

REMOVAL OF DISSOLVED ORGANIC MATTER FROM SURFACE WATERS/
BY COAGULATION WITH TRIVALENT IRON

by

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INTRODUCTION

Concern over potential public health risks posed by contamination of water supplies with organic chemicals has steadily risen over the past two decades. This concern is created by a continuous stream of research that produces a growing list of compounds detected and water sources tainted (e.g. Kleopfer and Fairless 1972, Cotruvo and Wu 1978, Smillie et al. 1978, Kelleher et al. 1981, Crathorne et al. 1984). At the same time, toxicological studies produce evidence that many of these contaminants have carcinogenic, mutagenic, or teratogenic properties. While it is more economical to control water pollution at point sources than to cleanse waters already contaminated, controlling emission of toxic compounds is only now becoming a major regulatory concern. Consequently, both the diversity and distribution of toxic contaminants are going to continue increasing, making the task of providing safe drinking water to the public more complex. New and costly treatment operations and analytical capabilities will have to be added at many water treatment facilities. Before opting for new treatment technologies to control organics, it is important to know what can be achieved with conventional water treatment operations.

Towards that end, the objectives of this research were to: (1) characterize organohalide precursors by size, charge, and reaction rate, (2) relate diel and seasonal

fluctuations in organic halide formation potential to changes in dissolved organic carbon (DOC) composition, (3) determine what types of organic compounds are removed by coagulation/flocculation, and (4) provide a conceptual model of DOC removal by the conventional treatment sequence of coagulation, flocculation, settling, and filtration. The approach was to characterize the DOC of raw and treated surface waters by analyzing the molecular size, charge, and solubility distributions. In addition, the distribution of organic precursors that react with chlorine to form organic halide compounds was studied, along with the rates of these reactions.

In the next section, background information on topics relevant to this project are reviewed. These topics include the nature and origin of DOM in surface waters, formation of organic halide compounds in drinking water, and previous work on DOM removal by coagulation.

LITERATURE REVIEW

DOM in Surface Waters

Organic compounds enter surface waters by direct deposition from the atmosphere, by dissolution in precipitation, by dissolution in surface and subsurface water, and by the metabolic activity of aquatic organisms. The fate of dissolved organic matter is complex. Some can be completely oxidized by microbial activity or solar radiation. Others may be modified and condensed through biological and chemical processes. A large portion becomes associated with organic and inorganic particles and is incorporated into sediments. Some eventually reaches the oceans.

The DOM pool can be partitioned into two components based on the rate of carbon cycling. The first is a labile component with high turnover rates, consisting of molecules readily utilized by microorganisms. The second, and much larger component, is refractory, consisting of molecules resistant to biological degradation. The labile component includes saccharides, peptides, nucleic acids, fatty acids, and other types of biologically active molecules. The refractory component consists primarily of complex molecules derived from plant cell wall polymers. These molecules, which have high molecular weights and are utilized by relatively few microorganisms, are referred to as humic compounds.

Humic compounds can be resolved into two categories, humic acids and fulvic acids, based on solubility differences. Humic acids are soluble under basic conditions, but precipitate under acidic conditions. Fulvic acids are soluble in both acidic and basic solutions. Generally, fulvic acids have smaller molecular weights, a higher proportion of oxygen (Blackman and Christman 1963), and a higher charge density than humic acids (Weber and Wilson 1975). Fulvic acids range in size from 200 to 20,000 daltons (Oliver and Visser 1980); humic acids can weigh up to 200,000 daltons (Gjessing and Lee 1967). In most waters examined, fulvic acids account for over 80% of the humic material present (Blackman and Christman 1963, Packham 1964).

It is difficult to generalize about the structure of humic molecules. Their properties have been investigated by size exclusion chromatography, infrared spectroscopy, nuclear magnetic resonance spectroscopy, mass spectroscopy, fluorescence, and elemental analysis (e.g. Ghassemi and Christman 1968, Hall and Lee 1974, Christman *et al.* 1981). The basic units are derived from the oxidative degradation of plant lignins. Lignin is a structural component of plant cell walls that is produced by the random condensation of *n*-propylphenolic units. These monomers usually have hydroxyl and methoxyl substitutions and can be joined together by ether, ester, or carbon linkages. During

decomposition, lignin fragments are cleaved by oxidative enzymes. Aliphatic side chains tend to be degraded, creating carbonyl and carboxylic acid groups. These modified molecules condense with one another and with many other types of molecules to form a complex and highly diverse assemblage of refractory compounds. A schematic summary of major DOM categories and their properties can be found in a review by Trussell and Umphres (1978b).

Formation of Organic Halide Compounds in Drinking Water

In 1974, the presence of chloroform and other trihalomethanes (THM) was reported in the drinking water of Rotterdam, Netherlands (Rook 1974). Bellar *et al.* (1974) found similar results in the United States. Rook established that the THM were produced by a reaction between chlorine and DOM. Two surveys conducted in the United States, the National Organics Reconnaissance Survey (Symons *et al.* 1975) and the follow-up National Organics Monitoring Survey (Cotruvo and Wu 1978) demonstrated the ubiquity of the problem. The most commonly encountered THM were chloroform, bromodichloromethane, dibromochloromethane, and bromoform. Brominated and iodinated THM are formed when chlorine oxidizes bromide and iodide ions (Bunn *et al.* 1975, Lange and Kawczynski 1978, Rook *et al.* 1978). The cleavage of THM from larger molecules is a base catalyzed hydrolysis reaction. Consequently, THM production increases with pH (Rook 1976, Stevens *et al.* 1976, Dore *et al.* 1982,

Fleischaker and Randtke 1983).

Other studies have focused on the organic precursors of THM. One allochthonous precursor source is agricultural runoff because of its humic content (Morris and Johnson 1976). Humic and fulvic acids have repeatedly been shown to produce high THM yields (Stevens *et al.* 1976, Rook 1977, Babcock and Singer 1979, Oliver and Lawrence 1979, Oliver and Vissar 1980, Christman *et al.* 1983, Kringstad *et al.* 1983, Reckhow and Singer 1984). Beside humic compounds, autochthonous precursors are generated by algal metabolism (Hoehn *et al.* 1977, 1978, 1980, Oliver and Shindler 1980, Crane *et al.* 1983, Wachter and Andelman 1984). More detailed work has shown that many types of functional groups can react with chlorine to ultimately generate THM (Arguello *et al.* 1979). The most studied precursor types are methyl ketones and dihydroxyl phenolic compounds (Rook 1976, Arguello *et al.* 1979, Dore *et al.* 1982). But virtually any organic molecule with hydroxyl or carbonyl groups is a potential THM precursor. For this reason, any category of DOM that can be isolated from surface waters will probably contain THM precursors.

The quantity of THM generated is a function of TOC concentration, chlorine dose, and reaction time (Bellar *et al.* 1974, Jolley 1975, Singer *et al.* 1976, Trussell and Umphres 1978a, Reckhow and Singer 1984). For water utilities, reaction time is defined by the distribution

system and therefore not adjustable. So methods for limiting THM production have concentrated on precursor removal and alternate disinfectants.

Precursor removal can be enhanced by several techniques. First, DOC removal by coagulation can be improved by manipulating pH, dose, and coagulant type (this topic is reviewed in a later section). Organic molecules can be sorbed onto powdered or granular activated carbon (Epton and Becnel 1981, Oulman *et al.* 1981, Randtke and Jepsen 1982, Roberts and Summers 1982, Weber *et al.* 1983, Glaze and Wallace 1984). Finally, pretreatment with ozone or chlorine dioxide can reduce THMFP by oxidizing precursors (Barnett and Trussell 1978, Trussell and Umphres 1978). The other approach is to circumvent THM formation by using alternate oxidants like ozone, chlorine dioxide, permanganate, and chloramines to replace or minimize the need for chlorination (Hubbs *et al.* 1979, Singer *et al.* 1980, Chow and Roberts 1981, Colthurst and Singer 1982). Extant THMs can be removed by carbon adsorption or aeration (McCarty *et al.* 1979). A thorough review of current strategies for THM control can be found in the AWWA publication "Treatment Techniques for Controlling Trihalomethanes in Drinking Water" (1982).

THM Regulation by the USEPA

Chloroform is a proven carcinogen in laboratory mice and rats; other THMs are also known or suspected carcinogens

or mutagens (Cotruvo and Wu 1978). These findings along with data on the ubiquity of THM occurrence in drinking water prompted the EPA in 1976 to propose limits on THM concentration in drinking water. The final regulations, promulgated in 1979, require quarterly collection of at least four samples from representative points in the distribution system (Cotruvo and Wu 1978). The four quarter running average of all such samples is not to exceed 0.10 mg/L. These regulations apply to all utilities which serve more than 10,000 persons.

Total Organic Halide Production

THM are not the only group of organic halide compounds generated by chlorination. Typically, only 20-30% of the organic halide produced by chlorination is THM (Chow and Roberts 1981, Reckhow and Singer 1984), but this ratio can vary because THM production is directly related to pH, while nonpurgeable organic halide production is inversely related (Fleischacker and Randtke 1983). Beside THM, major products include dichloroacetate, trichloroacetate, several halogenated acetones, and organic chloramines (Morris *et al.* 1980, Scully *et al.* 1984). Many of these compounds are known or suspected mutagens or carcinogens (Kringstad *et al.* 1983, Coleman *et al.* 1984). Unfortunately, these compounds are much more difficult to monitor than THM, because a gas chromatograph - mass spectrometer system is required. However, the concentration of total organic halide (TOX) is

relatively easy to estimate by sorbing DOM onto powdered carbon, pyrolyzing the carbon, and quantifying the halide ions liberated by microcoulometric titration. Currently, there are no regulations limiting TOX levels in potable water.

Many of the same precursor molecules that generate THM produce other organic halide molecules (Jolley 1975, Dore *et al.* 1982, Christman *et al.* 1983, Fleischaker and Randtke 1983, Miller and Uden 1983, Reckhow and Singer 1984). Rook (1977) and Dore *et al.* (1982) outlined mechanisms for generation of dichloroacetate, trichloroacetate, chlorine-substituted acetones, and chloroform from meta dihydroxyl phenolic moieties, a common functional group among humic compounds. But like THM formation, nearly all hydroxyl, carbonyl, or amine groups represent potential reaction sites for chlorine. Treatment strategies for reducing TOX formation potential (TOXFP) are the same as those employed to limit THM formation.

DOM Removal by Coagulation

Coagulation/flocculation is the process of coalescing entrained particles by neutralizing repulsive surface charges. Traditionally, coagulation of surface waters has been used to remove turbidity. Soluble salts of trivalent iron or aluminum are dispersed at concentrations typically less than 1 mM. The trivalent metal ions become hydrated, then hydrolyze to form metal hydroxides. The hydrolyzed

metal ions neutralize the negative surface charges of particles. Once neutralized, weaker Van der Waal's attractive forces cause particles to coalesce. At sustained low mixing energies, macroscopic particles consisting of hydrated metal oxides/hydroxides and enmeshed particulates form. As flocculation continues, the particles collide and adhere, forming larger particles termed "sweep floc". Particle size is ultimately limited by shear forces produced by mixing. When mixing ceases, the floc settles out of solution taking microorganisms, clay, silt, and organic detritus with it.

With the promulgation of an MCL for THM, there has been renewed interest in coagulation as a technique for removing organic carbon. Coagulation with metal salts can reduce DOC concentrations up to 60% (Kavanaugh 1978, Lange *et al.* 1978, Young and Singer 1979); removal rates up to 90% have been reported for humic compounds (Hall and Packham 1965, Narkis and Rebhun 1975, Scheuch and Edzwald 1981). In addition, reductions in THMFP and TOXFP often exceed organic carbon removal (Babcock and Singer 1979, Amy and King 1980, Johnson and Randtke 1983).

Many studies have focused on optimizing DOC removal by coagulation. From this work, several discoveries have been made. First, iron salts are somewhat more effective than aluminum for precipitating DOC (Kavanaugh 1978, Lange *et al.* 1978). Second, optimal removal occurs at pH values near 5

(Kavanaugh 1978, Lange *et al.* 1978, Semmens and Field 1980). Third, preozonation can reduce subsequent DOC removal by coagulation (Reckhow and Singer 1984). Fourth, No additional DOC removal is achieved by sequential coagulations compared to single coagulations of the same cumulative dose (Semmens and Field 1980). Fifth, humic acids are more readily precipitated than fulvic acids (Babcock and Singer 1979, Amy and King 1980). Finally, regardless of dose, a substantial DOC fraction remains unremovable (Lange *et al.* 1978).

In addition to the parameters mentioned above, DOC removal by coagulation is related to characteristics of the organic material itself. Molecular size, solubility, and charge may directly affect removal processes such as adsorption and direct precipitation. For example, Dempsey *et al.* (1984) studied fulvic acid removal by alum coagulation. At pH 5, hydrophilic acids were removed most effectively. As pH increased, removal preference shifted to more hydrophobic acids. This shift was attributed to the capacity of the different fractions to complex cations. Davis and Gloor (1981) found that adsorption of organics on aluminum oxide was size-dependent. These examples illustrate the type of research that is needed to understand the interaction between DOC and coagulants.

METHODS

Site Descriptions

The principal water source for this study was the Harwood's Mill Reservoir located in York County near Newport News, Virginia. The reservoir is managed by the public utilities department of the City of Newport News. Water quality characteristics for the reservoir during the study period April 1983 to June 1984 are summarized in Table 1 of the Results section. The high TOC (total organic carbon) concentration, TOXFP (total organic halide formation potential), and THMFP (trihalomethane formation potential) are typical of many surface waters of the Piedmont and Coastal Plain regions.

Finished water samples were collected from the Harwood's Mill Filtration Plant located at Harwood's Mill Reservoir. The plant has a treatment capacity of 40 ML/day (10 MGD) and operates a conventional treatment sequence of coagulation, flocculation, chlorination, settling, and filtration.

To provide a comparison for the Harwood's Mill data, Occoquan Reservoir water was collected in December 1983 and analyzed. The reservoir is managed by the Fairfax County Water Authority and supplies water to more than 600,000 residents (Hoehn et al. 1977). It receives agricultural and

urban runoff as well as effluent from wastewater treatment plants. Raw water characteristics for the sample collected 2 December 1983 are presented in Table 7 of the Results section.

Sample Collection

Water was collected in 24 L cartons with plastic liners by Newport News Public Utilities Department personnel. The plastic liners were tested to determine if they contributed DOC (dissolved organic carbon) by filling the liners with distilled water and incubating them at room temperature for several days. Little or no increase in TOC was detected.

Raw water samples were collected near the intake to the Harwood's Mill plant at a depth of about 3 m. Finished water was collected after sand filtration. Time of day, water temperature, and coagulant dose were recorded for each sample.

After collection, samples were taken to the water chemistry lab at the Lee Hall Filtration Plant. A flow chart of the sample processing scheme is shown in Figure 1. Measurements of alkalinity, hardness, turbidity, color, and pH were made by lab personnel. Algal count and taxonomic data were also provided. The chlorine residual of finished water samples was quenched with sodium sulfite. Subsamples for future DOC analyses were prepared by filtering water through prerinsed glass fiber filters into 4 L glass bottles. All water samples were refrigerated until

SAMPLE PROCESSING SCHEME

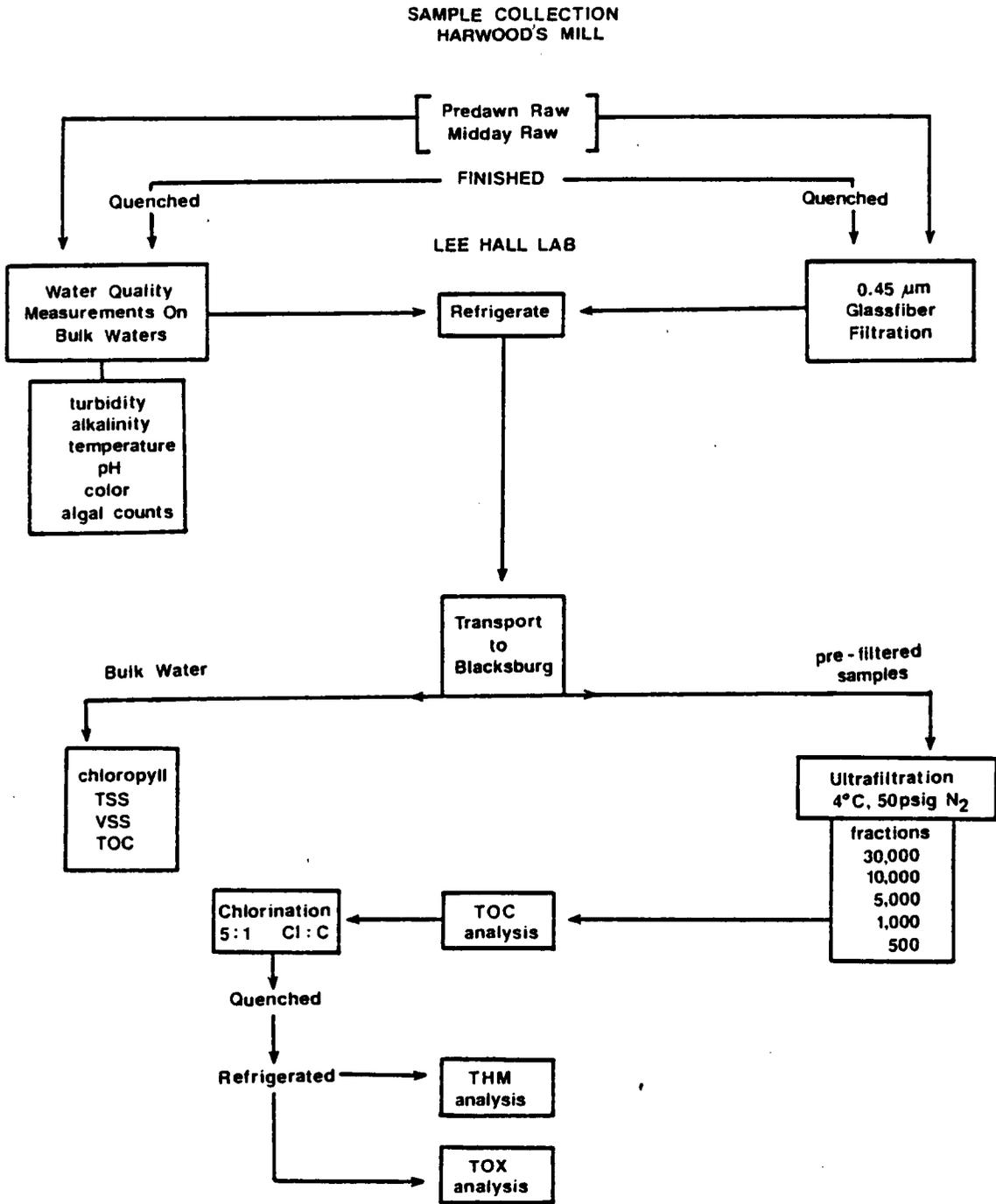


Figure 1. Sample collection and processing scheme.

transported to Blacksburg. The filtration and refrigeration steps were included to retard biological activity that might alter DOC characteristics. Additional preservation techniques, such as acidification or mercuric chloride addition, were not used because of the potential for precipitating humic compounds.

