidation and cleavage products which are resistant to further oxidation by hydroxyl radicals or ozone.

It is likely that the latter speculation best describes the process. It is well documented that ozonation can result in the formation of products that are resistant to further oxidation. The reaction of ozone with organic materials can be grouped into four major categories (Bollyky, 1977): 1) the reaction of organic olefins involves the formation of a pi complex between ozone and the olefin and can result in 1,3 -dipolar cyclo addition and ozonalysis products or forms sigma complexes which lose oxygen to produce epoxides 2) the reaction of nucleophiles is rapid and results in production of oxides 3) reaction with aromatic compounds often results in ring fragmentation and formation of phenolic or acidic intermediates 4) Aliphatic alcohols, acids, and hydrocarbons react slowly but oxidation is accelerated by UV/O_3 (which produces hydroxyl radicals). Many recalcitrant halogenated organics are oxidized under these conditions.

The ozonation of natural organic substances dissolved in water results in primarily a change in molecular structure (Maier, 1982). The ozonation of phenol results in the production of hydroquinone + catechol, glyoxylic acid, glyoxal, and finally oxalic acid. The ozonation of 2-propanol results in its total decay with the subsequent production of acetone. A overall NVTOC reduction of only about 15% is seen. The UV-ozonation of acetic acid results in the formation of oxalate which is fully oxidized only after 120 minutes of contact time (Bollyky, 1977).

An approximate 35% removal of UV absorbing (254nm) materials was observed during the initial 10 minutes of O_3/H_2O_2 treatment. UV absorbance at this wavelength has been correlated with the presence of humic substances. No significant reduction in absorption, at this wavelength, was observed for the additional 60 minutes of contact time (Figure 32). Duguet et al., (1985) observed a much more dramatic removal of UV₂₅₄ absorbance when O_3/H_2O_2 treating lake water. However, the initial optical densities in the lake water were much higher than the filtered effluent. A UV/visible scan of the water after 70 minutes of treatment indicated a slight reduction in UV/violet (~250 to 425 nm) absorption (Figure 33). Bourbigot and Dore (1982) suggest that the oxidation of aromatic compounds is evidenced by a reduction in UV absorbance between 254 to 270 nm.













Samples were taken, at 5 and 10 minutes intervals, from a O_3/H_2O_2 run (34.8 mg O_3/mg NVTOC and 34.8 mg $H_2O_2/$ mg NVTOC dose) to determine carbon adsorbability of the dissolved organic material as a function of O_3/H_2O_2 contact time (Figure 34). The plot includes equilibrium NVTOC observed after adsorption (C_e observed), surface concentrations observed (X/M observed), and equilibrium concentrations that would occur for a sample of filtered effluent that had the same NVTOC as the sample in question, but had not been treated with O_3/H_2O_2 (C_e calc.). This value was calculated from a mass balance utilizing the linear isotherm developed for filtered effluent at neutral pH:

$$C_{e calc} = (C_{o} + K^{*}C_{n}^{*}V)/(K^{*}x + V)$$
(48)

where C_e calc. is the equilibrium value (7 day) that would be observed without O_3/H_2O_2 treatment at the given initial NVTOC level C_o and volume V (see section on adsorption for other parameters). Although the NVTOC declined steadily throughout the run, it can be clearly seen that carbon adsorbability of the dissolved organic material decreases with increasing O_3/H_2O_2 dose. Much lower NVTOC levels are observed after carbon treatment for the unozonated water than for O_3/H_2O_2 treated samples. Clearly, a trade-off exists between physical removal vs. oxidation of NVTOC. It should be noted however, that research has shown that ozonation improves the removal of dissolved organic material on carbon that has been biologically activated (Bourbigot and Dore, 1982).





The effect of H_2O_2 dose on ozonation of the filtered effluent was examined using five different peroxide dosages (see Table 6). The use of ozone without peroxide resulted in an overall NVTOC removal of 18.3%. The addition of peroxide at a H₂O₂:O₃ (w/w) ratio of 0.343 : 1 dramatically improved NVTOC mineralization to 65.4 %. An increase in peroxide dosage at H_2O_2/O_3 (w/w) ratios of 0.685 : 1.0, 1.0 : 1.0, and 1.4 : 1.0 reduced terminal NVTOC removals to 54.1%, 40.6%, and 34.7% respectively (Figure 35). The effect of peroxide dosage on pseudo first-order rate constants is shown in Figure 36. All regressions used to obtain rate constants were significant at the 0.005 level except for the run without peroxide. Glaze and Kang (1988), using O_3/H_2O_2 to oxidize TCE in PCE in groundwater determined that maximum oxidation rates were observed for $H_2O_2:O_3$ (w/w) ratios of 0.7 to 1.0 for TCE. Aieta et al. (1988), conducting pilot studies on removal of TCE and PCE, suggested optimum H₂O₂:O₃ ratios (w/w) of 0.5. While a given amount of peroxide can catalyze the production of hydroxyl radicals, an excess results in radical quenching (see ozone literature review). The optimum ratio, for NVTOC removal, obtained here is near the stoichiometric ratio of 0.35 (w/w) for the production of hydroxyl radicals. However, as ozone levels in off-gases were not measured in this H_2O_2/O_3 ratios have been somewhat higher. study, actual may







Figure 36. Effect of H2O2 dose on pseudo first-order rate constants (avg. O3 dose 31.94 mg/mg NVTOC).

The effect of ozonation on trihalomethane precursors, synthetic chemicals, and specified chlorinated organics and pesticides has recently received a great deal of attention. With respect to trihalomethane precursors, results are somewhat source specific, but in general a decrease is observed with increasing ozone dose (Dore, 1982). The use of O_3/H_2O_2 , as a generator of hydroxyl radicals, to remove the larger, mostly undefined portion of halogenated dissolved organic matter (TOX), as well as its effect on TOX forming potentials remain largely unexplored and provide a new arena for research.