Water samples were collected and processed by Newport News personnel on Friday and transported on ice to Blacksburg Saturday morning. During the first phase of this project, water samples were collected on four occasions (7 May, 10 June, 1 July, 22 July 1983). On each date, two raw water samples and one finished water sample was collected. Two raw water samples were collected at different times, before dawn and at midday, to investigate potential diel fluctuations in DOC composition as a consequence of biological activity. Upon receipt in Blacksburg, TSS (total suspended solids), VSS (volatile suspended solids), chlorophyll a, TOC, THMFP, and TOXFP values were determined for each water sample.

During the second phase of the project, Harwood's Mill water was collected on 9 September 1983 for THM and TOX formation kinetics experiments, and again on 9 March 1984 for detailed chromatographic analysis of DOC. These samples were collected and processed in the same manner as the phase one samples. On 2 December 1983, water from the Occoquan Reservoir was collected at the dam from a depth of 9 m by

personnel of the Occoquan Watershed Monitoring Project, then brought to Blacksburg for analysis.

Preliminary Analyses

Preliminary characterization of water samples consisted of measuring pH, alkalinity, hardness, turbidity, color, TSS (total suspended solids), VSS (volatile suspended solids), chlorophyll a, and algal cell density. These parameters were quantified by established techniques described in Standard Methods for the Examination of Water and Wastewater (1980). Sample pH was measured potentiometrically with combination electrodes. Alkalinity was measured by titration with 0.02 N sulfuric acid to a pH of 4.2 and hardness was quantified by EDTA titration. Turbidity was measured nephelometrically. Color was estimated by comparison to platinum cobalt standards.

TSS was quantified by filtering three 500 mL aliquots of water through preweighed, precombusted Gelman A/E glass fiber filters; oven drying the filters at 105C for 24 h; then reweighing the filters on a Mettler balance. VSS was measured as weight loss upon ignition of oven dried filters at 550C for 60 min.

For chlorophyll a determinations, three 200 mL aliquots were filtered through 2.1 cm glass fiber filters to concentrate algal cells. One mL of magnesium carbonate suspension was added to each aliquot. Filters were ground in 10 mL of 90% aqueous acetone and extracted in the dark

for 24 h. The extracts were filtered and absorbance was recorded at 663, 645, and 630 nm using a Gilford model 260 spectrophotometer and 1 cm quartz cuvettes. Chlorophyll a values were corrected for the presence of pheophytin a by acidifying the extracts and recording absorbance at 665 nm after a 1 min delay.

Algal cell densities were determined by concentrating 500 mL aliquots to 5 mL on a sand filter. Ten 0.1 mL subsamples of the suspension were placed on Sedgewick-Rafter slides and scanned microscopically. Identifications were made to genus level.

Size Fractionation of Organic Carbon

Organic matter was fractionated into size categories through a series of filters of decreasing pore size. First, particulate organic carbon (POC) was excluded by filtering water through precombusted Gelman A/E glass fiber filters. This step was omitted for finished water samples since POC was negligible. The filtrate, containing only DOC, was then filtered through Amicon series YM ultrafilters with nominal exclusion sizes of 30, 10, 5, 1, and 0.5 kilodaltons (kd).

The ultrafilters were preserved with glycerol. Prior to use, soluble organics were leached for a minimum of four days in 2 L of distilled deionized water. The water was slowly mixed on a magnetic stirrer and replaced at least once daily. The membrane was then thoroughly flushed with organic-free water. These extensive preparations were

required to minimize sample contamination by membrane-associated DOC. Between uses membranes were gently washed with a mild detergent solution, rinsed, and stored individually in 10% aqueous ethanol at 4C as recommended by the manufacturer.

The ultrafiltration was performed in vigorously stirred 200 mL Amicon ultrafiltration cells under a nitrogen atmosphere of 2.8 kg/cm² at a temperature of 4C. Vigorous stirring helped reduce clogging. Flow rate through each ultrafilter was monitored to reduce errors caused by pore clogging. If flow rate fell 20% below its initial value, the ultracell was disassembled and its membrane cleaned. At the TOC concentrations encountered, clogging rarely occurred. Refilling the ultracell when the water level reached 50-100 mL also helped reduce clogging by keeping DOC concentrations lower. To minimize errors introduced by potential differences in exclusion properties among membranes, water was filtered through three membranes at each step in the fractionation. The three filtrates were then combined into a composite sample.

In preliminary trials, a serial filtration scheme was followed. Water was filtered through 30 kd ultrafilters; a portion of the filtrate was reserved for TOC, THM, and TOX analyses and the rest was filtered through the 10 kd ultrafilters. This procedure was repeated with the 5 kd, 1 kd, and 0.5 kd ultrafilters. This approach proved

unsatisfactory for two reasons. First, to obtain enough filtrate in every size range for the remaining analyses, a large volume of water was needed to commence the sequence. Filtering the required volumes of water was prohibitively time consuming. The second problem was that DOC introduced by contaminated filters accumulated as the sequence progressed, so there was little confidence in the accuracy of DOC estimates in the lower molecular weight ranges. Because of these problems, a parallel filtration scheme was adopted. In this scheme, particulate-free water was filtered through each set of ultrafilters in turn. Only enough filtrate was collected from each set of ultrafilters to complete desired analyses and cross-contamination was eliminated.

TOC Analyses

After fractionation, the organic carbon concentration in bulk waters and filtrates were determined with a Dohrmann Envirotech model DC-54 Ultralow Level TOC analyzer. Duplicate measurements were made on each sample. To be accepted, replicate values could differ by no more than 50 ug/L. Typically, differences between replicates were about half this value.

Chlorination

Filtrates and bulk waters were chlorinated at a Cl:OC weight ratio of 5:1 (1.7:1 molar ratio) and incubated in the dark at 22C. THM samples were incubated in 30 mL glass

vials, sealed headspace-free with PTFE (polytetrafluoroethylene) septa. TOX samples were incubated in 125 mL glass bottles sealed headspace-free with PTFE septa. Solution pH was buffered at 7.0 with 0.2 M phosphate buffer. Reactions were terminated by addition of sodium sulfite and sufficient nitric acid to reduce sample pH to 2 to inhibit hydrolysis of THM from organic halide intermediates (Peters *et al.* 1980). Quenched samples were refrigerated until analyzed, usually within a few days.

THM and TOX Measurements

THMFP was measured by the purge and trap method, described in Standard Methods (1980), using a Tracor model 560 gas chromatograph with a Hall electrolytic conductivity detector coupled to a Tracor LSC-2 purge and trap module. Replicate determinations usually differed by 2% or less. Because of this precision and the 45 min analysis time required per run usually only one THM determination was made per sample. TOXFP was measured by the carbon adsorption/pyrolysis technique with a Dohrmann Envirotech model DX-20 TOX Analyzer. Three 25 or 50 mL aliquots were used in the analysis, depending on the TOC concentration of the sample. Replicates usually differed by 3% or less. The efficiency of the adsorption and pyrolysis processes for various types of compounds has been discussed by Shorten (1983), Dressman and Stevens (1983), and Takahashi *et al.* (1980). The OC, THMFP, and TOXFP numbers given in Table 2

of the Results section for each molecular size class were obtained by subtracting the value determined for the filtrate from the value determined for the filter-applied water.

THM and TOX Generation Rates

During the first phase of the project (May-August 1983), only 7-day TOXFP (TOXFP-7) determinations were made while both THMFP-1 and THMFP-7 were estimated. TOXFP-1 values were not measured because of the time involved in collecting additional ultrafiltrates. The fraction of the THMFP-7 expressed after a one-day incubation was used as an index of rate of THM generation. The higher the fraction, the faster the initial THM production rate.

More detailed data on THM and TOX generation were collected during the second phase of the project. Raw and finished waters, collected at Harwood's Mill on 9 September 1983, were filtered to remove particulates. A subsample of the raw water was coagulated with a 0.35 mM Fe(III) dose at pH 5. The DOC in these three waters was resolved into three size ranges (bulk, <10 kd, <1 kd) by ultrafiltration through 10 kd and 1 kd membranes. THM and TOX determinations were made for all fractions at incubation times of 1, 6, 12, 24, 72, and 168 hr.

As a complement to chromatographic analysis, THM and TOX formation rates were followed for two size ranges (5-10 kd, 1-5 kd) of DOC in raw and lab treated Occoquan Reservoir

water collected on 2 December 1983. Raw water was treated in the lab at coagulant doses of 0.25 and 0.35 mM Fe. DOC from 1-5 kd and 5-10 kd was isolated, concentrated, dialyzed (these procedures are described in more detail later), then diluted to its original concentration for the kinetics experiments.

The final series of kinetics experiments were performed with raw and lab treated Harwood's Mill water collected 9 March 1984. The rate of formation of THM and TOX was traced for three size ranges of DOC (<10 kd, <5 kd, <1 kd) in the raw water and two lab treated waters coagulated with 0.10 and 0.25 mM Fe doses at pH 5. This work was done to complement chromatographic data collected for the same three size ranges.

Ultrafilter Evaluations

The performance of Amicon YM series ultrafilters was evaluated for several test compounds. Polyacrylic acids with average molecular weights of 5 kd and 2 kd were chosen as test compounds so that results could be compared to those of Aiken (1985), who evaluated Amicon series UM ultrafilters. Other test compounds selected were cytochrome c (12,384 d), cyanocobalamin (1,355.4 d), and nicotinamide adenine dinucleotide phosphate (765.4 d). YM10 membranes (10 kd exclusion) tests were conducted with the two polyacrylic acids and cytochrome c. YM2 membranes (1 kd exclusion) tests were conducted with cyanocobalamin and NADP.

Test solutions were prepared by dissolving the test compound in 1 L of organic-free water. The final DOC concentrations of stock solutions were: 5,000 d polyacrylic acid, 6.96 mg/L; 2,000 d polyacrylic acid, 6.32 mg/L; cytochrome c, 4.16 mg/L; cyanocobalamin, 5.17 mg/L; NADP, 2.74 mg/L.

For each test, 200 mL of stock solution was filtered under a nitrogen atmosphere of 2.8 kg/cm² at 4C until 100 mL of filtrate were collected. DOC measurements were made on the filtrate and the concentrate. Three membranes were tested with each compound to quantify variations in exclusion properties.

Sample Preparation for Chromatography

During the second phase of the project, dissolved organic compounds in raw and treated waters were analyzed chromatographically. DOC under 10 kd was analyzed by charge and solubility using ion exchange chromatography (IEC) and high-performance liquid chromatography (HPLC). The first series of samples were Occoquan waters collected on 2 December 1983. DOC from 1-5 kd and 5-10 kd was analyzed in raw and lab treated waters (0.25 and 0.35 mM Fe dosed). For the second series of samples, three size ranges of DOC (<1 kd, 1-5 kd, 5-10 kd) were analyzed. These samples consisted of one raw and two lab treated (0.10 and 0.25 mM Fe dosed) Harwood's Mill waters collected 9 March 1984.

The first step in the chromatographic analysis was DOC

concentration. Concentrated DOC samples with nominal molecular weight ranges of 5-10 kd, 1-5 kd, and <1 kd were prepared. To prepare a 5-10 kd concentrate, one liter of water that had been previously filtered through 10 kd ultrafilters was divided into two portions and concentrated against two 5 kd ultrafilters to a volume of approximately 100 mL. The volume of the concentrate was increased to 400 mL with deionized organic-free water (HPLC-grade water). The sample was again concentrated to 100 mL against two 5 kd ultrafilters to dialyze out salts and DOC under 5 kd. This dialysis procedure was repeated. Ideally, over 99% of the inorganic salts and low molecular weight organics were eliminated by this process. The concentrate was then frozen in liquid nitrogen and lyophilized, using a Labconco vacuum lyophilizer. The lyophilate was reconstituted with 10 mL of HPLC-grade water. The 1-5 kd concentrates were prepared in the same manner by concentrating one liter of 5 kd filtrate against two 1 kd ultrafilters. No precipitates were observed in any of the concentrates. Concentrating DOC without reducing inorganic solutes often results in coprecipitation of organic compounds with inorganic salts, reducing DOC recovery. Recovery from this procedure was consistently around 150% (range 140-156%) when compared to the DOC value determined for the same size range by the initial size fractionation. This excess recovery was probably the result of ultrafilter clogging which could not

avoided by this procedure, as it was during the initial DOC size fractionation.

The <1 kd concentrates were prepared somewhat differently since they could not be dialyzed by ultrafiltration. One liter of 1 kd filtrate was frozen in liquid nitrogen and lyophilized. The lyophilate was extracted with 100 mL of HPLC-grade methanol to recover as much DOC as possible while minimizing the dissolution of inorganic salts. The methanol was evaporated under vacuum, and the residual organics were dissolved in 10 mL of HPLC-grade water. DOC recovery averaged about 90%.

HPLC Analyses

A schematic summary of the chromatographic processing sequence is shown in Figure 2. The solubility distribution of DOC within each size class concentrate was analyzed by HPLC using a Beckman model 332 HPLC system and an octyldecyl reverse-phase column and precolumn (Ultrasphere ODS). HPLC-grade methanol and 10 mM ammonium dihydrogenphosphate buffer (pH 4) were used as solvents. The operating temperature was 22C, and the solvent flow rate was 1.0 mL/min at a pressure of 176 kg/cm². An Altex model 155 variable wavelength detector set at 254 nm was used for peak detection. Detector output was routed to an Apple II+ computer for data storage and analysis using a software package called Chromatohart (Interactive Microware Inc.).

After the system was equilibrated and calibrated, a

Protocol for Characterizing DOC Within Each Size Class

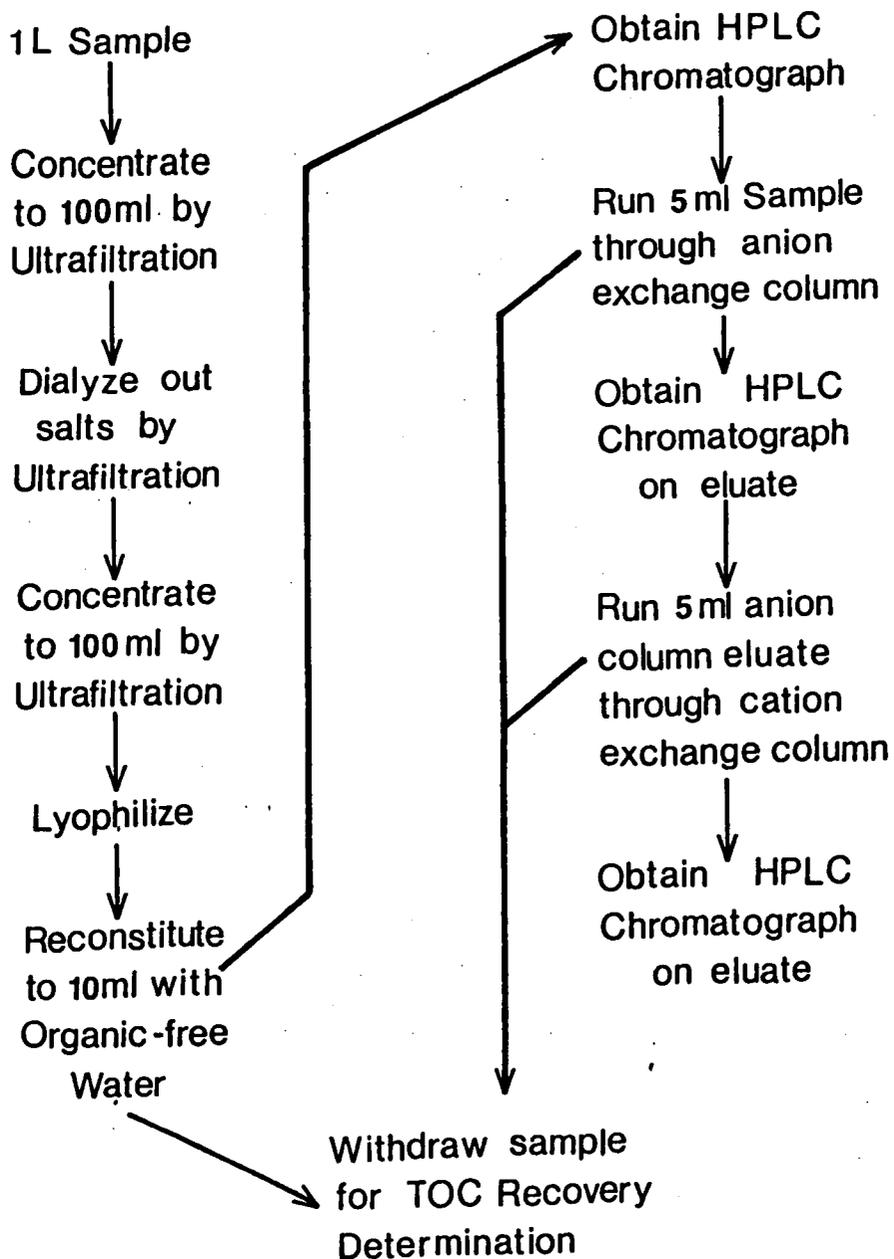


Figure 2. Protocol for chromatographic processing of DOC samples.

50-100 uL sample was injected onto the column. The operating program was as follows: 100% buffer for 5 min, a 2 min ramp to 50% methanol for 10 min, a 2 min ramp to 90% methanol for 20 min.

Peaks eluted by 100% buffer represented the most water soluble or polar organics. These peaks were collectively designated the philic fraction. Peaks eluted in 50% methanol were of intermediate solubility or polarity and were designated the mesic fraction. The least soluble compounds were eluted in 100% methanol and were designated the phobic fraction. The solubility distribution of DOC within each size class was assumed to be directly proportional to the area distribution under the three sections of the chromatogram. Three replicate chromatograms were obtained for each DOC concentrate analyzed.

IEC Analyses

After determining the solubility distribution of organics within each size class by HPLC, subsamples were eluted through ion exchange columns and reanalyzed by HPLC to determine the distribution of anionic, cationic, and neutral compounds within each solubility fraction. The ion exchange resins were Bio-Rad AG MP-50, a strong cation exchanger, and Bio-Rad AG MP-1, a strong anion exchanger. These resins are analytical grade, macroporous, and have a bead size of 20-50 mesh. The resins were prepared by boiling the beads in HPLC-grade methanol, followed by three

methanol rinses. This procedure was repeated several times until no discoloration of the methanol occurred on heating. The cleaned resin was stored under HPLC-grade methanol.

After slurrying the resin into columns (0.7 x 4.0 cm) about 100 bed volumes of 1 M HCl were eluted through the anion column to eliminate residual DOC contaminants. The resin was then charged with 100 bed volumes of 3 M NaOH. Finally, 100 bed volumes of HPLC-grade water were eluted from the column. The cation column was flushed with 3 M ammonium hydroxide to remove residual DOC contaminants, then charged with 2 M HCl and flushed with water.

A 5 mL subsample from a DOC concentrate was dripped through an anion exchange column and collected. The column was flushed with 2 mL of HPLC-grade water. The eluant was then analyzed by HPLC after incrementing the applied sample volume by 40% to compensate for the DOC dilution that resulted from the anion exchange procedure. The anionic portion of each solubility class was calculated by subtracting the peak area of the eluant chromatogram from the peak area of the corresponding section of the original HPLC chromatogram. This anionic area was assumed to be proportional to the concentration of anionic DOC. This assumption was substantiated by measuring the DOC concentration in the sample before and after anion exchange and correcting the values for dilution.

The next step was to apply a 5 mL subsample of the

anion column eluant onto a cation exchange column. The column was again flushed with 2 mL of HPLC-grade water. The eluant was analyzed by HPLC after the applied sample volume was corrected for the dilution introduced by the cation exchange procedure. The peak area under each section of the chromatogram was attributed to neutral organic compounds, while the differences in peak area compared to the anion column eluant chromatogram were attributed to cationic compounds. Again, DOC analysis was used to corroborate this procedure. Because anionic organic compounds are largely disassociated acids and cationic organics are largely protonated bases, these fractions are referred to as acidic and basic, respectively, in the text and tables.

Water Treatment

During the second phase of the project, portions of the raw waters collected on 9 September 1983, 2 December 1983, and 9 March 1984 were coagulated in the lab, and the DOC characteristics and organic halide formation rates of the raw and finished waters were compared. Laboratory treated waters were chosen over plant treated waters to assure uniformity of treatment. In addition to kinetic and chromatographic analysis of residual DOC, bench-top water treatment experiments were conducted to establish the relationship between coagulant dose and TOC precipitation for Harwood's Mill water (collected 9 March 1984) and Occoquan Reservoir water (collected 2 December 1983). After

determining the TOC concentration, water was coagulated with ferric sulfate at doses corresponding to molar Fe/OC ratios of 0.1, 0.2, 0.3, ..., 1.0.

A conventional six-place paddle mixer (Phipps and Bird, Richmond, VA) was used for laboratory simulation of water treatment. One liter samples were placed in rectangular jars. Ferric sulfate, from a stock solution, was added to each jar while the water was rapid mixed at a paddle speed of 150 rpm. The pH was adjusted to 5.0-5.2 during the rapid mix phase. This combination of coagulant and pH was chosen to optimize DOC removal. Following 3 min of rapid mixing, the paddle speed was reduced to 10 rpm for 20 min. The floc was allowed to settle for an hour. The supernatant was filtered through precombusted glass fiber filters into clean bottles. Residual DOC in these treated waters was analyzed by the procedures described earlier.

Statistical Analyses

Analysis of variance (ANOVA) was used to analyze the effects of size, charge, and solubility on DOC removal by coagulation from both Harwood's Mill and Occoquan Reservoir water. A three-level full-factorial model with size, charge and solubility as main effects was employed. DOC removal data for Occoquan Reservoir water coagulated at 0.25 mM and 0.35 mM doses and Harwood's Mill Reservoir water coagulated at 0.10 mM and 0.25 mM doses was analyzed. For the 0.25 mM coagulated Harwood's Mill water, removal efficiencies

relative to the composition of the 0.10 mM coagulated water were also analyzed. In all cases, the r^2 values for the models exceeded 0.99.

RESULTS

Preliminary Analyses of Phase 1 Samples

Phase 1 samples consisted of eight raw and four finished water samples collected at Harwood's Mill on four dates between May and August 1983. Preliminary analyses included measurements of temperature, pH, alkalinity, color, turbidity, TSS, VSS, chlorophyll a, algal cell density, TOC, THMFP-7, and TOXFP-7. These raw water data are summarized in Table 1.

Harwood's Mill Reservoir is typical of many surface waters of the Piedmont and Coastal Plain regions. The water is low in alkalinity with a greenish brown color due to algae and humic substances. TOC was moderately high, ranging from 5.9 to 6.9 mg/L over the sampling interval. Upon chlorination, as much as 660 ug/L THM and 2200 ug/L TOX could be generated.

Algal taxonomic data are presented in Table 2. Nineteen genera were identified. By number, chlorophytes were the dominant group, followed by bacillariophytes and cyanophytes. The three most common genera were Ankistrodesmus, a solitary rod-shaped chlorophyte, Sphaerocystis, a colonial coccoid chlorophyte, and Staurastrum, a desmid. Other common genera were the filamentous cyanophytes Anabaena and Aphanizomenon, the pennate diatoms Fragilaria, Pinnularia, and Synedra, the dinoflagellate Ceratium and the chrysophyte Mallomonas.

TABLE 1

Preliminary water quality analyses
of Phase 1 samples from Harwood's
Mill Reservoir.

Temperature	15-29°C
pH	7.0-7.7
Alkalinity	50-76 mg/L
Color	35-60 Pt/Co units
Turbidity	1.4-3.2 NTU
Algal Count	49-94 cells/mL
Chlorophyll a	9-17 mg/m ³
TSS	2.2-3.9 mg/L
VSS	1.6-2.3 mg/L
TOC	5.9-6.9 mg/L
THMFP-7	570-660 ug/L
TOXFP-7	1500-2200 ug/L

TABLE 2

Algal taxonomy data for Phase 1 samples from Harwood's Mill

<u>Genus</u>	<u>Algal Density (number/mL)</u>				
	5/7/83 Predawn	6/10/83 Predawn	6/10/83 Midday	7/1/83 Predawn	7/22/83 Predawn
<u>Anabaena</u>	0	4	8	4	0
<u>Ankistrodesmus</u>	19	12	12	14	10
<u>Aphaninomention</u>	25	0	0	0	0
<u>Asterionella</u>	7	0	0	2	0
<u>Ceratium</u>	0	12	6	3	0
<u>Chlorella</u>	0	2	0	0	0
<u>Closteriopsis</u>	2	0	0	0	0
<u>Coelosphaerium</u>	0	0	0	2	5
<u>Dinobryon</u>	0	2	0	0	2
<u>Euglena</u>	0	0	0	0	1
<u>Fragilaria</u>	3	4	4	8	2
<u>Mallomonas</u>	0	3	10	7	0
<u>Navicula</u>	2	1	0	1	3
<u>Pinnularia</u>	1	0	2	4	10
<u>Scenedesmus</u>	1	0	0	0	3
<u>Sphaerocystis</u>	2	4	38	3	5
<u>Staurastrum</u>	11	13	14	8	5
<u>Synedra</u>	6	1	0	5	2
<u>Ulothrix</u>	0	0	0	0	1

Water quality remained fairly constant over the sampling period. Expected diel shifts in parameters such as pH, algal cell numbers, and TOC were not apparent. Consequently, one of the initial objectives of the project, which was to account for diel fluctuations in THM production by analyzing the effects of biological activity on the composition of the DOC pool, could not be accomplished. Another objective was to relate changes in DOC composition over a seasonal cycle to algal succession, but unfortunately no significant shifts in algal density or taxonomic composition were observed. The lack of variation during this period may be attributed to a severe drought that persisted throughout the spring and summer of 1983. Because of the consistency of water quality there was little information to be gained by continued sampling so the program was suspended after four collection dates.

Preliminary data for finished water samples are given in Table 3. Since raw water quality was similar on all four sampling dates, differences in finished water quality must have been due to treatment variations. Applied coagulant dose decreased at each successive sampling date, ranging from 0.35 mM to 0.15 mM (as Fe or Al). Consequently, removal of organic carbon and organic halide precursors tended to decline also (Table 4). The TOXFP-7 and THMFP-7 values in Table 3 are underestimates because settled water was chlorinated prior to filter application.

TABLE 3

Preliminary analyses of Phase 1 finished water samples from the Harwood's Mill Filtration Plant.

Date	5/7/83	6/10/83	7/1/83	7/22/83
Temperature, C	15	24	26	28
pH	5.9	6.5	6.6	6.6
Alkalinity, mg/L	8	36	34	46
TOC, mg/L	2.166	3.080	3.056	3.638
THMFP-7, ug/L	29	82	147	159
TOXFP-7, ug/L	143	234	373	362
Coagulant	Fe(III)	Fe & Al	Al(III)	Al(III)
Dose, mM	0.35	0.28	0.18	0.15

TABLE 4

Organic carbon and organic halide precursor removal in relation to coagulant dose for Phase 1 finished water samples.

Date	5/7/83	6/10/83	7/1/83	7/22/83
Coagulant Dose (mM)	0.35	0.28	0.18	0.15
TOC Reduction (%)	68	53	49	41
THMFP-7 Reduction (%)	95	89	74	75
TOXFP-7 Reduction (%)	94	87	88	76

Even though the chlorine was quenched after the filtered water samples were collected, some of the THM that had already been produced was lost during subsequent sample processing. The magnitude of the error is probably not unacceptably large, since comparable THM values were determined independently from distribution system samples collected during the same period.

Size Distribution of OC and OHP in Phase 1 Samples

There were no consistent differences in the molecular weight distributions of DOC in samples collected at midday and predawn or on different sampling dates. The data for the eight raw water samples were averaged to generate a composite distribution (Table 5). The coefficients of variation for each size class ranged from 10-22%. The largest fraction (26%) consisted of organics under 0.5 kd. About 82% of the TOC was under 10 kd with the median molecular weight about 2.7 kd.

The distribution of OHP (organic halide precursors) generally paralleled the DOC distribution (Table 5). However, specific yields (ug/mg OC) for DOC under 1 kd and over 30 kd were 40-60% lower than yields for organics between 1 kd and 30 kd. These differences were statistically significant ($P < 0.05$, T-test). The mean THM/TOX weight ratio for the eight samples was 0.38 ± 0.03 (SD). No statistically significant differences in this ratio were found among precursor size classes. About 95% of

Table 5

Composite molecular size distribution of organic carbon and organic halide precursors in eight water samples collected from Harwood's Mill Reservoir between 7 May 1983 and 22 July 1983.

size range (kd)	OC ug/L \pm SE	THMFP-7 ug/L \pm SE	THM SY ¹	TOXFP-7 ug/L \pm SE	TOX SY ¹	1/7 THM ²
POC	270 \pm 50	25 \pm 3	94	110 \pm 20	421	.50
>30	550 \pm 80	25 \pm 6	44	125 \pm 30	226	.52
10-30	310 \pm 40	40 \pm 10	129	125 \pm 20	406	.50
5-10	1290 \pm 240	170 \pm 21	131	480 \pm 75	371	.56
1-5	1320 \pm 290	190 \pm 21	147	460 \pm 70	348	.48
0.5-1	950 \pm 180	60 \pm 12	62	190 \pm 30	196	.41
<0.5	1680 \pm 170	110 \pm 13	65	300 \pm 40	177	.26
Bulk	6370	620	97	1790	281	.52

1 SY = specific yield (ug/mg OC)
 2 ratio of THMFP-1 to THMFP-7

the THM production was chloroform; dichlorobromomethane was the only other THM detected.

Cumulative TOC distributions for the finished water samples are shown in Figure 3 in relation to the raw water distribution. Two trends were apparent. First, TOC removal was directly related to coagulant dose. The 0.35 mM dose (70 mg/L ferric sulfate) removed 68% of the TOC, the 0.28 mM dose (35 mg/L alum and 35 mg/L ferric sulfate) 53%, the 0.18 mM dose (60 mg/L alum) 49%, and the 0.15 mM dose (50 mg/L alum) 41%. Second, DOC removal was size dependent. Larger molecules were precipitated more effectively than smaller ones. The median molecular weight of raw water organic compounds was 2.7 kd. After coagulation with 0.15 mM Fe, the median molecular weight of residual DOC was 955 d. As coagulant dose increased from 0.18 to 0.35 mM, the medians continued to decrease from 465 to 455 to 390 d.

OHP were precipitated more effectively than DOC, but precursor removal was also closely related to molecular size (Figure 4). There was no bias in THMFP reduction compared to TOXFP reduction, so only TOX removal is shown in Figure 4. Because of selective precursor removal, THM and TOX specific yields were lower in finished waters than in the raw water.

In addition to THMFP-7, THMFP-1 determinations were made on both untreated and finished samples. The ratio of THMFP-1/THMFP-7 is an index of THM formation rate. Mean

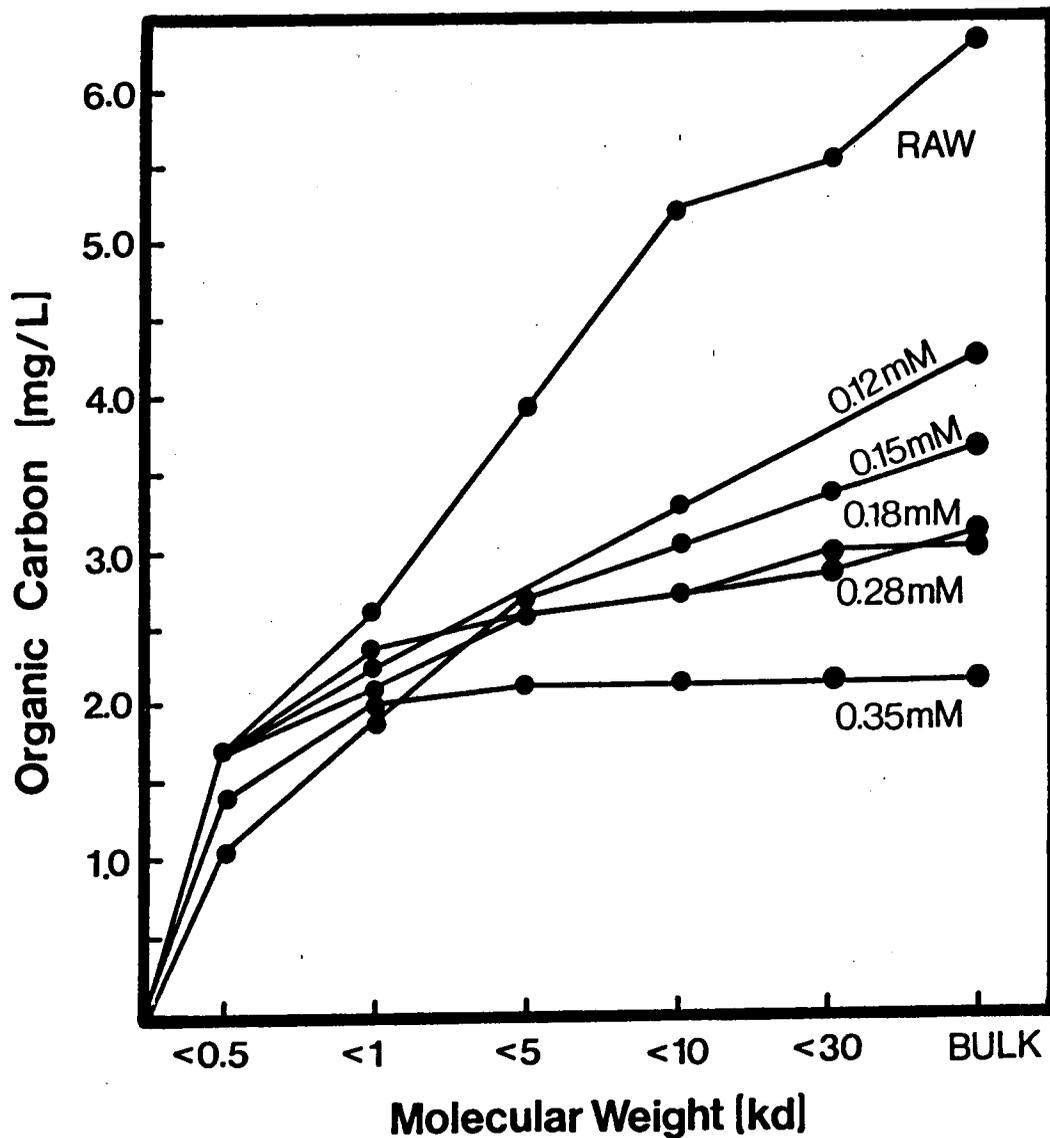


Figure 3. Cumulative size distribution of TOC in five finished water samples from Harwood's Mill Filtration Plant. The raw water distribution is shown for reference. Coagulant doses shown are those that were being applied at the time of sampling.