Filtered secondary effluent samples (Aqua II) were treated with O_3/H_2O_2 at an applied dose of 34.8 mg $O_3/$ mg NVTOC and a $H_2O_2:O_3$ dose of 1.0 : 1.0 (w/w). Samples removed for TOX analyzes indicate that TOX values, while generally decreasing, fluctuate during the process (Figure 37). The increase in TOX, after an initial reduction, may be due to the presence and oxidation of bromide (and possible chloride) ions to hypohalous acids which can then react with chlorinated substances to form addition TOX. Comparing the relative redox potentials of the couples $O_3/O_2 = 2.07V$, HOCl/Cl⁻ = 1.49V, and HOBr/Br⁻ = 1.33V, to that of the redox potential of the hydroxyl radical = 2.8 V, it is apparent that ozone and hydroxyl radicals could oxidize chlorides or bromides in water.

Hoigne et al. (1985) report rate constants for the consumption of ozone by the halogens: for Cl⁻, K = 0.003 M⁻¹s⁻¹ and for Br⁻, K = 160 \pm 20 M⁻¹s⁻¹, at pH 8 and 20-23 °C. Thus, it may be the production of hypobromous acid that is responsible for the observed fluctuations in TOX. Indeed, the formation of bromoform has been observed in the ozonation of seawater (Dore, 1982).
Applied peroxide doses (40 minutes, $34.8 \text{ mg O}_3/\text{ mg NVTOC}$) markedly effect total terminal reductions in TOX levels upon ozonation (Figure 38). Ozonation alone removes only 13.9% of the initial TOX, while the addition of hydrogen peroxide at a $H_2O_2:O_3$ ratio (w/w) of 0.343 reduces TOX by 79.1%. Increases in H_2O_2 addition to a ratio of 1.40 results in consistently inferior removals of TOX.





TOX (ug/I as CI)

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Analysis of the above samples for TOX forming potentials (TOXFP) indicate that the ozone/peroxide method is highly effective in removing these substances (Figure 39). Treatment with ozone alone causes an increase of TOXFP by 21.2% and an increase in the ratio of TOXFP/NVTOC of 39.6% when compared to unozonated filtered secondary effluent. This phenomena may be due to the cleavage of larger molecules into subunits more susceptible to halogen addition and substitution reactions. Addition of peroxide to ozonation, at a H₂O₂:O₃ ratio (w/w) of 0.343, results in an 90.8% removal of TOXFP and a 72.2% reduction in the TOXFP/NVTOC ratio when compared to unozonated effluent. The overall reduction in TOXFP is likely due to oxidation of NVTOC. The marked decrease in the observed TOXFP/NVTOC ratio may be explained by the fact the remaining NVTOC may have been partially oxidized by hydroxyl radicals or ozone making it resistant to further electrophilic attack by chlorine. The ozone/peroxide treatment compares favorably, with respect to these parameters, with the Aqua II final effluent (99.3% removal of TOXFP and 80.6% reduction in TOXFP/NVTOC ratio compared to unozonated) which, after filtration, has been treated with reverse osmosis, air stripping, and carbon adsorption.





TOXFP's of ozone/peroxide treated secondary effluent (Aqua II) to effluent untreated and Aqua II final effluent.

DISCUSSION

Statement of Purpose

An increasing awareness of the potential toxicological hazards and carcinogenic risks associated with consumption of drinking water has occurred in the past decade. Trace quantities of synthetic chemicals and disinfection by-products, known to be hazardous to human health, have been detected in waters reaching the consumer. Close to 1000 organic contaminants, at nanogram to microgram concentrations, have been identified in drinking waters (Ram, 1986). However, much of dissolved organic material found in water remains unidentified and has unknown health risks.

In addition to dealing with trace contaminants in drinking water, public and private water suppliers are facing increasing water shortages, particularly in the southwestern portion of the United States. These deficits demand the development of additional water sources. Recently, the City of San Diego proposed reclamation of municipal wastewaters, with a subsequent retention in surface reservoirs, as an additional source of potable water. An advanced treatment facility (Aqua II) was constructed and is being evaluated for this purpose.

An unknown, but high level of treatment will be required if municipal wastewater effluents are to meet drinking water standards. Trace organic and metallic contaminants must be removed in addition to "conventional pollutants" such as coliforms, BOD, COD, suspended solids, color, and odor. In addition, many bacterial and viral contaminants are present which threaten public health. Therefore, disinfection is of prime importance in providing a safe product for consumption. The water resources engineer, faced with the responsibility of providing the consumer with water of high quality, must determine the most efficient and costeffective method to treat raw water sources. Adequate disinfection, prerequisite to providing a safe product, often results in compromise of chemical integrity. Aqueous chlorine has been used for many decades as a cost effective and efficient disinfectant for both drinking and waste waters. However, the use of chlorine has come under scrutiny following the discovery that chlorine reacts with naturally present organics in water (precursors) to form trihalomethanes (THM's) and other potentially hazardous chlorinated organics (TOX). It is the ability of chlorine to maintain a residual disinfecting action during water distribution, unlike many other disinfectants, that it is so difficult to find a suitable replacement exhibiting less hazardous side reactions (Morris, 1986). The continued use of aqueous chlorine as a disinfectant must be accompanied by modifications or additions to the treatment processes to minimize the formation of potentially hazardous by-products.

In the assessment of various treatment methods, the engineer must either target particular classes of contaminants or choose a given set analyses for process evaluation. The analytical difficulty, as well as high cost and labor requirements, needed to identify the plethora of organic contaminants in raw waters preclude the exact evaluation of treatment technologies to remove contaminants from complex organic mixtures (Ram, 1986). The engineer must choose analyses that identify and quantitate specific chemicals and evaluate treatments for these constituents or rely on surrogate parameters that define the potential toxicity of the much larger, complex, total organic matrix.

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Conventional surrogate parameters such as BOD, COD, and TOC have not proven extremely valuable for ascertaining the safety of drinking water. Although correlations between TOC and THMFP have been developed, these are subject to fluctuations such as changes in weather and reservoir conditions. The ideal gross surrogate parameter should require modest capital investment, be capable of rapid measurement, and be correlatable to one or more toxic responses. The TOX parameter, although not totally ideal, represents the closest approximation (Glaze, 1986).

A review of the literature concerning methods to minimize levels of and precursors to THM's and TOX indicate that a variety of treatment methods are effective: coagulation and flocculation followed by sedimentation or filtration, reverse osmosis, carbon adsorption, and the use of alternative disinfectants. Marked reductions in THM levels have also been achieved by combining the use of alternative disinfectants, such as ozone, with various physical treatment methods. However, much of the reported work to date has been conducted on natural, rather than reclaimed, water sources. Although many natural water sources have high levels of dissolved organic material (potential THM or TOX precursors), levels of pathogens are generally far below those to be encountered in reclaimed wastewater sources. The lower levels of pathogens permit the use of less powerful disinfectants.