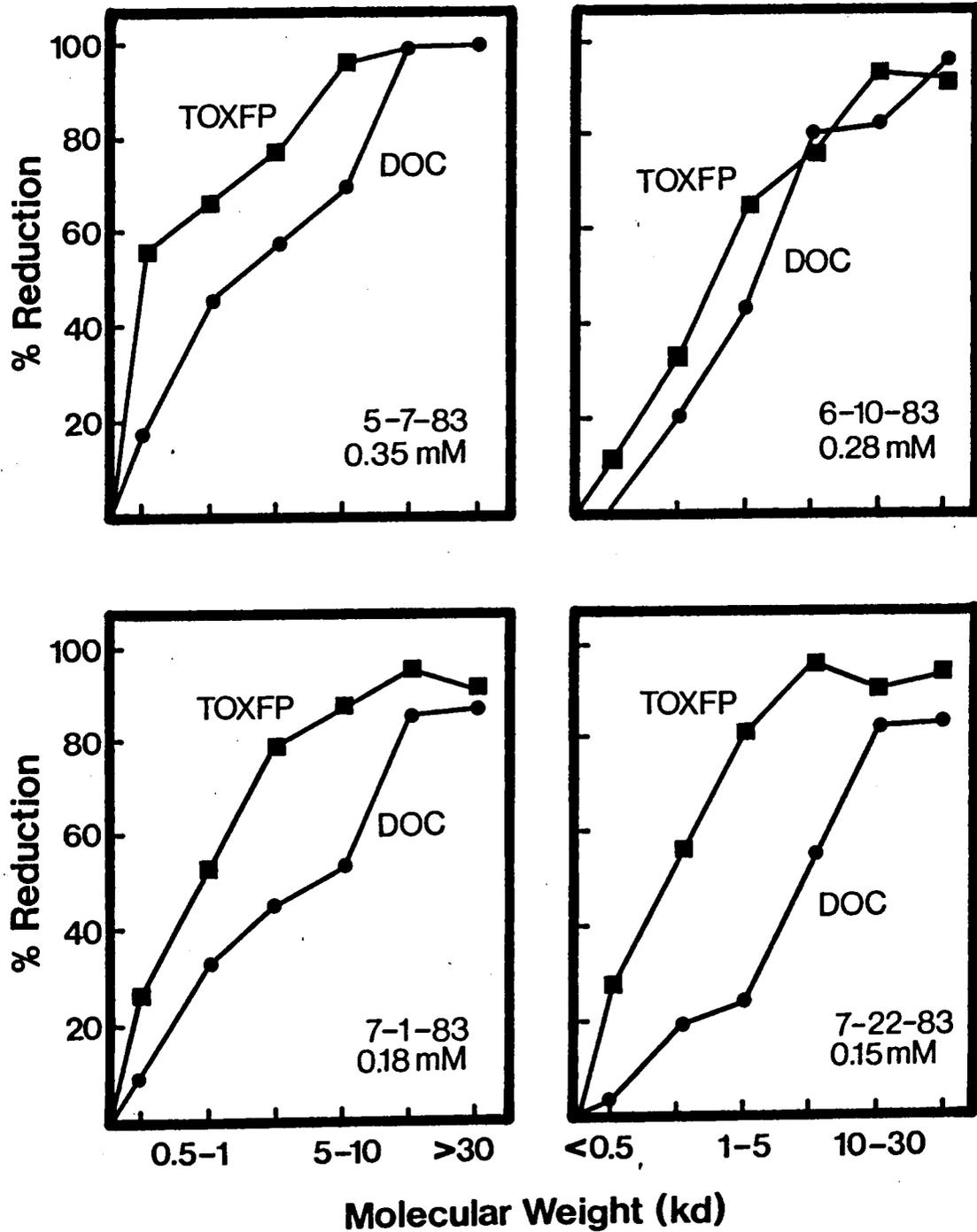


Figure 4a-d. DOC and TOXFP removal by molecular size for Phase 1 finished water samples from Harwood's Mill Filtration Plant. Collection date and coagulant dose are shown in the lower right hand corners.

values are listed in Table 5 for untreated samples. For DOC under 500 d, only 27% of the THMFP-7 was exerted in one day. For organics over 5 kd the proportion stabilized at approximately 50%. Values are not given for finished water samples. They were anomalously high as a consequence of THM generation prior to sample collection.

Phase 2 THM and TOX Formation Rate Experiment

The production rate of THM and TOX in untreated and 0.35 mM Fe treated waters was followed for seven days, with determinations made after incubations of 1, 6, 12, 24, 72, and 168 h. But the essence of the data can be summarized by tabulating 1-day/7-day formation potential ratios (Table 6). Three trends were apparent. First, ratios were higher for TOX generation than for THM generation, showing that TOX formation was faster. Second, like the Phase 1 samples, formation rates were related to precursor size, but the effect was smaller for TOX generation than for THM generation. TOX production by precursors under 1 kd was only 20% slower than that in bulk water, while THM generation was 50% slower. Third, faster reacting molecules must have been selectively removed by coagulation because 1-day/7-day ratios in every size range declined after treatment.

Occoquan Sample: Size Distribution of TOC and OHP

Preliminary data for Occoquan water collected 2 December 1983 are given in Table 7. Compared to Harwood's

TABLE 6

Cumulative 1-day/7-day THMFP and TOXFP ratios for three size ranges of DOC in raw and lab treated (0.35 mM Fe) Harwood's Mill water collected 9 September 1983.

<u>size range (kd)</u>	<u>1/7 THMFP</u>		<u>1/7 TOXFP</u>	
	<u>raw water</u>	<u>treated water</u>	<u>raw water</u>	<u>treated water</u>
Bulk	0.58	0.51	0.68	0.65
<10	0.56	0.44	0.63	0.59
<1	0.32	0.25	0.55	0.52

TABLE 7

Preliminary water quality analyses of
Occoquan Reservoir water collected 2
December 1983.

Temperature	80C
pH	6.4
Alkalinity	32 mg/L
Chlorophyll a	not detected
TSS	15.8 mg/L
VSS	3.4 mg/L
TOC	8.885 mg/L
THMFP-7	1.11 mg/L
TOXFP-7	3.59 mg/L

Mill water (Table 1), this sample had lower pH and alkalinity and higher suspended solids, TOC, THMFP-7, and TOXFP-7. The TOC distribution was skewed toward heavier molecules (Table 8). The largest size class (28% of TOC) was DOC from 10-30 kd. The median molecular weight was 9.7 kd compared to 2.7 kd for Harwood's Mill water. Only 51% of the TOC was under 10 kd.

The size distribution of THM and TOX precursors is also presented in Table 8. Like Harwood's Mill water, DOC under 1 kd yielded less organic halide per mg OC than heavier molecules. Unlike Harwood's Mill, low specific yields were not characteristic of DOC above 30 kd. In general, THM and TOX specific yields were similar to those of Harwood's Mill water. The overall THM/TOX weight ratio was 0.31 compared to 0.38 for Harwood's Mill.

Cumulative TOC size distributions for lab treated Occoquan water are presented in Figure 5 in relation to the raw water distribution. The 0.25 mM Fe dose removed 66% of the TOC, while 76% was precipitated by the 0.35 mM Fe dose. Again, DOC removal was biased toward heavy molecules. The median molecular weight of residual organic matter was 870 d after the 0.25 mM Fe treatment and 605 d after the 0.35 mM Fe treatment. In both cases, little organic carbon under 1 kd was removed.

OHP (organic halide precursors) were precipitated more effectively than DOC though removal rates were closely

TABLE 8

Molecular size distribution of OC and OHP in Occoquan Reservoir water collected 2 December 1983.

size range (kd)	OC ug/L	THMFP-7 ug/L	THM SY ¹	TOXFP-7 ug/L	TOX SY ¹
POC	240	45	192	340	1425
>30	1620	285	176	760	467
10-30	2455	315	128	1030	419
5-10	1890	265	140	660	351
1-5	955	140	145	440	463
0.5-1	805	30	37	200	252
<0.5	890	35	39	150	168
Bulk	8855	1115	126	3580	404

1 SY = specific yield (ug/mg OC)

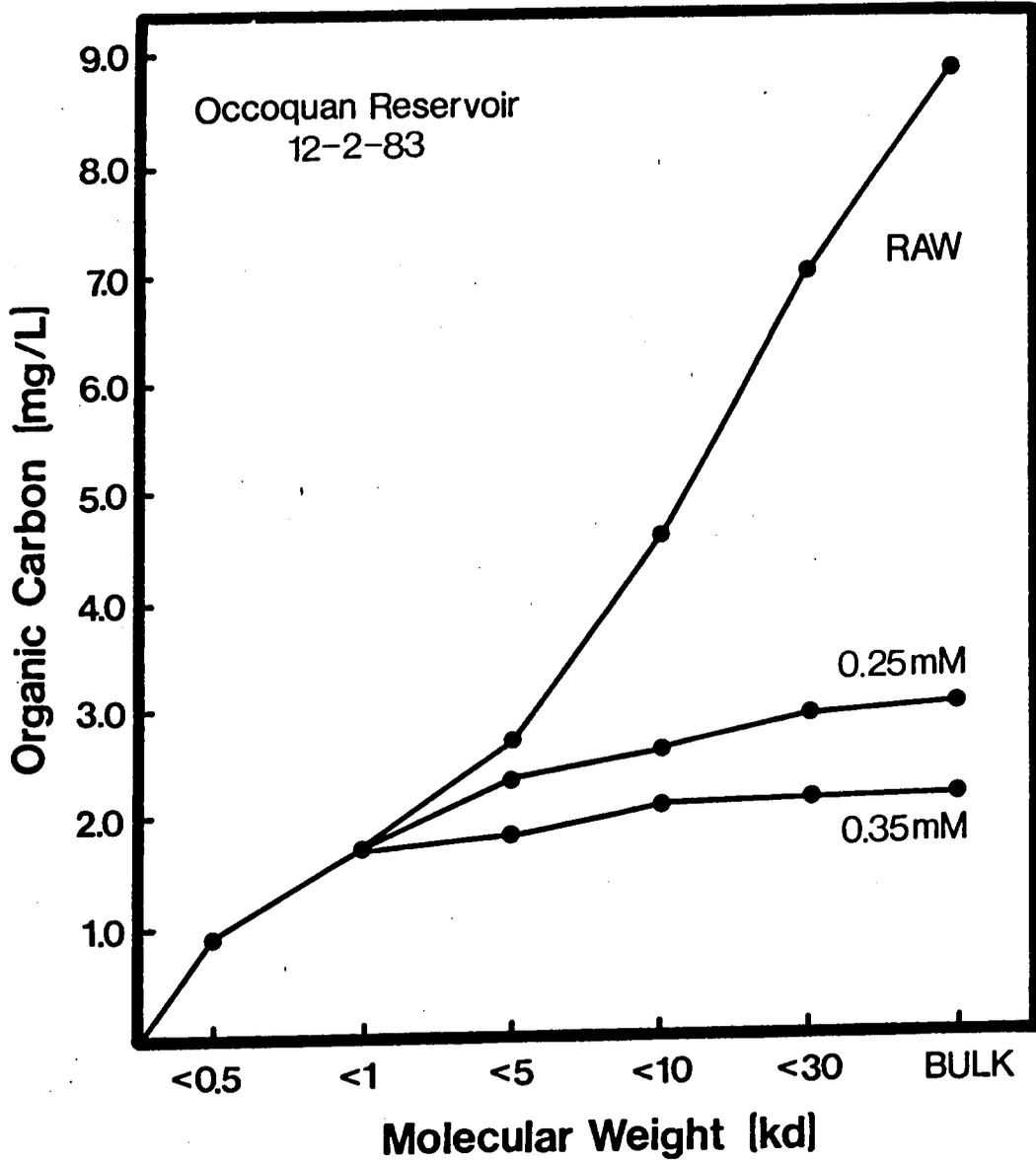


Figure 5. Cumulative DOC size distribution for 0.25 and 0.35 mM Fe coagulated Occoquan Reservoir water. The raw water distribution is shown for reference.

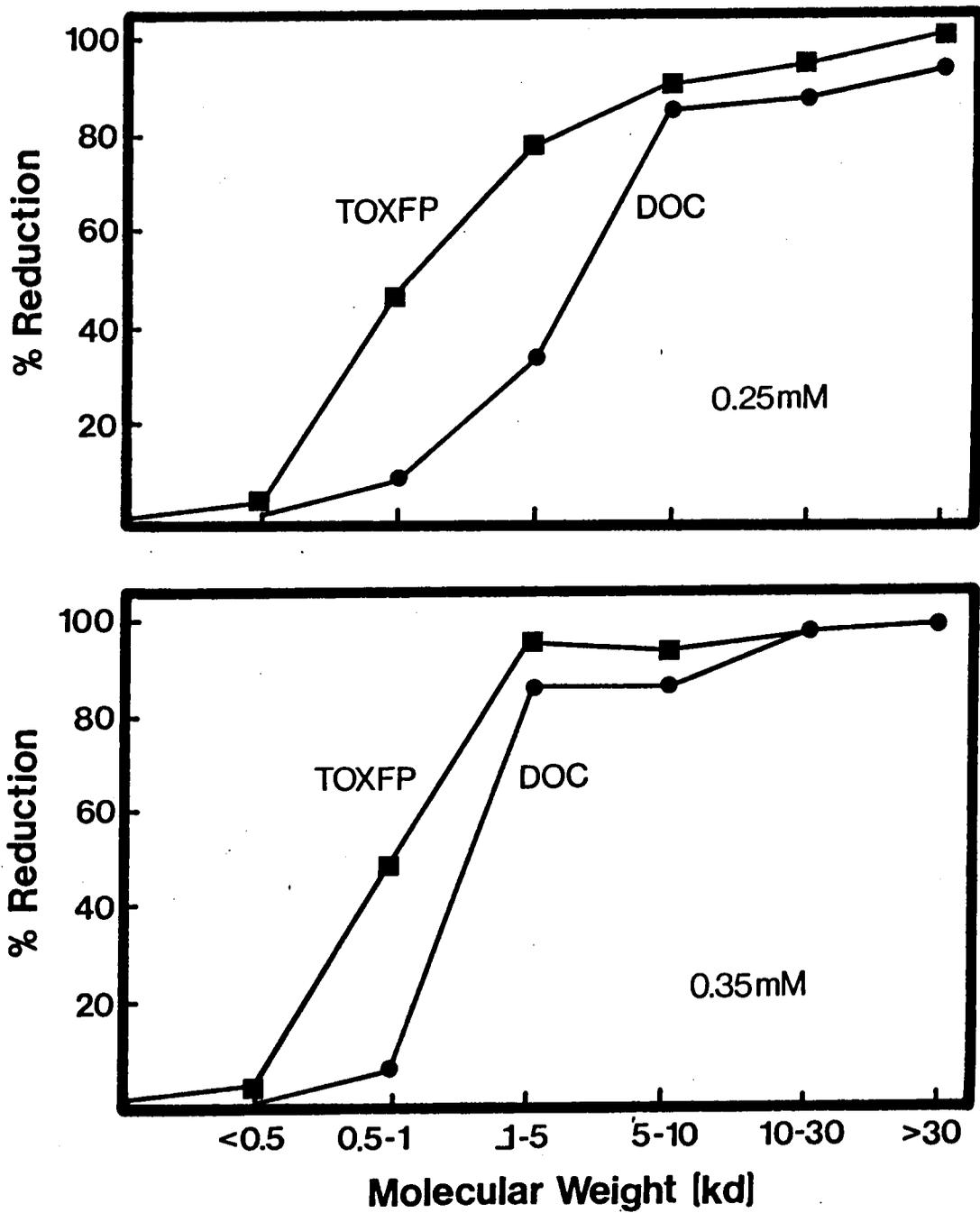


Figure 6a,b. DOC and TOXFP removal by molecular size for 0.25 and 0.35 mM Fe coagulated Occoquan Reservoir water.

related to molecular size (Figure 6). At the 0.35 mM dose, THMFP-7 and TOXFP-7 were reduced by 88% and 89%, respectively, by precipitating 76% of the TOC. At the 0.25 mM dose, removal of 66% of the TOC reduced THM and TOX production by 84% and 87%. There was no apparent bias in THM precursor removal relative to TOX precursors.

Occoquan Sample: THM and TOX Formation Rates

THM and TOX formation was followed for seven days for two size ranges of organic compounds. As was the case for Harwood's Mill, the formation rate data can be summarized by 1-day/7-day FP ratios (Table 9). Again, ratios were higher for TOX generation than for THM generation, indicating that THM hydrolysis proceeded more slowly at pH 7 than initial chlorine substitution reactions. In the 5-10 kd range, TOX formation rates were rapid with 91% of the TOXFP-7 exerted in the first day. Laboratory treatment reduced this formation rate index to 78% with a 0.25 mM Fe dose and to 66% with a 0.35 mM Fe dose. This trend did not extend to the 1-5 kd range, where coagulation apparently had no impact on organic halide formation rate. Except for the rapid TOX formation in the 5-10 kd range, formation rates were similar to those in Harwood's Mill samples (Table 6).

Occoquan Sample: Charge X Solubility Distribution of DOC

Charge x solubility matrices for DOC in the 5-10 kd and 1-5 kd size ranges are presented in Table 10 for untreated Occoquan water. Organic matter in these two size ranges was

TABLE 9

1-day/7-day THMFP and TOXFP ratios for two size ranges of DOC in raw and lab treated Occoquan Reservoir water collected 2 December 1984.

<u>size range (kd)</u>	<u>raw</u>	<u>1-day/7-day THMFP Ratio</u>	
		<u>0.25 mM treated</u>	<u>0.35 mM treated</u>
5-10	0.45	0.38	0.34
1-5	0.37	0.45	0.32
		<u>1-day/7-day TOXFP Ratio</u>	
5-10	0.91	0.78	0.66
1-5	0.59	0.60	0.51

TABLE 10

Charge x solubility matrix for DOC in two size ranges of Occoquan Reservoir water collected 2 December 1983.

5-10 kd Range

	<u>%Philic</u>	<u>%Mesic</u>	<u>%Phobic</u>	<u>Total</u>	<u>DOC¹</u>
%Acids	13.5	59	5	77.5	83
%Bases	0	0	0	0	0
%Neutrals	0.5	11	10	21.5	17
Total	14	70	15	100	

1-5 kd Range

	<u>%Philic</u>	<u>%Mesic</u>	<u>%Phobic</u>	<u>Total</u>	<u>DOC¹</u>
%Acids	31.5	55	0.5	87	92
%Bases	2	0	0	2	0
%Neutrals	1.5	8	2.5	12	8
Total	35	63	3	100	

1 DOC is the estimated charge distribution based on DOC measurements rather than area calculations from chromatograms.

similar in composition. By solubility, about 2/3 of the DOC was mesic; by charge, acidic compounds accounted for more than 3/4 of the DOC. Nearly all the remaining organics were neutral compounds. Basic compounds were not detected in the 5-10 kd range and constituted only 2% of the DOC in the 1-5 kd range. The main distinctions between the two size ranges were a solubility shift toward philic compounds and an elevated proportion of acids in the 1-5 kd range.

The charge x solubility distribution of residual organics after coagulation is given in Tables 11 and 12; 86% of the DOC from 5-10 kd and 33% from 1-5 kd was removed by the 0.25 mM Fe dose. Solubility distributions were not greatly affected by coagulation, but the charge distributions were. Because of selective precipitation of anionic compounds, neutral compounds accounted for 94% of residual DOC in the 5-10 kd range and 18% in the 1-5 kd range. Removal efficiencies for all charge x solubility groups are shown relative to DOC removal in Figures 7 and 8. These plots show that acidic and basic compounds were selectively removed while neutral compounds remained in solution and that removal of charged organics corresponded to preferential reductions in THM and TOX formation potentials.

The 0.35 mM Fe dose removed 86% of the DOC from the 5-10 kd range and 85% from the 1-5 kd range. Compared to the 0.25 mM dose, no additional DOC was removed in the 5-10

TABLE 11

Charge x solubility matrix for DOC in two size ranges of lab treated (0.25 mM Fe) Occoquan Reservoir water.

5-10 kd Range

	<u>%Philic</u>	<u>%Mesic</u>	<u>%Phobic</u>	<u>Total</u>	<u>DOC1</u>
%Acids	0.5	5	1	6.5	5.5
%Bases	0	0	0	0	0
%Neutrals	9.5	77	7	93.5	94.5
Total	10	82	8	100	

1-5 kd Range

	<u>%Philic</u>	<u>%Mesic</u>	<u>%Phobic</u>	<u>Total</u>	<u>DOC1</u>
%Acids	13	65.5	1	79.5	83
%Bases	2	0	0	2	0
%Neutrals	2	12.5	4	18.5	17
Total	17	78	5	100	

1 DOC is the estimated charge distribution based on DOC measurements rather than area calculations from chromatograms.

TABLE 12

Charge x solubility matrix for DOC in two size ranges of lab treated (0.35 mM Fe) Occoquan Reservoir water.