Adequate disinfection will be critical for the treatment of reclaimed wastewater for potable use. Free chlorine remains the ideal disinfectant for this purpose. It is highly effective, easy to use, cost efficient, and maintains a residual throughout the distribution system providing protection to the consumer. To capitalize upon these benefits treatment methods must be found to minimize the hazardous halogenated by-products associated with chlorine disinfection.

The purpose of this dissertation is to fulfill this need by identifying unit operations effective in both minimizing levels of disinfection by-products (THMS's and TOX) and removal of existing organohalogens in reclaimed wastewaters treated with free chlorine.

Summary of Results

Earlier studies by Fam (1987) and Fam and Stenstrom (1987, 1988) at the selected study site (Aqua II) in San Diego, showed that 1) the use of chloramines, in lieu of free chlorine, as a disinfectant reduced levels of chlorinated by-products, and 2) that dechlorination, with sulfites, of previously disinfected effluents resulted in decreases in existing levels of non-volatile gas chromatographable chlorinated by-products. A further examination of the literature indicated that removal of organic material (precursors) prior to disinfection with chlorine is also a potentially effective method to control by-product levels in reclaimed wastewaters.

Research, in this study, using THM, TOC, and TOX parameters as a measure of contaminant levels, focused upon alternative methods to remove organohalogens and organohalogen precursors. A surrogate removal profile of the Aqua II facility determined the effectiveness of the various unit operations currently in use. Fractionation and classification of the total organic carbon and halogen content of filtered secondary effluent at Aqua II and at the City's existing water source, Miramar reservoir, provided a measure of the relationship between the dissolved organic matter and THM and TOX forming potentials as well as a comparison

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between polluted and unpolluted sources. Finally, various unit operations were evaluated for their effectiveness in removal of organohalogens and organohalogen precursors from water: review of the use of chloramines, organic dechlorination with sulfites, carbon adsorption, and advanced oxidation processes. The experiments and significant results are summarized in tabular form below. A more detailed summary follows.

Table 15. Synopsis of results.

Experiment/Purpose

Literature review of chloramine disinfectants. Ammonia already present in wastewaters forms chloramines upon reaction with chlorine.

Reaction of sulfites with pure compounds. Quantitate extent of reaction and determine susceptible functional groups.

Kinetic studies of the reaction between sulfites and pure compounds. Allows determination of rate of reaction and effect of pH.

Reaction of sulfites with drinking and reclaimed wastewaters. To estimate terminal reductions in TOX levels upon dechlorination.

Profile of organohalogen removal at the San Diego Water Reclamation Plant. To determine efficiency of background pollutant removal.

Profile of TOX/THM precursors at the San Diego Water Reclamation Plant. To determine efficiency of plant and to identify critical unit operations.

Development of surrogate correlations between easily measured parameter (UV or TOC) and TOX and THM forming potentials.

XAD-8 fractionation of dissolved organics at San Diego Miramar drinking water reservoir.

XAD-8 fractionation of dissolved organics in sand filtered secondary effluent at San Diego Water Reclamation Plant.

<u>Results</u>

Chloramines reduce levels of TOX and THM's. Questionable health effects and disinfection ability limit utility.

Bromine substituted alkene highly reactive.

Rate constants highly compound and pH dependent.

Reaction and terminal reduction levels highly source and pH dependent. Source specific results preclude dechlorination as unit operation to remove TOX.

Treatment scheme highly efficient. Terminal carbon adsorption step results in diminishing returns.

Treatment scheme highly efficient. Terminal carbon adsorption step redundant with respect to precursor removal.

Provides a rapid method of measurement of precursor concentrations. Data will be valuable for both laboratory and pilot and plant scale monitoring.

Defines physical and chemical characteristics (solubilities, TOX, TOXFP's, acidities, UV absorption spectra) of precursors in unpolluted source waters. Provides important comparison to polluted water.

Defines physical and chemical characteristics (solubilities, TOX, TOXFP's, acidities, UV absorption spectra) of precursors in treated water. Provides data important to design of effective treatment scheme. Carbon adsorption isotherm studies of coagulated sand filtered secondary effluent from San Diego.

Batch dynamic adsorption studies of coagulated sand filtered secondary effluent from San Diego.

Anion exchange studies of coagulated sand filtered secondary effluent from San Diego.

Oxidation studies using ozone and advanced oxidation processes for removal of organic halogens and precursors from coagulated sand filtered secondary effluent at San Diego. Establishes the effectiveness of carbon for multicomponent adsorption (precursors and background organohalogens). Optimal pH determined and isotherms developed for capacity estimates.

Confirmed operational parameters critical to design of adsorbers. Dynamic and equilibrium results can be used to determine economics of carbon as treatment alternative.

Demonstrated significant interaction between anion exchange resins and dissolved organic material. Implications for inorganic removal by ion exchange.

Established effectiveness of ozone/peroxide method for substantial mineralization of both precursors and background TOX in influent. Demonstrated decrease in carbon absorbability of ozone/peroxide treated effluents.

Chloramines

Literature indicates that chlorination with chloramines, in lieu of free chlorine, results in significant reductions in levels of THM's and other halogenated organics. Furthermore, the presence of significant levels ammonia nitrogen in wastewater effluents makes chloramination an attractive process for disinfection of reclaimed wastewaters. However, because of uncertainties concerning the efficacy of chloramines with respect to disinfection and health effects, no experimental work was pursued concerning disinfection with chloramines as a unit operation in reducing levels of halogenated byproducts.

Dechlorination

The reduction in concentrations of non-volatile chlorinated organics (NVCO), an unknown fraction of TOX, upon dechlorination of reclaimed water was first observed by Fam and Stenstrom (1988). The authors envisioned this as a potential unit operation to reduce concentrations of NVCO in effluents; dechlorination followed by rechlorination prior to discharge. However, while results indicated that this process results only in a partial reduction of organohalogen residuals, total dechlorination resulted in significant reductions.

The effect of sulfites on the total halogen content (TOX) of various waters and pure compounds was investigated in this study. The purpose of this work was to examine the reaction in more detail and to provide quantitative data on terminal TOX reductions. The reaction of aqueous sodium sulfite with eleven chlorinated compounds and total organic halogen (TOX) content of seven water sources was studied by Purge and Trap Gas Chromatography and by TOX analyzer. Significant reductions of bromopropene in the presence of sulfite were observed. Reaction kinetics were pseudo first-order kinetics and highly pH dependent. Slight reductions were observed for other compounds at short reaction times and room temperatures.

For natural and drinking waters, significant differences (>25%) were observed in TOX concentrations after dechlorination with sodium sulfite under acidic and basic conditions. Reactivity of sulfite ions with TOX appears to be dependent upon initial TOX concentrations, pH, and duration of reaction.

From this work it can be concluded that dechlorination with sulfites has important implication with respect to analysis of organohalogens and release of effluents to the environment. Recommendations have been made to minimize sulfite-organohalogen reactions as sulfites are used extensively in procedures for analysis of various organohalogens. With respect to release of effluents to the environment, significant reductions in TOX concentrations can be achieved with dechlorination, as has been demonstrated here, making it a favorable process. Indeed, several researchers have confirmed decreases in mutagenicity following dechlorination with sulfites (Cheh et al., 1979; Cheh et al., 1980; Wilcox and Horth, 1984).

As a unit operation for minimizing TOX concentrations in drinking and reclaimed waters for potable purposes, treatment with sulfites has several important limitations: 1) experimental evidence indicates that reductions in TOX

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concentrations never exceed 50% within time periods to be encountered in treatment processes; 2) chlorine residuals necessary for distribution cannot be maintained; and 3) a certain percentage of the population is allergic to sulfites.

Unit Operation Removal of Precursors

A profile of organic removal throughout the Aqua II facility indicated that treatment of secondary effluent by coagulation/filtration and reverse osmosis resulted in a very high quality effluent (with respect to total non-volatile organic, organohalogen, and organohalogen concentrations). The additional aeration and carbon adsorption steps effected very little additional treatment. Background organohalogen concentrations in the influent (107.8 $\mu g/l$) were essentially removed after reverse osmosis (2.6 $\mu g/l$). Aeration and carbon adsorption removed the trace residual (0.6 $\mu g/l$). Total organic carbon and organohalogen precursors (measured as THMFP and TOXFP) show a similar pattern: the final aeration and carbon adsorption step removing only 1.4%, 0.08%, and 0.0% of NVTOC, THMFP, and TOXFP of secondary effluent concentrations respectively. This observations suggest, that for these components of the dissolved organic carbon, the final aeration and carbon steps result in diminishing returns.

XAD-8 Organic Fractions.

Fractionation, using XAD-8 resin, of the organic content of the Miramar reservoir water and the filtered secondary effluent at AQUA II indicated a great deal of similarity between the two sources. Fractions were analyzed for NVTOC, THMFP, TOX, TOXFP, and UV absorbance. The average NVTOC content of the filtered

sewage is roughly 2.3 times higher than the reservoir water which has a NVTOC averaging around 3.0 mg/l. Hydrophilic acids and bases account for nearly 2/3 of the total organic carbon, while hydrophobic acids account for about 1/4 of the level. Hydrophobic neutrals and bases account for the remainder of the carbon.

Highly significant correlations were observed between UV absorbance (pH 7, 254 nm) and NVTOC as well as TOXFP and THMFP for all fractions. Significant absorption at 254 nm and adsorbability under acid conditions, of XAD-8 hydrophobic fractions of both the Miramar and Aqua II samples, suggest that these fractions be characterized operationally as humic.

The relative THMFP and TOXFP distributions between the reservoir and sewage effluent samples paralleled the distribution of NVTOC. However, total THMFP and TOXFP concentrations are much higher in the wastewater effluent. The dependence of THMFP and TOXFP on initial NVTOC concentrations, somewhat independent of the fraction in these samples, was demonstrated by the similarity of the ratio of THMFP and TOXFP to organic carbon between the two sources. The distribution of concentrations of background organohalogens paralleled NVTOC distribution with the largest fractions in the hydrophilic portions of the samples.

Carbon Adsorption

A review of the literature indicated that carbon adsorption is an effective method to reduce THM (and presumably TOX) precursors. Data from Culp et al. (1980) indicate that a use of carbon in lieu of reverse osmosis may substantially reduce costs. They present data concerning costs and efficiencies associated with various levels of treatment of secondary municipal effluents. Treatment trains were organized into 13 levels, with each level generally increasing in complexity. Level 11 treatment consists of reverse osmosis following biological physical-chemical treatment and is similar to the process at Aqua II. Level 9 consists of carbon adsorption of lime and ion exchange treated effluent. Both processes produce high quality effluent. Average process train performance data indicate that the level 9 process is capable of producing effluents with extremely low dissolved carbon concentrations (NVTOC = 0, BOD = 0, COD = 8 mg/l) and metal concentrations below drinking water MCL's (except for mercury and silver). However, cost and total energy consumption differences between the two processes is significant (see Table 16).

	Plant Capacity (mgd)		
Treatment Process	1	<u>10</u>	<u>50</u>
Level 9: (Carbon Adsorption Based)			
Total Energy: Electrical, 1000 kwh/yr Fuel, mil Btu/yr	1,050 10,948	7,165 54,465	33,308 261,310
Total Cost: (Reverse Osmos \$1000/yr ¢/1000 gal	is Based) 870 238.3	3,725 102.1	14,069 77.1
Level 11:			
Total Energy: Electrical, 1000 kwh/yr Fuel, mil Btu/yr	4,183 27,252	35,040 68,008	167,290 329,096
Total Cost: \$1000/yr	1,328	6,926	28,640
¢/1000 gal	368.6	190.2	157.0

Table 16. Cost^{*} and Energy Consumption of Level 9 and 11 treatment processes (Modified after Culp et al., 1980).

* Cost in 1977 dollars. Capital costs amortized for 20 yrs. at 7%.

Although operating costs of reverse osmosis treatment may have been reduced by the development of thin film composite membranes, it is likely that carbon adsorption still represents a cost effective method of treatment for reclamation. Research, in this study, indicated that direct carbon treatment of filtered secondary effluent results in a high level of treatment for removal of background TOX and dissolved organic material.