5-10 kd Range

Distribution is the same that shown for the 0.25 mM treated water (Table 11).

1-5 kd Range

	<u>%Philic</u>	<u>%Mesic</u>	<u>%Phobic</u>	<u>Total</u>	<u>DOC¹</u>
%Acids	0.5	5	0	5.5	11
%Bases	0	0	0	0	0
%Neutrals	10.5	77	7	95.5	89
Total	11	82	7	100	

1 DOC is the estimated charge distribution based on DOC measurements rather than area calculations from chromatograms.

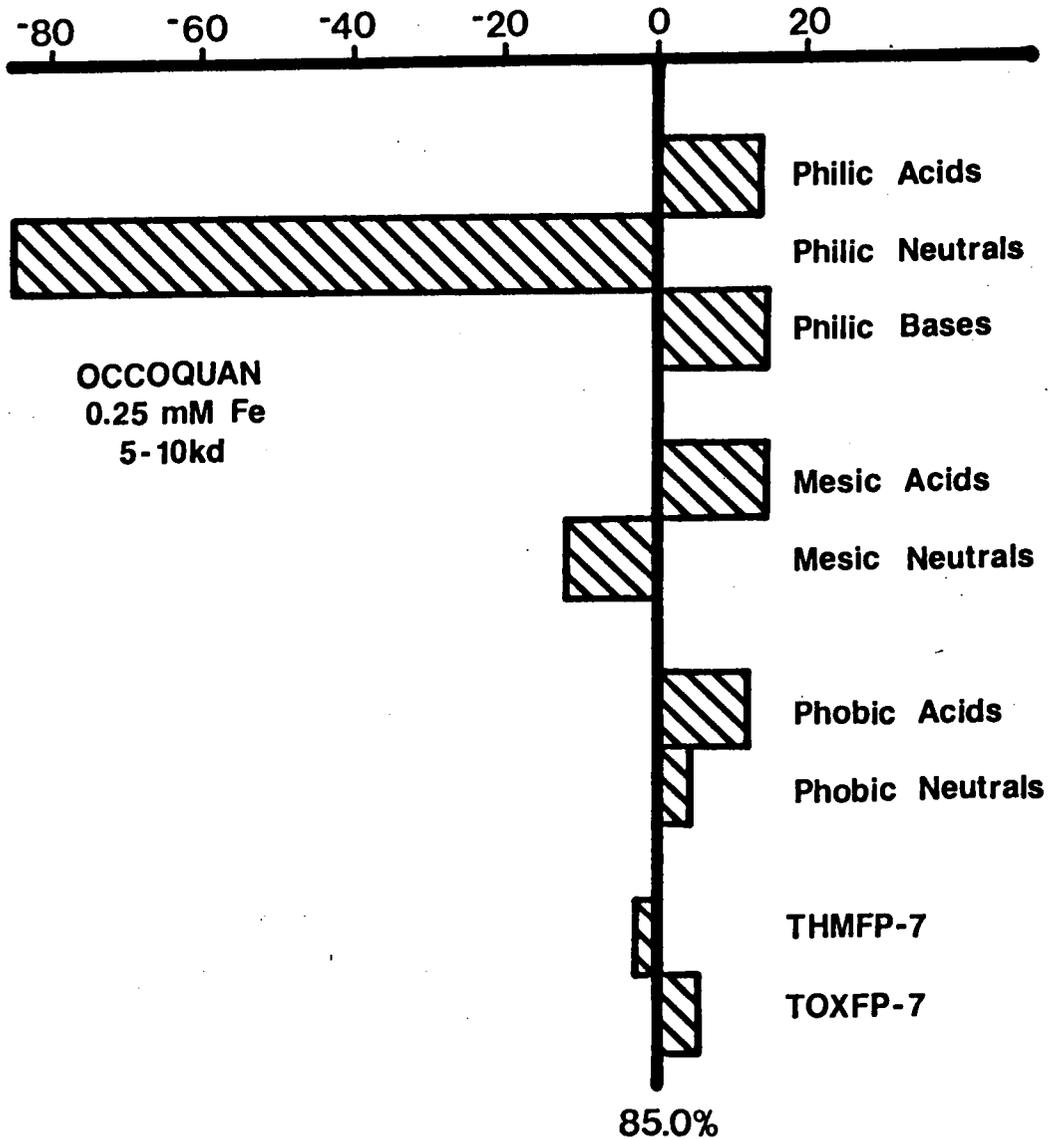


Figure 7. Removal efficiencies for charge and solubility groups in the 5-10 kd size range of 0.25 mM Fe coagulated Occoquan Reservoir water. Removals are shown relative to DOC removal which was 85%.

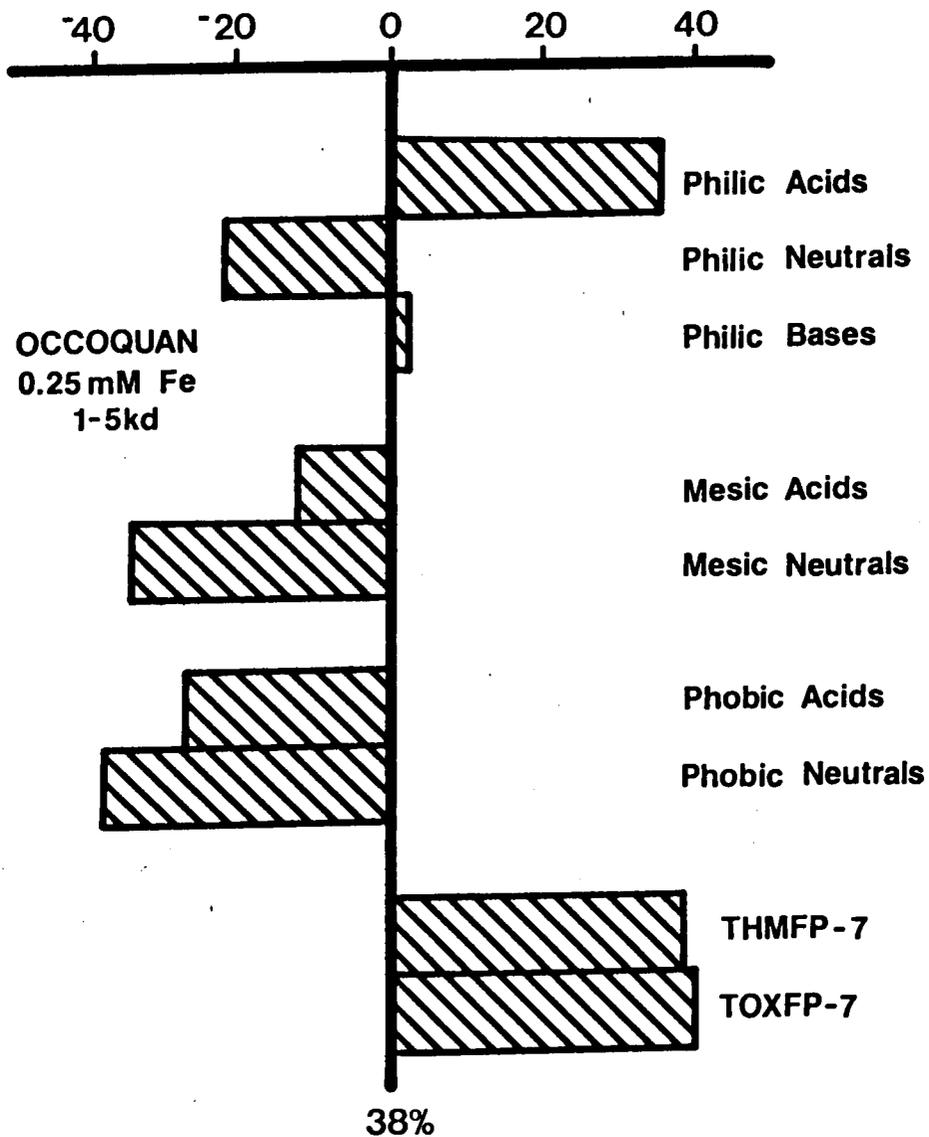


Figure 8. Removal efficiencies for charge and solubility groups in the 1-5 kd size range of 0.25 mM Fe coagulated Occoquan Reservoir water. Removals are shown relative to DOC removal which was 38%.

kd range, but removal in the 1-5 kd range was greatly enhanced (85% vs. 33%). Because no additional DOC was removed, the charge x solubility distribution of compounds from 5-10 kd was the same as that shown in Table 11 for the 0.25 mM treatment. The results of this treatment were similar to those at the lower coagulant dose. 94% of the residual DOC was identified as neutral compounds in the 1-5 kd range. Removal efficiencies for each charge x solubility group in the 1-5 kd class are shown in Figure 9. The product of abundance and removal efficiency gives the actual quantity of DOC precipitated. This calculation showed that 91% of the precipitated organics from 1-10 kd were acidic, 8% were neutral, and 1% were basic.

Analysis of variance (ANOVA) was used to analyze the effects of size, charge, and solubility on DOC removal. The ANOVA established that all three main effects were significant ($P < 0.01$) factors in DOC removal. Size was the largest factor at the 0.25 mM dose, but not at the 0.35 mM dose where DOC removal was about 85% in both the 1-5 kd and 5-10 kd ranges. Acidic and basic compounds were removed at approximately the same levels, but the removal rate for neutral compounds was only 1/3 that of charged compounds. Philic and phobic compounds were precipitated with about equal frequency while removal of mesic compounds was only about 1/2 that of the other solubility categories. The second order interactions were all statistically significant

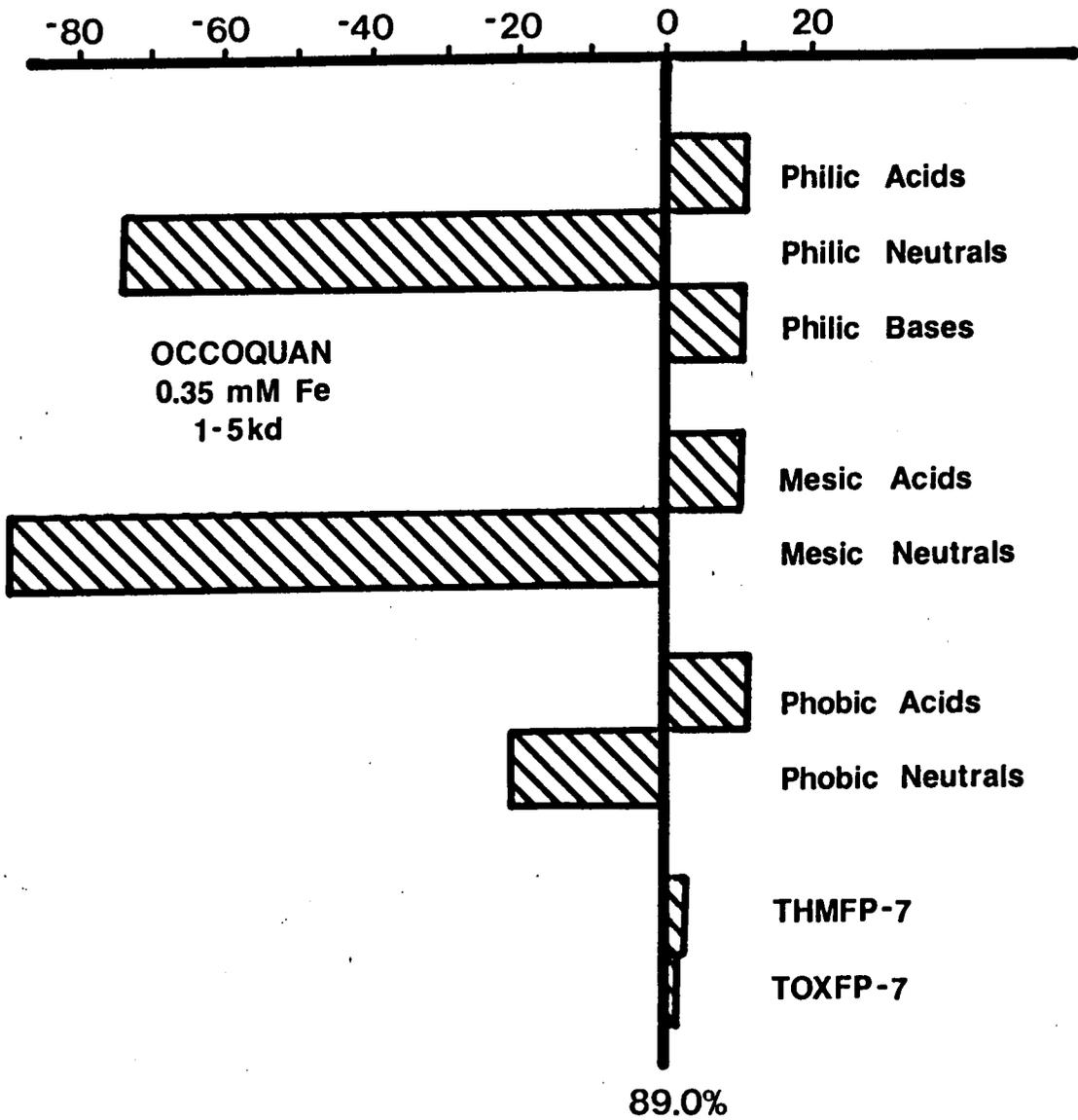


Figure 9. Removal efficiencies for charge and solubility groups in the 1-5 kd size range of 0.35 mM Fe coagulated Occoquan Reservoir water. Removals are shown relative to DOC removal which was 89%.

($P < 0.01$), indicating synergistic relationships among size, charge, and solubility.

As explained in the methods section, the charge and solubility distributions presented here were based on the assumption that organic carbon distribution was directly related to the area distribution under HPLC chromatograms. Where possible DOC measurements were used to corroborate this assumption. In Table 13 reductions in peak areas of treated water chromatograms are compared to DOC reductions calculated from the original size fractionation procedure. These numbers compare quite well although area reductions were larger than DOC reductions, probably a result of selective precipitation of strong ultraviolet-absorbing molecules. Within each size class, the distribution of acids, bases, and neutrals was confirmed by DOC determinations. These data are listed to the right of the areal charge distribution summary column in Tables 10-12. Again, charge distributions based on area calculations were similar to those generated from DOC measurements. Although the uv absorbance of natural DOC typically declines with molecular size, these results support the assumption that within a suitably narrow size range the DOC distribution can be adequately estimated from uv absorbance data.

Occoquan Sample: TOC Precipitation vs. Coagulant Dose

The effect of coagulant dose on TOC removal is shown in Figure 10. Coagulant dose is expressed as the molar ratio

TABLE 13

Comparison of DOC removal efficiencies, calculated from area reductions in HPLC chromatograms, to values obtained from the initial DOC size fractionation of Occoquan Reservoir water.

<u>Treatment</u>	<u>Removal by Size Range</u>			
	<u>5-10 kd</u>		<u>1-5 kd</u>	
	<u>OC</u>	<u>Area</u>	<u>OC</u>	<u>Area</u>
0.25 mM	86%	85%	33%	38%
0.35 mM	86%	85%	86%	89%

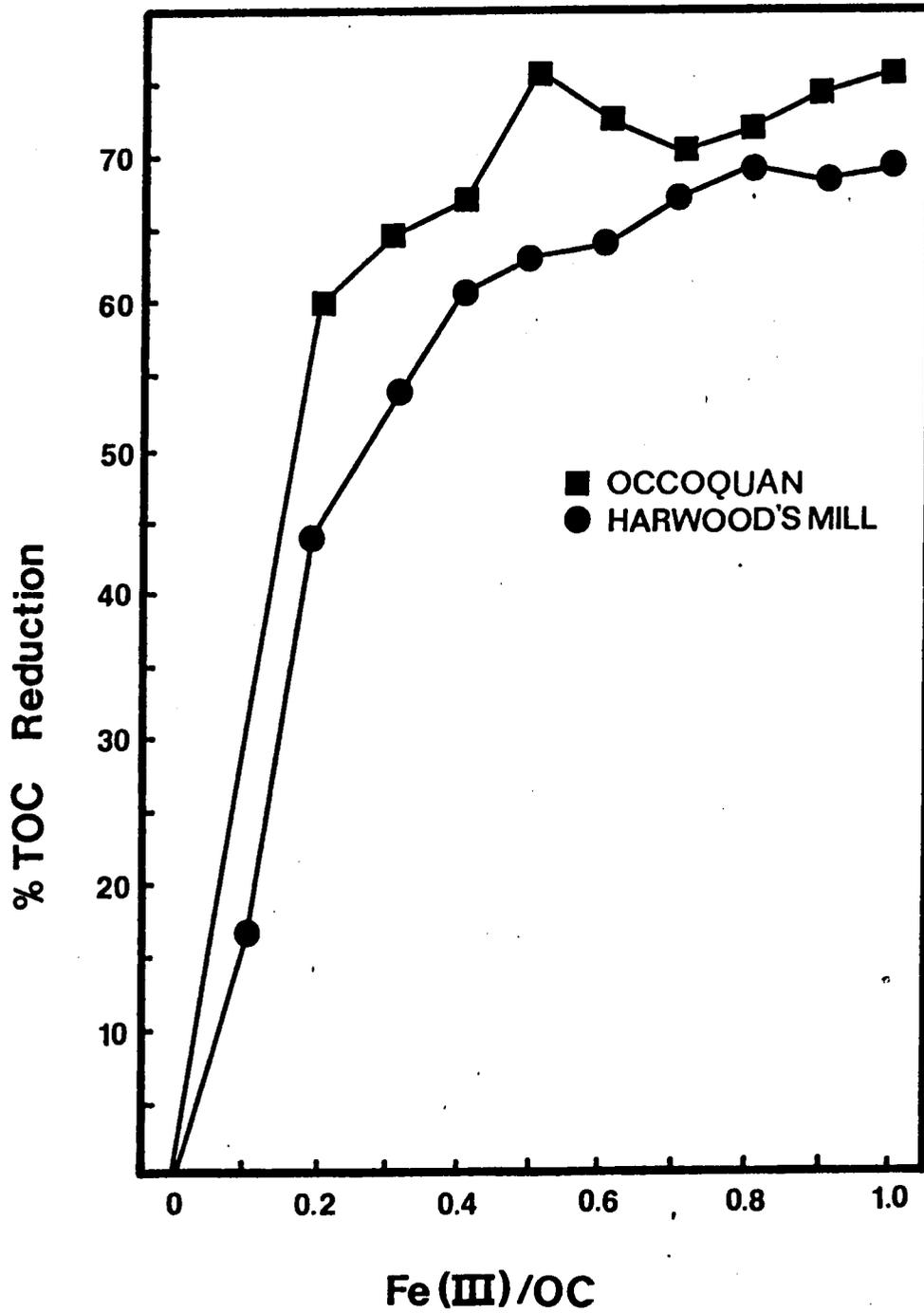


Figure 10. TOC removal by ferric sulfate coagulation as a function of the molar ratio of Fe(III) to organic carbon.

of Fe(III) to TOC. With this ratio, waters of different initial TOC concentrations can be compared on a common basis. TOC removal rapidly increased with dose up to an Fe/TOC ratio of 0.2. At ratios from 0.2 to 0.5, removal continued to increase, but at a much reduced rate. At ratios above 0.5 no additional removal occurred. The upper limit for TOC removal from Occoquan water was 76%, leaving a residual molecular weight distribution skewed sharply toward small molecules.

Harwood's Mill Sample: Size Distribution of TOC and OHP

The final Harwood's Mill sample was collected 9 March 1984. Preliminary data are given in Table 14. Water quality was very similar to that of the phase 1 samples except that suspended solids concentrations were about 50% higher. The TOC distribution is presented in Table 15. This size distribution resembled the phase 1 distribution, though DOC above 30 kd and POC levels were somewhat higher. Approximately 75% of the TOC was under 10 kd, compared to 82% in the phase 1 samples. The median molecular weight was 4.0 kd, again higher than the 2.7 kd median of the phase 1 samples. The size distribution of OHP also resembled that of earlier samples (Table 15). Specific yields for DOC under 0.5 kd and over 10 kd were lower than those of DOC between 0.5 and 10 kd, trends similar to those observed in phase 1 samples.

Cumulative size distributions for 0.10 mM and 0.25 mM

TABLE 14

Preliminary water quality analyses
of Harwood's Mill water collected
9 March 1984.

Temperature	9°C
pH	7.3
Alkalinity	58 mg/L
Chlorophyll a	17.6 mg/m ³
TSS	7.3 mg/L
VSS	3.6 mg/L
TOC	5.42 mg/L
THMFP-7	490 ug/L
TOXFP-7	1300 ug/L

TABLE 15

Molecular size distribution of organic carbon and organic halide precursors in Harwood's Mill Reservoir water collected 9 March 1983.

size range (kd)	OC ug/L	THMFP-7 ug/L	THM SY ¹	TOXFP-7 ug/L	TOX SY ²
POC	580	40	67	80	134
>30	620	25	37	105	166
10-30	300	20	66	20	73
5-10	895	75	86	275	306
1-5	1250	120	94	315	251
0.5-1	520	105	206	265	513
<0.5	1255	105	83	235	188
Bulk	5420	490	90	1295	239

1 SY = specific yield (ug THM/mg OC)

2 SY = specific yield (ug Cl/mg OC)

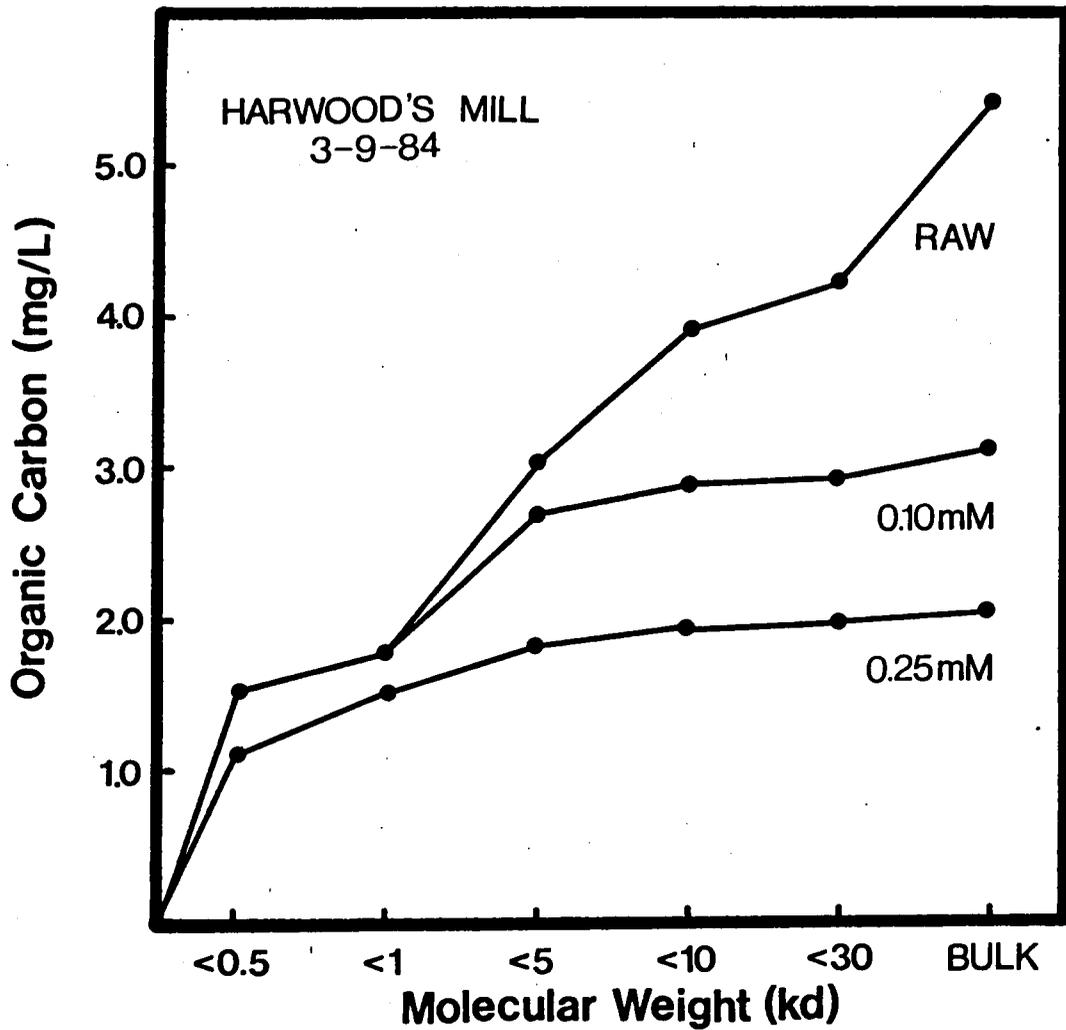


Figure 11. Cumulative size distribution of DOC in 0.10 and 0.25 mM Fe coagulated Harwood's Mill Reservoir water. The raw water distribution is shown for reference.

Fe treated waters are shown in Figure 11 with the raw water distribution as a reference. 43% (2.33 mg/L) of the TOC was precipitated at the 0.10 mM Fe dose and 62% (3.36 mg/L) at the 0.25 mM Fe dose. In comparison, 66% (5.85 mg/L) of the TOC in Occoquan water was precipitated with a 0.25 mM coagulant dose, an increase of 74%. The median molecular weight of residual organic matter decreased to 650 d with the 0.10 mM Fe dose, even though no DOC under 1 kd was removed. The median was further depressed to 470 d by the 0.25 mM Fe dose. Because of its heavier organic constituency, a 0.25 mM dose reduced the median molecular weight of Occoquan DOC to only 870 d. As was the case for prior samples, OHP were selectively removed compared to DOC (52% vs. 43% at the 0.10 mM dose and 70% vs. 62% at 0.25 mM) with removal efficiency directly related to molecular size (Figure 12).

Harwood's Mill Sample: THM and TOX Formation Rates

THM and TOX production was monitored for three size ranges of precursors (<1 kd, 1-5 kd, 5-10 kd). These data are summarized in the form of 1-day/7-day formation potential ratios in Table 16. The results were similar to those obtained from the September 1983 kinetics experiments (Table 6). As in previous experiments, it was found that TOX generation at pH 7 was more rapid than THM generation, that reaction rates declined with the molecular size of the precursors, and that precursor removal by coagulation was

TABLE 16

1-day/7-day THMFP and TOXFP ratios for three size ranges of DOC in raw and lab treated Harwood's Mill water collected 9 March 1983.

<u>size range (kd)</u>	<u>raw</u>	<u>1-day/7-day THMFP Ratio</u>	
		<u>0.10 mM Treated</u>	<u>0.25 mM Treated</u>
<10	0.48	0.40	0.38
<5	0.40	0.35	0.33
<1	0.31	0.31	0.27
		<u>1-day/7-day TOXFP Ratio</u>	
<10	0.61	0.58	0.57
<5	0.53	0.51	0.51
<1	0.45	0.46	0.41

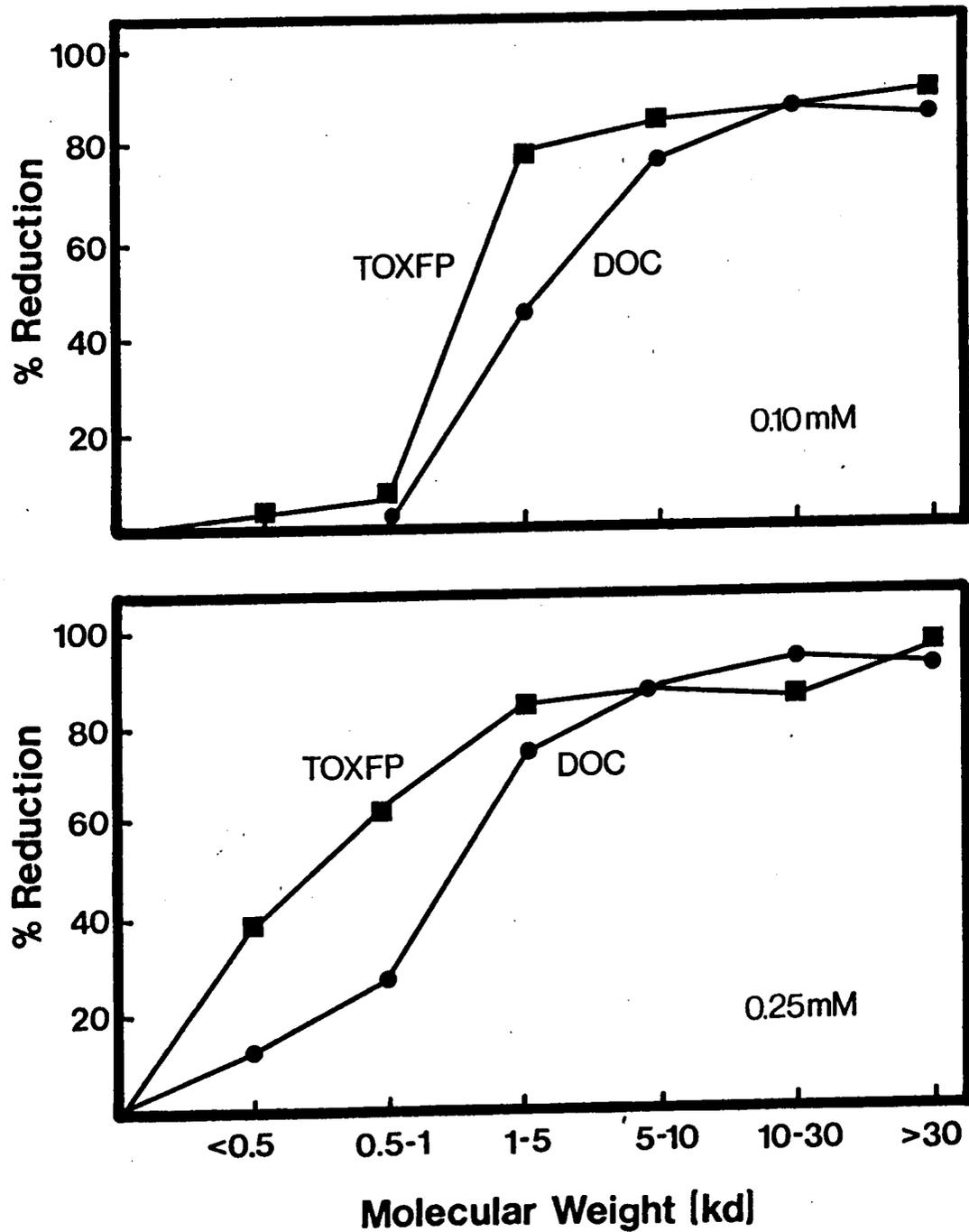


Figure 12a,b. DOC and TOXFP removal by molecular size for 0.10 and 0.25 mM Fe coagulated Harwood's Mill Reservoir water.

slightly biased toward faster reacting molecules.

Harwood's Mill Sample: Charge X Solubility Distributions

The solubility and charge distributions of DOC in three size ranges are presented in Table 17 for untreated Harwood's Mill water. The 1-5 kd and 5-10 kd size ranges were similar in composition. Like the Occoquan Reservoir samples, the dominant solubility fraction for DOC from 1-10 kd was the mesic, accounting for about 2/3 of the total. For compounds under 1 kd, there was a marked decline in polarity with the phobic fraction increasing to nearly 2/3 of the DOC, while the philic fraction declined to only 4%. Collectively, 15% of the DOC under 10 kd was classified as philic, 51% as mesic and 34% as phobic.

By charge, acidic compounds constituted 65% of DOC in the 5-10 kd range. This share dropped to 46% in the 1-5 kd class and further diminished to 40% for compounds under 1 kd. In contrast, the distribution of basic compounds was inversely related to molecular size. Only 2% of the DOC was present as basic compounds in the 5-10 kd range, but this share increased to 25% for the <1 kd class. The neutral fraction showed no relationship to molecular weight, but the solubility of neutral compounds steadily declined with molecular size. Nonpolar neutrals became the largest charge x solubility fraction for DOC under 1 kd.

As in the Occoquan sample, the charge distribution of residual DOC was radically different after coagulation,

TABLE 17

Charge x solubility matrix for DOC in three size ranges of Harwood's Mill water collected 9 March 1983.

5-10 kd Range

	<u>%Philic</u>	<u>%Mesic</u>	<u>%Phobic</u>	<u>Total</u>	<u>DOC*</u>
%Acids	11	45	9	65	58
%Bases	2	0	0	2	2
%Neutrals	10	17	6	33	40
Total	23	62	15	100	

1-5 kd Range

	<u>%Philic</u>	<u>%Mesic</u>	<u>%Phobic</u>	<u>Total</u>	<u>DOC*</u>
%Acids	5	38	4	46	51
%Bases	8	2	0	9	2
%Neutrals	12	27	5	44	47
Total	24	67	9	100	

0-1 kd Range

	<u>%Philic</u>	<u>%Mesic</u>	<u>%Phobic</u>	<u>Total</u>	<u>DOC*</u>
%Acids	2	17	21	40	46
%Bases	1	8	17	26	23
%Neutrals	1	9	24	34	31
Total	4	34	62	100	

* DOC is estimated charge distribution based on DOC measurements rather than area calculations from chromatograms.

while the solubility distribution remained approximately the same. Results for the 0.10 mM Fe treated water are given in Table 18. No data are presented for compounds under 1 kd because DOC, THMFP-7, and TOXFP-7 measurements indicated only marginal reductions in that size range. About 81% of the DOC was removed from the 5-10 kd class and 57% from the 1-5 kd class. Removal efficiency for each charge x solubility category is compared to DOC removal in Figures 13 and 14. Generally, acidic and basic compounds were selectively removed while neutral organics remained in solution. Actual DOC removal is the product of removal efficiency and abundance. Those calculations show that 58% of the precipitated DOC in the 1-10 kd range was acidic, 32% was neutral, and 10% basic. THMFP-7 and TOXFP-7 reductions also exceeded DOC removal, implying that the acidic fraction contained a disproportionate share of OHP.

The charge x solubility matrices for residual DOC after coagulation with a 0.25 mM dose is given in Table 19. DOC reductions were 92%, 84%, and 20% in the 5-10 kd, 1-5 kd, and <1 kd size classes, respectively. Trends in DOC removal were similar to those of the lower dose treatment. Charged compounds were precipitated more effectively than neutral compounds (Figures 15-17). The precipitated DOC was 58% acidic, 11% basic, and 30% neutral, nearly identical in composition to DOC precipitated by the 0.10 mM Fe dose, but quite different in composition from precipitated Occoquan

Table 18

Charge x solubility matrix for DOC in two size ranges of Harwood's Mill water treated at a coagulant dose of 0.10 mM Fe.

5-10 kd Range

	<u>%Philic</u>	<u>%Mesic</u>	<u>%Phobic</u>	<u>Total</u>	<u>DOC*</u>
%Acids	0	36	3	39	42
%Bases	0	0	0	0	0
%Neutrals	29	22	10	62	58
Total	29	58	13	100	

1-5 kd Range

	<u>%Philic</u>	<u>%Mesic</u>	<u>%Phobic</u>	<u>Total</u>	<u>DOC*</u>
%Acids	3	46	0	49	42
%Bases	0	0	0	0	0
%Neutrals	15	30	6	51	58
Total	18	76	6	100	

* DOC is the estimated charge distribution based on DOC measurements rather than area calculations from chromatograms.

TABLE 19

Charge x solubility matrix for DOC in three size ranges of Harwood's Mill Reservoir water treated at a coagulant dose of 0.25 mM Fe.

5-10 kd Range

	<u>%Philic</u>	<u>%Mesic</u>	<u>%Phobic</u>	<u>Total</u>	<u>DOC*</u>
%Acids	0	7	7	14	6
%Bases	0	0	0	0	0
%Neutrals	11	48	27	86	94
Total	11	55	34	100	

1-5 kd Range

	<u>%Philic</u>	<u>%Mesic</u>	<u>%Phobic</u>	<u>Total</u>	<u>DOC*</u>
%Acids	0	14	0	14	8
%Bases	0	0	0	0	0
%Neutrals	5	65	16	86	92
Total	5	79	16	100	

0-1 kd Range

	<u>%Philic</u>	<u>%Mesic</u>	<u>%Phobic</u>	<u>Total</u>	<u>DOC*</u>
%Acids	1	11	20	32	35
%Bases	1	5	17	23	24
%Neutrals	2	11	32	46	41
Total	4	27	69	100	

* DOC is the charge distribution based on DOC measurements rather than area calculations from chromatograms.