Equilibrium isotherm results indicated favorable adsorption of NVTOC from Aqua II filtered secondary effluent. As previous results have indicated, NVTOC is an excellent predictor of THMFP and TOXFP for this water. Isotherms fit both modified linear and Freundlich isotherm models. A slightly better fit was observed for the modified linear model. Slope of the isotherms increased with decreasing pH. At low pH a three-fold increase in the slope of the isotherm and an almost 50% reduction of the "non-adsorbable" fraction of the TOC was observed. Rate studies, using powdered GAC, indicated NVTOC removal rates decreased with pH.

Equilibrium TOX data were modeled by the Freundlich isotherm to provide for estimates of background halogenated organic removal by carbon. Initial TOX concentrations were $69.22 \mu g/l$ and required dosages were, at pH 3.0, 0.176 g/l and 2.49 g/l to reduce terminal concentrations to $12.8 \mu g/l$ and $3.9 \mu g/l$ respectively. TOX removal must be considered multicomponent as NVTOC concentrations of approximately 7 mg/l in the samples. It is expected that the column mode of operation would improve TOX, as well as TOC, removal efficiencies.

Equilibrium studies with NVTOC in Aqua II effluent and pulverized activated alumina (AA) indicated that it exhibited extremely poor adsorption characteristics.

Advanced Oxidation Processes.

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Substantial oxidation of NVTOC to mineral products was effected by treatment of filtered secondary effluent (Aqua II) with ozone/hydrogen peroxide (O_3/H_2O_2) at a dosage ratio of 0.343:1 (w/w).

An approximate 35% removal of UV absorbing (254nm) materials was observed during the initial 10 minutes of O_3/H_2O_2 treatment at a weight ratio of 1:1. UV absorbance at this wavelength has been correlated with the presence of humic substances.

Carbon adsorbability of the dissolved organic material as a function of O_3/H_2O_2 contact time indicated that although the NVTOC declined steadily throughout the run, that carbon adsorbability of the dissolved organic material decreases with increasing O_3/H_2O_2 dose. Much lower NVTOC concentrations are observed after carbon treatment for the unozonated water than for O_3/H_2O_2 treated samples. Clearly, a trade-off exists between physical removal by carbon vs. oxidation of NVTOC.

The effect of H_2O_2 dose on ozonation of the filtered effluent was examined. The use of ozone without peroxide resulted in an overall NPTOC removal of 18.3%. The addition of peroxide at a $H_2O_2:O_3$ (w/w) ratio of 0.343 : 1 dramatically improved NVTOC mineralization to 65.4 %. Further increase in peroxide dosage (w/w) to ratios of 1.4 : 1.0 reduced terminal NVTOC removals.

Filtered secondary effluent samples (Aqua II) treated and ozone/peroxide indicated that TOX values, while generally decreasing, fluctuate during the process. The increase in TOX, after an initial reduction, may be due to the presence and

oxidation of bromide (and possible chloride) ions to hypohalous acids which can then react with chlorinated substances to form addition TOX. Ozonation alone removes only 13.9% of the initial TOX, while the addition of hydrogen peroxide at a $H_2O_2:O_3$ ratio (w/w) of 0.343 reduces TOX by 79.1%. Increases in H_2O_2 addition to a ratio of 1.40 results in consistently inferior removals of TOX.

Analysis of the above samples for TOX forming potentials (TOXFP) indicate that the ozone/peroxide method is highly effective in removing these substances. Addition of peroxide to ozonation, at a $H_2O_2:O_3$ ratio (w/w) of 0.343, results in an 90.8% removal of TOXFP and a 72.2% reduction in the TOXFP/NVTOC ratio when compared to unozonated effluent. The ozone/peroxide treatment compares favorably, with respect to these parameters, with the Aqua II final effluent.

CONCLUSION

Many organic pollutants in drinking water are halogenated and can be potential health risks. In fact, the U.S. EPA has set primary drinking water standards specifying maximum allowable contaminant levels (MCL's) for halogenated organic chemicals including chlorinated pesticides, chlorophenoxy herbicides, and trihalomethanes. Furthermore, precursors or uncharacterized dissolved organic substances in water can react with chlorine, upon disinfection, to produce concentrations (as Cl) of organohalogens comparable or greater than the organohalogen concentrations (as Cl) of the combined organics specified in the Primary Drinking Water Standards MCL's.

This dissertation examined removal of organohalogens and organohalogen precursors from drinking water and reclaimed wastewater that is being proposed as a potential water source. An existing water reclamation facility was evaluated for removal efficiency of these contaminants. Results indicated that removal was highly efficient and resulted in effluent concentrations lower than the existing drinking water source. However, the terminal aeration and carbon adsorption steps effected little additional removal of these contaminants and may provide diminishing returns.

Fractionation and classification of dissolved organic material in specific source and polluted waters indicated that *all* fractions of dissolved organic carbon can form significant concentrations of organohalogens upon chlorination. This is in contrast to the classic assumption that humic and fulvic acids are the primary precursors and indicated that design of unit operations should be directed to total organic carbon removal.

Finally, unit operations were evaluated for their effectiveness in removal of organohalogens and/or organohalogen precursors directly from filtered secondary effluent. The purpose of this research was to evaluate alternative unit operations that could replace the existing advanced treatment train at San Diego to result in a more efficient and economically viable reclamation facility.

The effectiveness of chemical reduction of halogenated organics by sulfite treatment was highly dependent upon source waters and reaction conditions. Large scale treatment would not likely result in effective contaminant removal.

Direct treatment of filtered secondary effluent by powdered activated carbon resulted in significant removal of both background organohalogens and organohalogen precursors. It is expected that the large scale column mode of treatment would result in increased efficiencies. Carbon adsorption combined with ion exchange could provide a reasonably economical substitute to the existing advanced treatment train at San Diego.