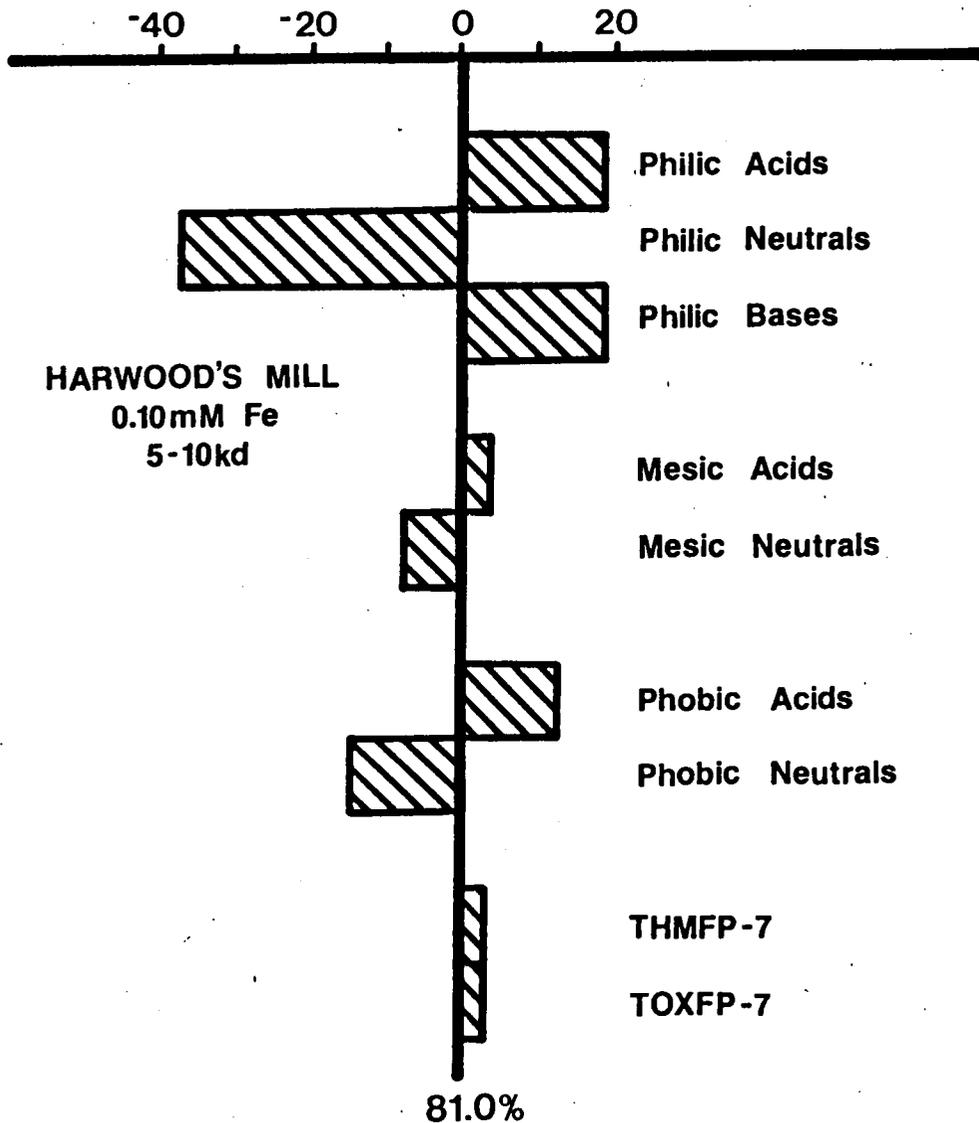


Figure 13. Removal efficiencies for charge and solubility groups in the 5-10 kd size range of 0.10 mM Fe coagulated Harwood's Mill Reservoir water. Removals are shown relative to DOC removal which was 81%.

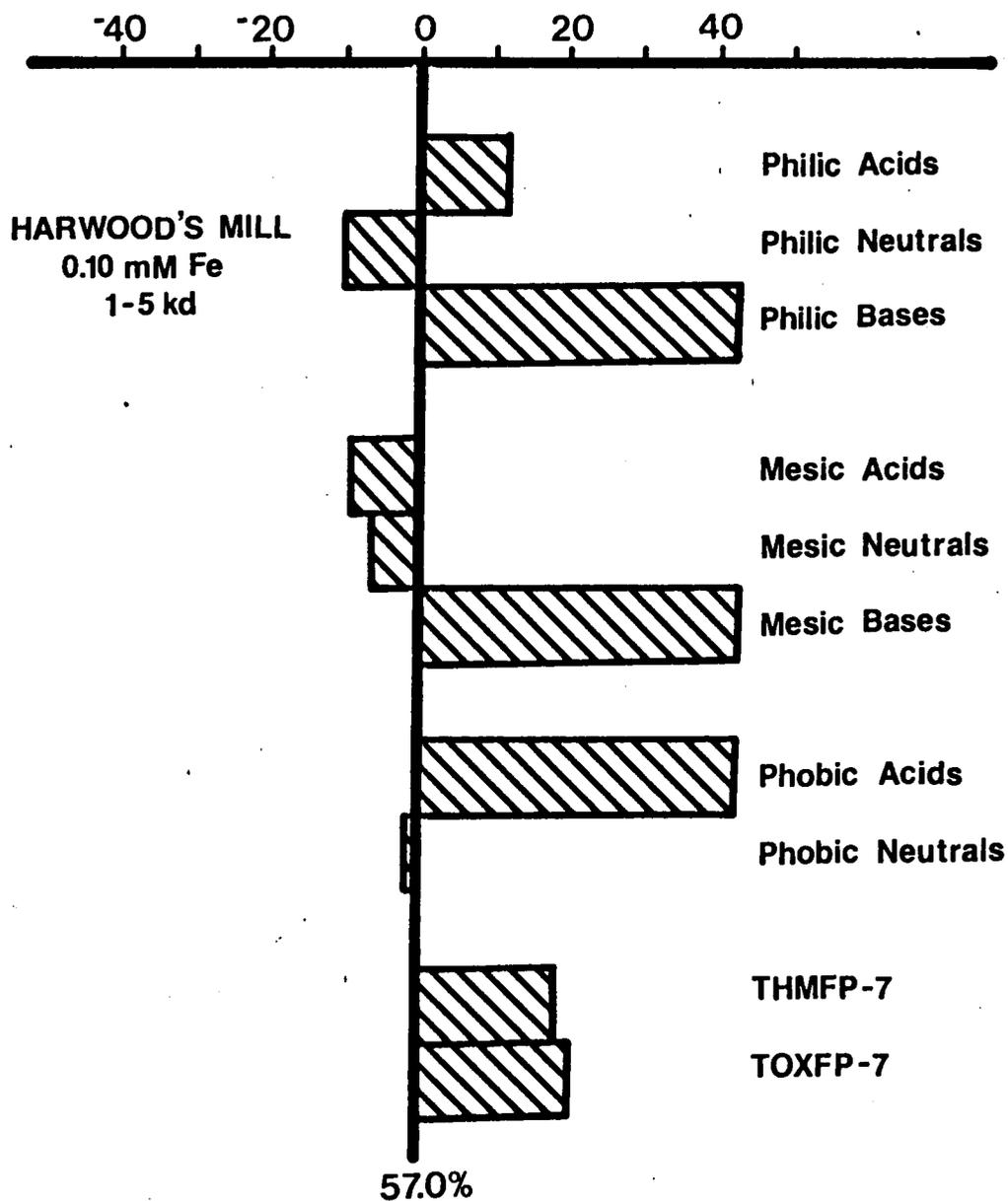


Figure 14. Removal efficiencies for charge and solubility groups in the 1-5 kd size range of 0.10 mM Fe coagulated Harwood's Mill Reservoir water. Removals are shown relative to DOC removal which was 57%.

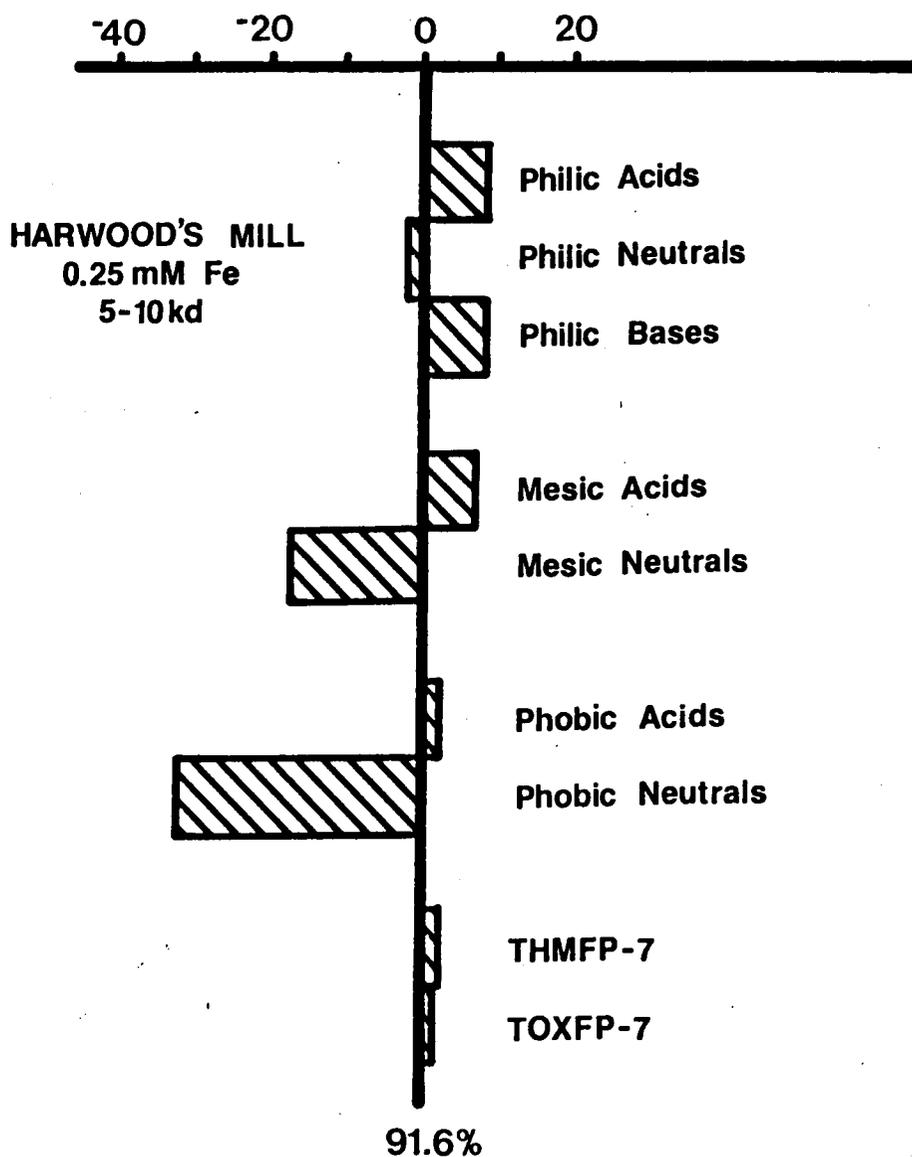


Figure 15. Removal efficiencies for charge and solubility groups in the 5-10 kd size range of 0.25 mM Fe coagulated Harwood's Mill Reservoir water. Removals are shown relative to DOC removal which was 92%.

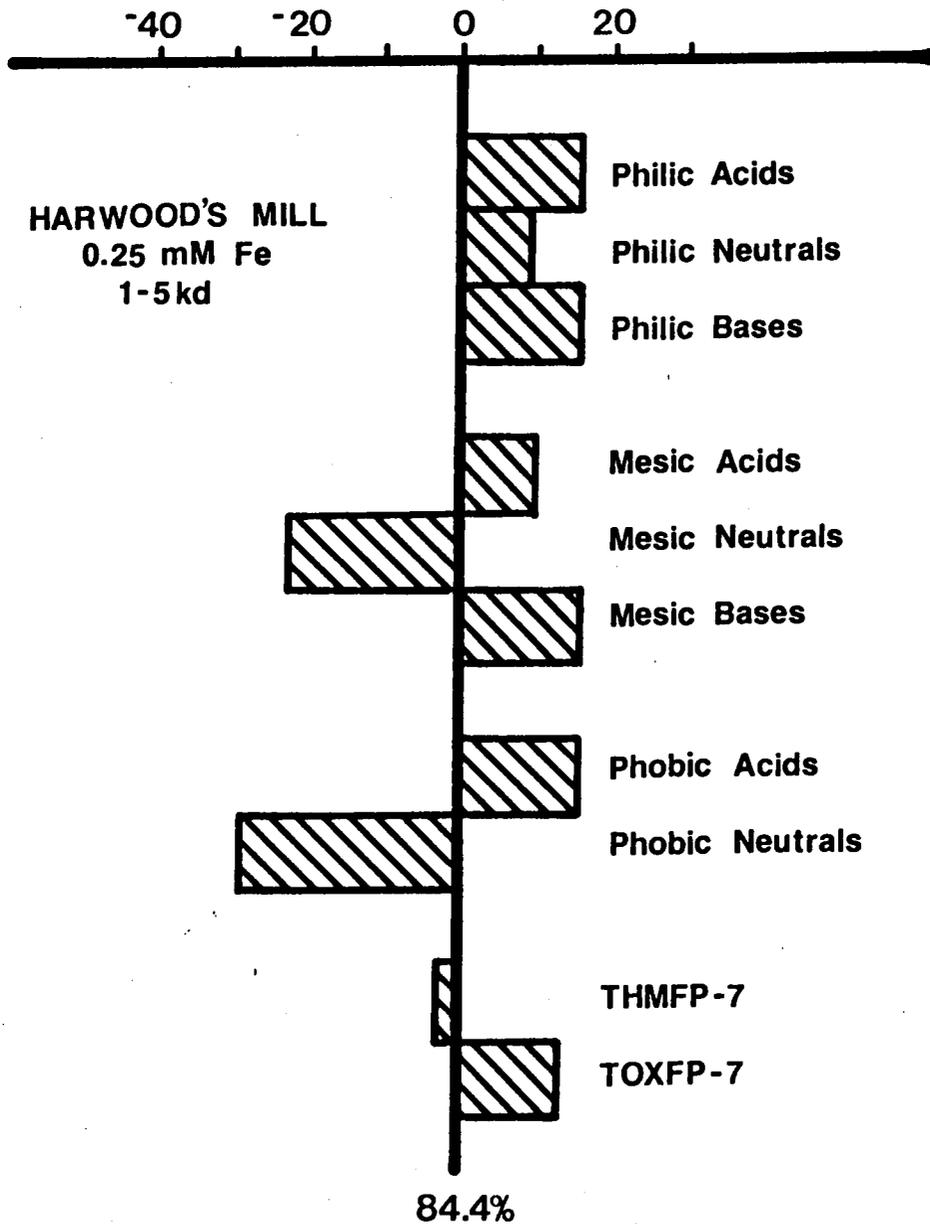


Figure 16. Removal efficiencies for charge and solubility groups in the 1-5 kd size range of 0.25 mM Fe coagulated Harwood's Mill Reservoir water. Removals are shown relative to DOC removal which was 84%.

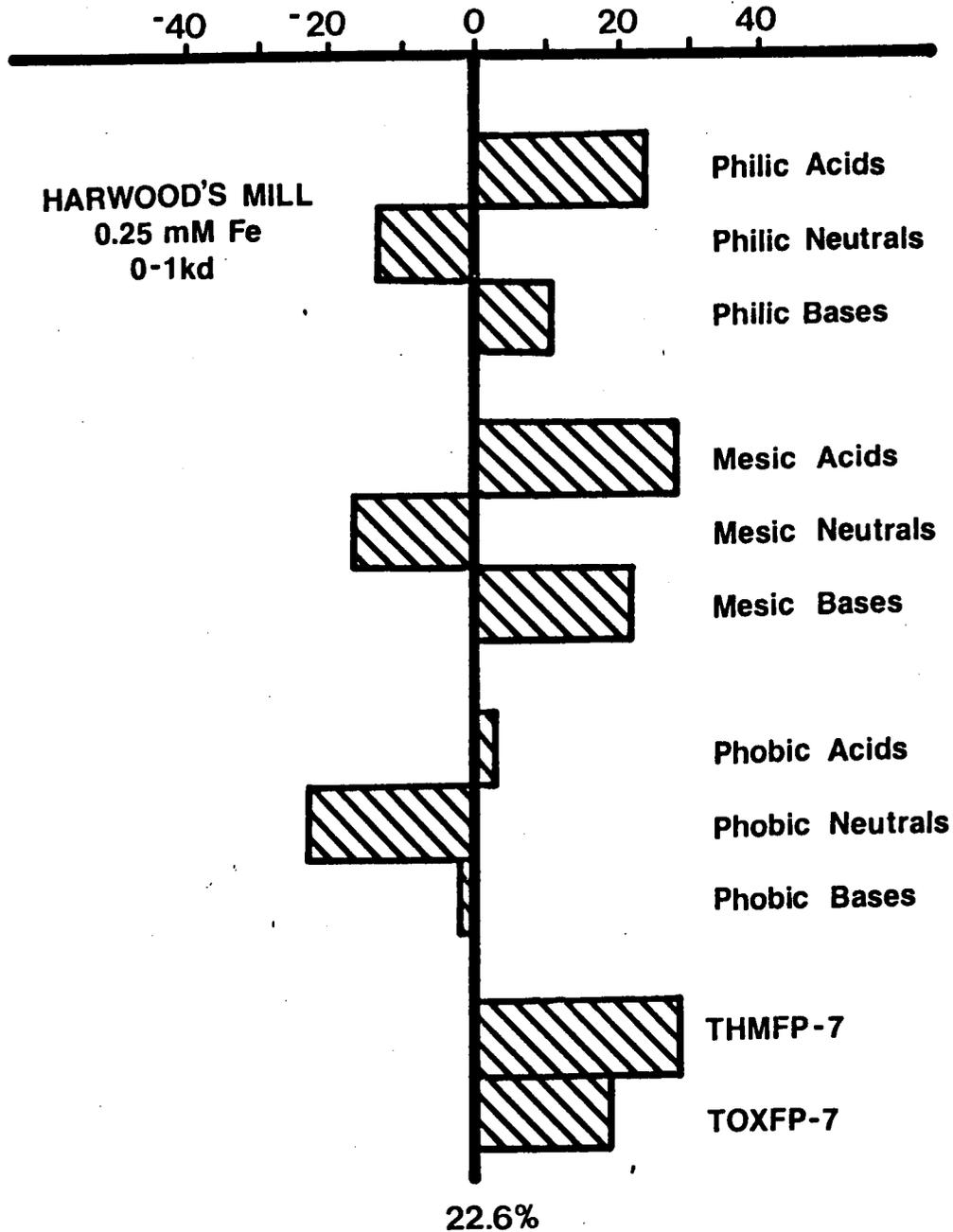


Figure 17. Removal efficiencies for charge and solubility groups in the 0-1 kd range of 0.25 mM Fe coagulated Harwood's Mill Reservoir water. Removals are shown relative to DOC removal which was 23%.

organics, which were 91% acidic, 8% neutral, and 1% basic. The major differences in DOC removal at the 0.25 mM Fe dose were enhanced removal of DOC under 1 kd (20% vs. 0%) and a more pronounced solubility effect on DOC removal. The greater the solubility, the higher the removal efficiency.