Finally, the direct treatment of filtered secondary effluent by ozone/peroxide, in appropriate stoichiometric ratios, resulted in substantial mineralization of both precursors and background organohalogens. After treatment, the remaining dissolved organic carbon is resistant to further chlorine addition upon disinfection. Furthermore, the literature indicates that ozonated organic carbon is more easily biodegraded. These observations suggest that the ozone/peroxide process may be a good alternative to the existing advanced treatment train at San Diego. Direct treatment of filtered secondary effluent would result in mineralization of organohalogen and organohalogen precursors with the simultaneous destruction of

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pathogens. Subsequent chlorination, for storage or transport, would produce few byproducts and the remaining dissolved organic material would likely be biodegraded during storage in surface reservoirs.

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APPENDICES

Appendix 1. GC-ECD Calibration for THMFP experiments.

Concentration (ppb)

Compound	0.01	0.025	0.05	0.2	0.5	1
Chloroform:			26227	50556	82369	154550
			30164	5047 8	78873	
			32149			-
average area	9:		29513	50517	80621	154550
Bromodichlo	8277	14487	22650	94873	219860	527980
methane	: 7954	14332	24158	94949	217680	
average area	a: 8115.	5 14409.5	23404	94911	218770	527980
Dibromo-	463	9 8530	15957	54216	132990	354130
dichlorometh	nane:440	5 8343	13963	53511	133220	
			14980			
average area	a: 440	5 8343	14471.5	53511	133220	354130
Bromoform:	157	4 3569	21505	28523	141410	127400
	152	1 3790	20693	30162	51101	
average area	n: 1547	.5 3679.5	5 21505	60477	9625	6 127400

Linear Regressions

Chloroform:

~

Regression Output:			
Constant	0		
Std Err of Y Est	0.10319		
R Squared	0.93936		
No. of Observations	4		
Degrees of Freedom	3		
R:	0.96920		

X Coefficient(s) 6.1062×10^{-6} Std Err of Coef.0.00000

Bromodichloromethane:

Regression Output:			
Constant	0		
Std Err of Y Est	0.03300		
R Squared	0.99220		
No. of Observations	7		
Degrees of Freedom	6		
R:	0.99609		

X Coefficient(s) 1.9556×10^{-6} Std Err of Coef.0.00000

Dibromochloromethane:

Regression Output:

Constant	0.02213
Std Err of Y Est	0.05085
R Squared	0.98457
No. of Observations	7
Degrees of Freedom	5
R:	0.99225

X Coefficient(s) 2.869 x 10 ⁻⁶ Std Err of Coef.0.00000

Bromoform:

Regression Ou	tput:
Constant	0
Std Err of Y Est	0.12261
R Squared	0.89236
No. of Observations	7
Degrees of Freedom	6
R:	0.94465

X Coefficient(s) 6.371 x 10 ⁻⁶ Std Err of Coef.0.0000

Linear Regressions

-

Chloroform:

Regression Output:	
Constant	0
Std Err of Y Est	12.753
R Squared	0.9807
No. of Observations	7
Degrees of Freedom	6

X Coefficient(s) 6.9858 x 10⁻⁴ Std Err of Coef.0.000

Bromodichloromethane:

Regression	Output:
Constant	0
Std Err of Y Est	2.855
R Squared	0.998
No. of Observations	6
Degrees of Freedom	5

X Coefficient(s)	8.1667 x 10 ⁻⁴
Std Err of Coef.	0.0000

Dibromodichloromethane:

	Regression Output:
Constant	0
Std Err of Y Est	4.295
R Squared	0.996
No. of Observati	ons 6
Degrees of Freed	om 5
X Coefficient(s)	9.3729 x 10 ⁻⁴
Std Err of Coef.	0.0000

Bromoform:

Regr	egression Output:			
Constant	0			
Std Err of Y Est	4.722			
R Squared	0.997			
No. of Observations	6			
Degrees of Freedom	5			
X Coefficient(s)	1.1260 x 10 ⁻³			
Std Err of Coef.	0.0000			

Appendix 3. Quality Control Data for TOX and TOC analyses.

WATER 1	OTAL TOX				
micr	microgram/100 ml Statistics				
	••••••				
Whittier effluent:	18.17				
(0.18 mg/l Total Cl)	16.80				
	18.35				
	17.77				
	17.73 Sample size: 8.00				
	17.48 Average: 17.93				
	18.45 S.D.: 0.61 or 3.41%				
	18.68 *95% C.I. : 0.44 or 2.45%				
UCLA tap water:	10.94 Sample size: 3.00				
	10.94 Average: 10.96				
	10.99 S.D.: 0.03 or 0.28%				
	*95% C.I.: 0.06 or 0.57%				
Trichlorophenol:	9.53 Sample size: 3.00				
(100 ppb)	8.56 Average: 9.41				
	10.13 S.D.: 0.79 or 8.40%				
	*95% C.I. : 1.63 ot 17.34%				
Trichlorophenol:	14.87				
(155 ppb)	15.14				
	15.53				
	15.50				
	15.14				
	15.26				
	15.06				
	15.28 Sample size: 12				
	15.45 Average: 15.32				
	15.59 S.D.: 0.25 or 1.61%				
	15.72 *95% C.I. : 0.13 or 0.87%				
	15.31				

*confidence interval: Tc x S.D./sqrt(N-1)

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Appendix 4. Reaction kinetics analysis of bromopropene decay in aqueous sulfite. Observed data vs. pseudo 1st order kinetics (Calculated from regressions)

		рн				
time	8.1	8.1	10	10	3	3
t	ln(C)	ln reg.	ln(C)	ln reg	ln(C)	ln reg
0.00	4.41	4.40	4.59	4.53	4.32	4.28
2.00	4.39	4.38		4.51		4.28
30.00	4.10	4.05		4.19	4.25	4.27
31.25		4.04	4.23	4.18		4.27
58.00	3.69	3.73		3.88		4.26
63.50		3.67	3.87	3.82		4.26
70.00		3.59		3.74	4.22	4.25
86.00	3.33	3.41		3.56		4.25
91.83		3.34	3.50	3.50		4.24
97.83		3.27		3.43	4.22	4.24
115.00	3.09	3.08		3.24		4.23
120.33		3.02	3.15	3.18		4.23
126.00		2.95		3.11	4.25	4.23
150.66		2.67	2.66	2.84		4.22
154.00		2.63		2.80	4.22	4.22
180.00		2.33	2.45	2.51		4.21
181.00	2.35	2.32		2.50		4.21
189.00		2.23		2.41	4.22	4.20
225.00		1.81		2.00	4.18	4.19
238.00		1.66	1.99	1.86		4.18
240.00		1.64		1.83		4.18

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Appendix 5. Reaction of pure compounds with sulfite.

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CONTROL		TIME
		(approx. hrs.)
Compound:	3 bromopropene	•
Area:	Concentration	
21946000	241.40	0
21750000	239.25	1.5
21134000	232.47	3
20217000	222.38	4.5
19140000	210.54	6
17538000	192.91	7.5
16472000	181,19	9
	AVERAGE:	217.16
	STD. DEV.:	21.59
SULFITE		11ME
Compounds		(approx. nrs.)
compound:	5 bi dilopi opene	
Area:	Concentration	
12614000	138.75	0
2753100	30.28	1.5
71160	0.78	3
224670	2.47	4.5
243750	2.68	6
97896	1.08	7.5
83246	0.92	9
87789	0.97	10.5
AVERAGE :	22.241060735	
STD. DEV.:	45.039686766	
FERROUS SULFA	ITE	TIME
		(approx. hrs.)
Compound:	3 bromoprópene	
Area:	Concentration	
21260000	233.86	0
20352000	223.87	1.5
20098000	221.07	3
19579000	215.37	4.5

198.94

176.03

173.07

18086000

16003000

15734000

181

6

9

7.5

AVERAGE:	206.0293968	
STD. DEV.:	22.176180388	

CONTROL

Compound:	3 chlorobutene	TIME	
		(approx. hrs.)	
Area:	Concentration		
225580	200.16	0	
32903	29.20	1.5	
. 0	0.00	3	
0	0.00	4.5	
0	0.00	6	
0	0.00	7.5	
0	0.00	9	
AVERAGE:	32.76490997	10.5	
STD. DEV.:	69.08		

STD. DEV.:

SULFITE

Compound:

TIME (approx. hrs.)

Area:	Concentration	
119040	105.63	0
10286	9.13	1.5
٥	0.00	3
0	0.00	4.5
0	0.00	6
0	0.00	7.5
0	0.00	9
0	0.00	10.5

3 chlorobutene

AVER/	AGE:	14.3440203165
STD.	DEV.:	34.630182085

FERROUS SULFATE

		(approx.	hrs.)
Compound:	3 chlorobutene		
Area:	Concentration		
71008	63.01	0	
0	0.00	1.5	
0	0.00	3	
0	0.00	4.5	
0	0.00	6	

182

TIME

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0	0.00	7.5
0	0.00	9
		10.5

AVERAGE:	9.0008655392
STD. DEV.:	22.047527814

CONTROL

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		TIME	
Compound:	Chlorobenzene	(approx.	hrs.)
Area:	Concentration		
64688	3 1038.54	0	
64353	1033.16	1.5	
64694	1038.64	3	
69394	1114.09	4.5	
66988	1075.47	.6	
66608	1069.37	7.5	
67385	5 1081.84	9	
	1066 6636663		

VALUNGE	•	100414430043
STD. DE	V.:	27.331157007

SULFITE

TIME (approx. hrs.)

Compound: Chlorobenzene

Area:	Concentration		
	61833	992.70	0
	62802	1008.26	1.5
	62429	1002.27	3
	64748	1039.50	4.5
	66184	1062.56	6
	60881	977.42	7.5
	64748	1039.50	9
	62845	1008.95	10.5
AVERAG	ε:	1016.39737314	
STD. D	EV.:	26.458206132	

FERROUS SULFATE

TIME	
(approx.	hrs.)

Area:	Concentration		
	62993	1011.33	0
	63860	1025.25	1.5
	65208	1046.89	3
	68739	1103.58	4.5
	67379	1081.74	6
	69607	1117.51	7.5
	67536	1084.26	9

10.5

AVERAGE:	1067.2234056	
STD. DEV.:	37.132387625	

CONTROL

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TIME

Compound:	bromobenzene	(approx.	hrs.)
Area:	Concentration		
2204600	248.19	0	
2250200	253.33	1.5	
2031900	228.75	3	
2140900	241.02	4.5	
2303800	259.36	6	
2274200	256.03	7.5	
2282100	256.92	9	

AVERAGE:	249.08713033
STD. DEV.:	10.0886517748

SULFITE

TIME

Compound: bromobenzene		(approx.	hrs.)	
Area:	Concentration			
2173700	244.72	0		
2219000	249.82	1.5		
2179000	245.31	3		
2067800	232.79	4.5		
2189700	246.52	6		
2207600	248.53	7.5		
2064300	232.40	9		
2094000	235.74	10.5		
AVERAGE:	241.97868957			
STD. DEV.:	6.6949636821			

FERROUS SULFATE

TIME

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Compound:	bromobenzene	(approx.	hrs.)
Area:	Concentration		
2200000	247.68	0	
2225300	250.52	1.5	
2261900	254.65	3	
2350600	264.63	4.5	
2270600	255.62	6	
2285700	257.32	7.5	

2312100	260.30

9

AVERAGE:255.81782398STD. DEV.:5.2876505404

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Appendix 6. GC-ECD calibration for aqueous sulfite decay experiments.

Concentrations in ppb

Compound:Chlorobenzene Regression data:

Area:	Conc.:	Constant	0.0
		Std Err of Y Est	26.169
61029.5	964.4	R Squared	0.9970
27939	482.2	No. of Observations	3
0	0	Degrees of Freedom	2

X Coefficient(s) 1.6054611298E-02 Std Err of Coef. 0.0003898819

Compound:Bromobenzene

Regression data:

Area:	Conc.:	Constant	0.0
		Std Err of Y Est	5.9918
2014350	229.6	R Squared	0.9953
1081650	114.8	No. of Observations	3
475210	57.4	Degrees of Freedom	2

X Coefficient(s) 1.1258032612E-04 Std Err of Coef. 0.0000025658

Compound:3-chloro-1-butene

Regression data:

Area:	Conc.:	Constant	0.0
		Std Err of Y Est	8.8460
293670	260.4	R Squared	0.9920
1516000	130.2	No. of Observations	3
60136	65.1	Degrees of Freedom	2

 X Coefficient(s)
 8.8730931603E-04

 Std Err of Coef.
 0.000026334

Compound:3-bromo-propene

Regression data:

Агеа:	Conc.:	Constant	0.0
		Std Err of Y Est	6.6300
22071500	241.12	R Squared	0.9948
11010500	120.56	No. of Observations	3

4642700 60.28 Degrees of Freedom 2

X Coefficient(s)	1.0999781E-05	
Std Err of Coef.	0.000002642	

Compound:hexaclorobutadiene

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Regression data:

Area:	Conc.:	Constant	0.0
		Std Err of Y Est	0.0861
626190	0.44	R Squared	0.9906
1697300	1.1	No. of Observations	3
3776300	2.2	Degrees of Freedom	2
X Coeffi	cient(s)	5.96E-07	

Appendix 7. Calibration curve for Nessler Ammonia determinations using Spectronic 20 Colorimeter at 420 nm.

Ammonium				
Chloride	Ammonium			
Conc.(mg/l)	Conc.(mg/	U)	Trans.	Absorbance
10.00		3.40	0.27	0.57
7.00		2.38	0.35	0.46
5.00		1.70	0.422	0.37
3.00		1.02	0.53	0.28
1.00		0.34	0.858	0.07
0.50		0.17	0.933	0.03

Regression Output:

Constant	0
Std Err of Y Est	0.292247
R Squared	0.945126
No. of Observations	6
Degrees of Freedom	5
X Coefficient(s)	5.269470
Std Err of Coef.	0.336793

Regression equation:

Std Err of Coef.

mg/l as NH4 = 5.27*(-log [transmittance @ 420nm])

Appendix 8. Reaction kinetics of 3 bromopropene and hexachlorobutadiene in the presence of sulfite. Data analysis.

Compound: 3-Bromopropene

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Assuming pseudo 1st order Kinetics pH=8.1

regression data

Co	С	t	ln(C/Co)	κ	ln(C)	(ln)
82.37	82.37	0	-	. ·	4.411221	4.398690
82.37	80.38	2	-0.02445	0.012227	4.386765	4.375706
82.37	60.59	30	-0.30709	0.010236	4.104129	4.053928
82.37	40	58	-0.72234	0.012454	3.688879	3.732149
82.37	28	86	-1.07901	0.012546	3.332204	3.410371
82.37	22	115	-1.32017	0.011479	3.091042	3.077100
82.37	10.51	181	-2.05889	0.011375	2.352327	2.318622

AVG.	K: 0.011720	
STD:	0.000801	6.84%

Assuming form of Y=mX + b with ln(C)=-Kt + ln(Co)

Regression Out	:put:	y intercept
Constant	4.398690	81.34431
Std Err of Y Est	0.049218	
R Squared	0.996461	
No. of Observations	7	
Degrees of Freedom	5	
R	0.998228	

X Coefficient(s) -0.01149 Std Err of Coef. 0.000306

Assuming pseudo 1st order Kinetics pH=10.0

regression data

Co	C	t	ln(C/Co	5) K	ln(C)	(ln)
98.6	98.6	0	-	-	4.591071 4.5	28516
98.6	68.86	31.25	-0.35899	0.011487	4.232075 4.1	69388
98.6	47.87	63.5	-0.72258	0.011379	3.868489 3.7	98768
98.6	33.187	91.83	-1.08891	0.011857	3.502158 3.4	73197
98.6	23.33	120.33	-1.44133	0.011978	3.149740 3.14	45673
98.6	14.327	150.66	-1.92892	0.012803	2.662145 2.7	97118
98.6	11.636	180	-2.13696	0.011872	2.454103 2.4	59940
98.6	7.348	238	-2.59664	0.010910	1.994428 1.7	93399

AVG. K: 0.011755 STD: 0.000547 4.66%

Assuming form of Y=mX + b with ln(C)=-Kt + ln(Co)

Regression Output:

Constant	4.528516 92.62106		
Std Err of Y Est	0.108658		
R Squared	0.984721		
No. of Observations	7		
Degrees of Freedom	5		

X Coefficient(s) -0.01123 Std Err of Coef. 0.000625

R:

Assuming pseudo 1st order Kinetics pH=3.0

0.992331

regression data

Co	С	t	ln(C/Co)	κ	ln(C)	(ln)
75.52	75.52	0	-	-	4.324397	4.284770
75.52	70.118	30	-0.07421	0.002473	4.250179	4.271501
75.52	68.113	70	-0.10322	0.001474	4.221168	4.253809
75.52	68.22	97.83	-0.10165	0.001039	4.222737	4.241500
75.52	70.13	126	-0.07404	0.000587	4.250350	4.229041
75.52	67.88	154	-0.10665	0.000692	4.217741	4.216656
75.52	67.7	189	-0.10931	0.000578	4.215086	4.201176
75.52	65.5	225	-0.14234	0.000632	4.182050	4.185253

AVG. K: 0.001068 STD: 0.000648 60.70%

Assuming form of Y=mX + b with ln(C)=-Kt + ln(Co)

Regression Output:

4.284770
0.026145
0.666439
8
6

X Coefficient(s) -0.00044 Std Err of Coef. 0.000127

Assuming pseudo 1st order Kinetics pH=8.8 Hexachlorobutadiene

regression data

R:

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Co	C	t	ln(C/Co)	K	ln(C)	(ln)
1.568	1.568	0	-	-	0.449800	0.448771
82.37	1.617	33.83	-3.93064	0.116188	0.480572	0.438764
82.37	1.497	75.3	-4.00775	0.053223	0.403463	0.426496
82.37	1.373	.143.5	-4.09422	0.028531	0.316998	0.406321
82.37	1.5875	183.16	-3.94906	0.021560	0.462160	0.394589
82.37	1.456	214.6	-4.03552	0.018804	0.375692	0.385289
82.37	1.4738	249.5	-4.02337	0.016125	0.387844	0.374965
82.37	1.434	294	-4.05075	0.013778	0.360467	0.361801

AVG. K: 0.038316 STD: 0.034096 88.99%

Assuming form of Y=mX + b with ln(C)=-Kt + ln(Co)

Regression Output:

Constant	0.448771		
Std Err of Y Est	0.050139		
R Squared	0.310220		
No. of Observations	8		
Degrees of Freedom	6		

X Coefficient(s) -0.00029 Std Err of Coef. 0.000180

R: 0.556974