In Figures 18 and 19, the removal rate for each charge x solubility group is presented relative to the composition of the 0.10 mM Fe treated water rather than to the raw water. These figures highlight the DOC fractions that were most affected when the coagulant dose was incremented from 0.10 mM to 0.25 mM. Residual acids were still selectively removed, but for the first time, philic neutral compounds, which tended to remain in solution at the lower dose, also were preferentially precipitated. The removal of less polar mesic and phobic neutrals still lagged far behind DOC removal. THMFP-7 and TOXFP-7 reductions, which exceeded DOC removal at the 0.10 mM Fe dose, lagged behind DOC removal when the dose was incremented to 0.25 mM Fe, suggesting that after most acidic compounds have been removed the largest precursor group remaining is the nonpolar neutral fraction.

Additional information about the influence of size, charge, and solubility on DOC removal was obtained by analysis of variance (ANOVA). The ANOVA procedures confirmed that size, charge, and solubility were all significant factors ($P < 0.01$) affecting DOC removal. At the 0.10 mM dose, the largest factor was size, followed by

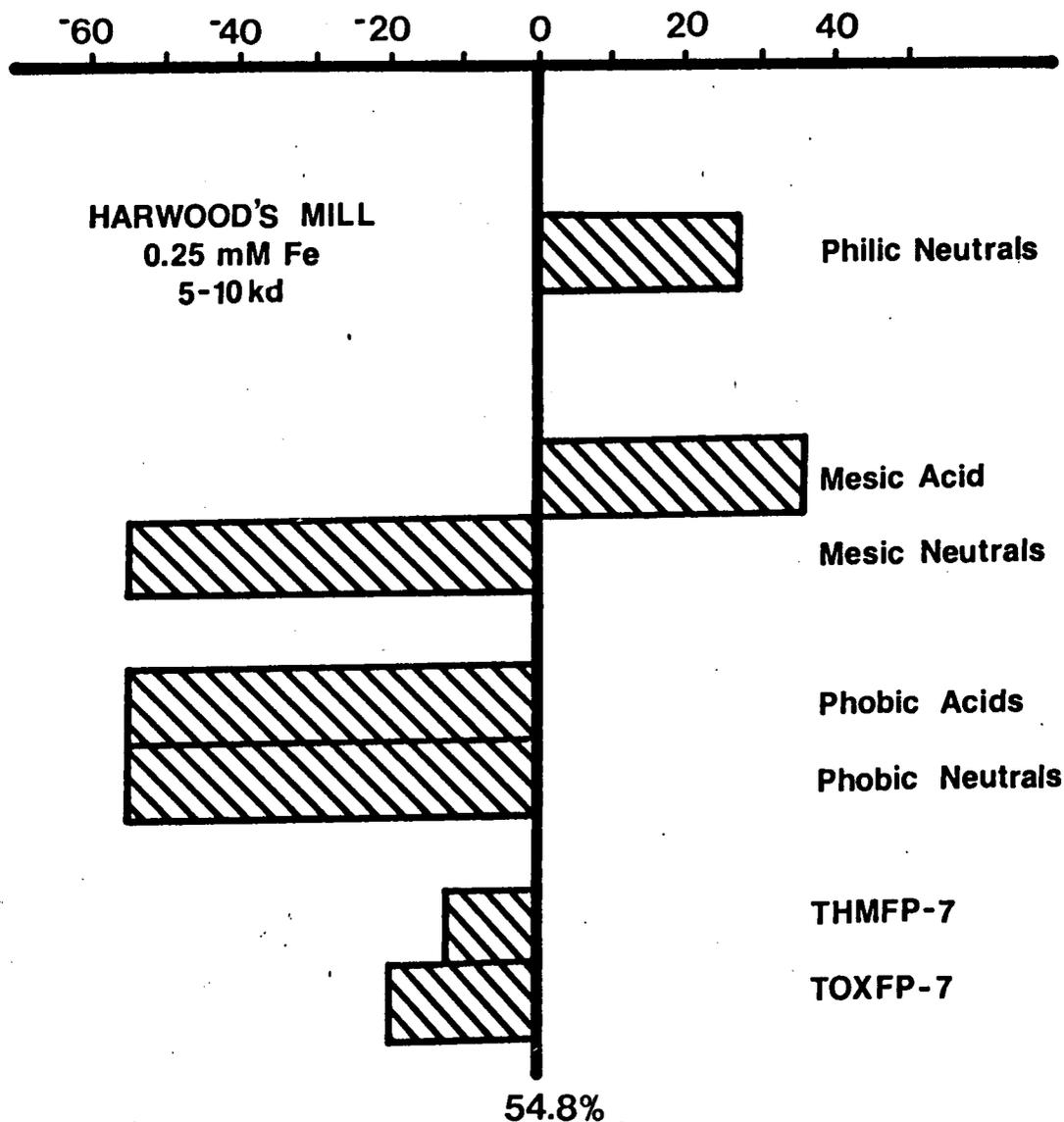


Figure 18. Removal efficiencies, relative to the composition of the 0.10 mM Fe coagulated water, for charge and solubility groups in the 5-10 kd size range of 0.25 mM Fe coagulated Harwood's Mill Reservoir water. Removals are shown relative to DOC removal which was 55%.

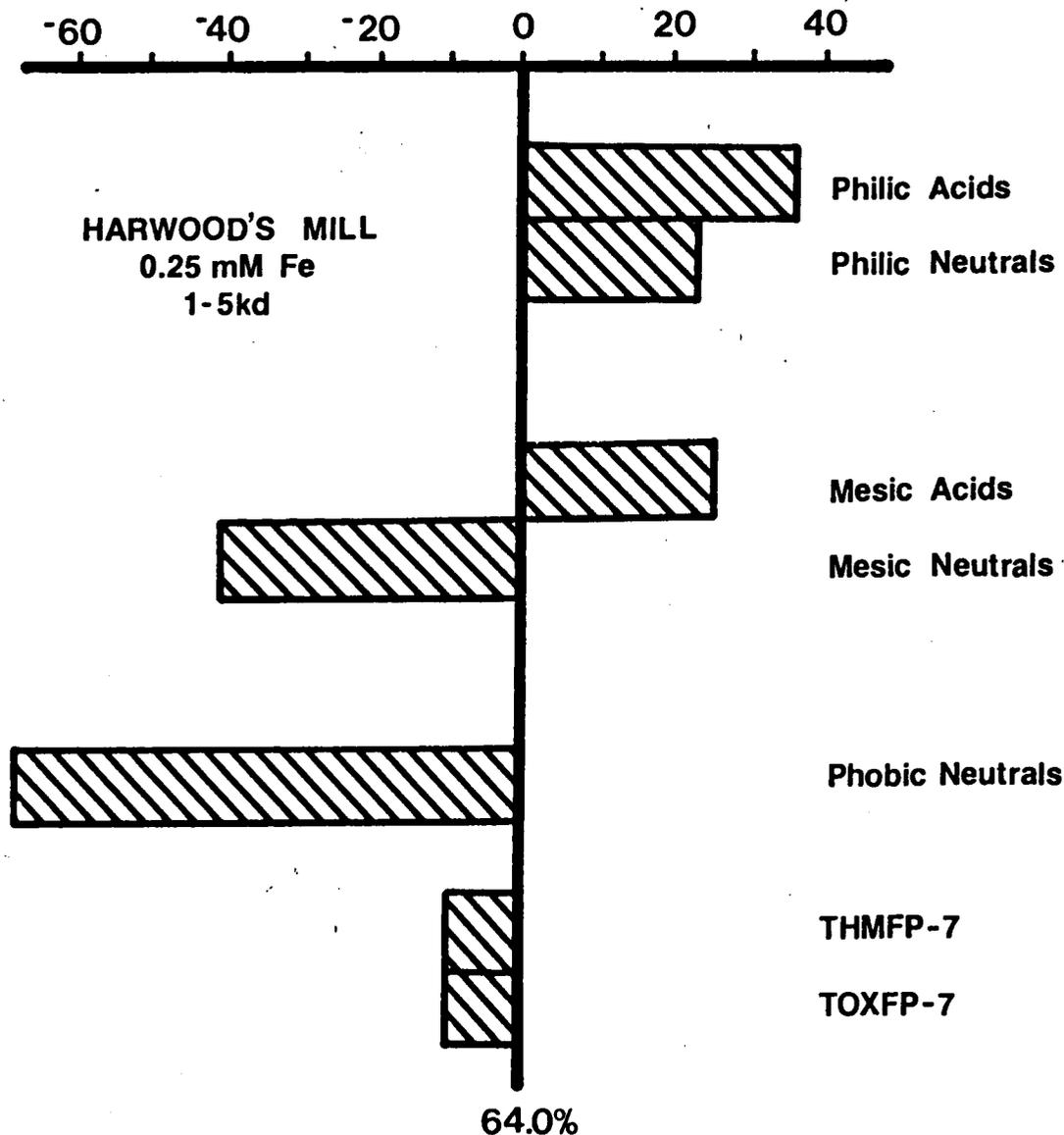


Figure 19. Removal efficiencies, relative to the composition of the 0.10 mM Fe coagulated water, for charge and solubility groups in the 1-5 kd size range of 0.25 mM Fe coagulated Harwood's Mill Reservoir water. Removals are shown relative to DOC removal which was 64%.

charge, then solubility. The results are similar to those obtained from analysis of the Occoquan data. Larger molecules were removed more effectively than smaller ones. Removals of acidic and basic compounds were similar, but statistically distinct. Neutral compounds were removed at about half the level of charged compounds. Philic compounds were removed at somewhat higher rates than phobic compounds, which in turn, were removed more effectively than mesic ones.

Similar results were found for 0.25 mM Fe treated water. Like the 0.35 mM treated Occoquan water, there was no difference in DOC removal in the 1-5 kd and 5-10 kd size ranges. This pattern reflects a serial relationship between DOC removal in successive size classes and coagulant dose. Again, acidic compounds were removed slightly more effectively than cationic compounds, while both were removed much more completely than neutrals. The effect of solubility was accentuated at this higher dose, with philics removed better than mesics and phobics removed least of all.

The results of analysis of DOC removal at the 0.25 mM dose relative to the composition of the 0.10 mM treated water were similar to those obtained by comparing the removal to the raw water composition. The analyses of variance also showed that all interaction effects were significant ($P < 0.01$), verifying that the effects of any combination of size, charge, and solubility on DOC removal

are not simply additive, but synergistic.

A comparison of estimated DOC reductions in treated waters based on chromatogram area calculations and DOC measurements of ultrafiltrates is shown in Table 20. Like Occoquan water, there was good agreement between the two estimates, though reductions based on area calculations were consistently higher. Comparison of charge distributions within size ranges also showed good agreement between area estimates and DOC estimates (Tables 17-19), confirming the validity of uv absorbance to estimate DOC distribution within a given size range.

Harwood's Mill Sample: TOC Precipitation vs. Coagulant Dose

TOC removal from Harwood's Mill Reservoir water as a function of coagulant dose is shown in Figure 10. Like treated Occoquan water, removal increased rapidly with coagulant dose up to an Fe/TOC ratio of 0.2, which corresponds to a 0.10 mM Fe dose, then continued to slowly increase to about 0.5, which corresponds to a 0.25 mM Fe dose. No additional removal occurred at ratios beyond 0.5. The upper limit for TOC removal in the Harwood's Mill water was approximately 70% (3.79 mg/L) compared to 76% (6.73 mg/L) for Occoquan water, an increase of nearly 78%.

Ultrafilter Performance Evaluations

Data on ultrafilter performance tests are given in Table 21. Good replicability was observed between membranes. It was also found that virtually all the organic

TABLE 20

Comparison of DOC removal efficiencies, calculated from area reductions in HPLC chromatograms, to values obtained from the initial DOC size fractionation of Harwood's Mill water.

<u>Treatment</u>	<u>Removal by Size Range</u>					
	<u>5-10 kd</u>		<u>1-5 kd</u>		<u>0-1 kd</u>	
	OC	Area	OC	Area	OC	Area
0.10 mM	76%	81%	44%	56%	0%	0%
0.25 mM	87%	92%	74%	84%	20%	23%

carbon applied to the ultrafiltration system was recoverable. However, the results also confirmed that molecular weight cutoffs of YM series ultrafilters were broad. Polyacrylic acids, with their linear polymeric structure and polyanionic charge were largely retained by 10 kd exclusion membranes even when the average molecular weight of the acid molecules was 2 kd. The smaller the charge and the more globular the molecule, the closer the results conformed to the ideal.

TABLE 21

Summary of ultrafilter performance evaluations.

<u>Test Compound</u>	<u>Molecular Weight</u>	<u>Test Filter</u>	<u>Expected Retention</u>	<u>Actual Retention</u>
Polyacrylic Acid	5,000	YM-10	50%	89.5 + 0.8*
Polyacrylic Acid	2,000	YM-10	50%	77.4 + 0.9
Cytochrome c	12,384	YM-2	100%	78.0 + 1.3
Cyanocobalamin	1,355	YM-2	100%	87.8 + 1.9
NADP	765	YM-2	50%	74.6 + 1.1

* standard deviation

DISCUSSION

Overview

The Phase 1 samples provided baseline data for the more comprehensive work that followed. Many of the results have been reported by other researchers (see the section on DOC removal by coagulation in the Introduction). Among these are that coagulation is effective for DOC removal, that DOC removal is a function of dose, that some portion of the DOC remains in solution regardless of coagulant dose, and that organic halide precursors are usually removed selectively. Other results have not been previously reported; these provided some insight into DOC removal mechanisms. Among these were that DOC removal, organic halide formation rate, and organic halide specific yields were related to molecular size. These observations raised additional questions. Was molecular size a real factor in DOC removal or was removal related to some other factor that was correlated with molecular size? Why did specific yields and formation rates vary so much among size ranges? To address these questions, a comprehensive sample processing scheme was developed during the second phase of the project. This approach provided data on the size, charge, and solubility distribution of DOC, as well as on the formation rate of THM and TOX within discrete size ranges of precursors. With

detailed descriptions of the DOC characteristics of both raw and coagulated waters, conclusions about DOC removal by coagulation could be drawn.

Unlike the results section, the discussion is organized by subject rather than by experiment. The topics that will be covered include: the DOC fractionation scheme, the size distribution of DOC in untreated water, the role of molecular size in DOC removal, the role of charge and solubility in DOC removal, and the effect of coagulation on the kinetics of organic halide formation.

DOC Fractionation Scheme

The combination of ultrafiltration, IEC, and HPLC made possible quantitative analysis of the size, charge, and solubility characteristics of DOC. With these techniques, DOC compositional changes effected by any treatment operation or sequence can be studied in detail. This approach to DOC analysis was adapted from a preparative fractionation scheme presented by Leenheer (1981). Leenheer fractionated DOC by selective sorption onto XAD and ion exchange resins, followed by desorption and concentration for further analyses. With this procedure, Leenheer was able to resolve DOC into hydrophilic and hydrophobic acids, bases, and neutrals. In my approach, reverse-phase HPLC was substituted for XAD resins for partitioning DOC into arbitrary solubility categories. HPLC offers enhanced resolution, reduced analysis time, and, depending upon the

system, can operate in either an analytical or preparative mode. Leenheer's ion exchange procedure, with macroporous resins, was retained because the available HPLC system was not equipped for preparative IEC. However, instead of desorbing organics from resins for quantification, anionic and cationic DOC within each solubility category was determined analytically by area reductions in HPLC chromatograms generated before and after sample elution through ion exchange columns. This method was simpler and faster than preparative isolation and circumvented problems of sample dilution and variable desorption efficiency. This conventional column IEC procedure could be replaced by preparative HPLC with ion exchange columns, just as reverse-phase HPLC was substituted for XAD resins. The addition of ultrafiltration to isolate DOC in nominal size ranges added a further dimension to the fractionation scheme.

One limitation of this scheme was that DOC heavier than 10 kd could not be processed without compromising the performance of the HPLC column. Another problem was that the molecular weight exclusion limits of the ultrafilters are broad. Many factors influence the movement of molecules across the ultrafilter: molecular characteristics, such as shape and charge; membrane characteristics, like pore-size variation and surface charge; and operating conditions, including temperature, pressure, DOC concentration, and

clogging (Staub *et al.* 1984). Aiken (1985) evaluated Amicon series UM ultrafilters using polyacrylic and fulvic acids. These anionic compounds were repelled by the negative surface charge of the membranes and by one another, especially as concentrations increased. The result was that compounds were retained by membranes which they should have permeated based on a strict molecular weight criterion. For polyacrylic acids, the effect was compounded by the linear structure of the molecules and the large number of anionic sites along the polymer. Several compounds were tested, with three membranes used per test; good reproducibility was found among membranes (Table 21). However, these analyses also demonstrated that polymeric and/or charged molecules were retained by YM series membranes to a greater extent than had been expected on the basis of a strict molecular weight criterion. Consequently, the molecular weight distributions of DOC presented here can be considered only approximate. The actual distributions were quite probably shifted toward the lower molecular weights, especially among acidic compounds, the largest DOC fraction.

Unfortunately, errors caused by molecular shape and charge also plague size exclusion chromatography, the most commonly used alternative for assigning approximate molecular weights. Also, DOC recovery is constrained by variable desorption efficiency and irreversible adsorption. In contrast, the membrane evaluation tests demonstrated that

nearly 100% of the DOC applied to an ultrafiltration system can be recovered. For these reasons and because ultrafiltration is faster and simpler than size exclusion chromatography, it is probably the better method for processing large numbers of samples.

Size Distribution of DOC in Untreated Water

The molecular weight distribution of DOC was constructed for several Harwood's Mill Reservoir raw water samples (Tables 5 and 15) and one Occoquan Reservoir sample (Table 8). As detailed in the Results section, the size distribution in the two reservoirs was quite different. The median molecular weight of DOC in the Occoquan sample was 9.7 kd compared to 2.7 kd for Phase 1 Harwood's Mill samples.

Other researchers have analyzed the size structure of dissolved organic material. Schnoor *et al.* (1979), using size exclusion chromatography, found that 90% of the DOC in the Iowa River was under 3.0 kd and that 75% of the THM originated from precursors in that size range. In a Swiss lake, 42% of the DOC was under 0.5 kd and only 18% was heavier than 4 kd (Davis and Gloor 1981). These weight distributions are much lighter than those determined for the Occoquan and Harwood's Mill Reservoirs. At the other extreme, the distribution in a Vermont lake, determined by ultrafiltration, included many heavy molecules (Allen 1976). Compounds larger than 100 kd accounted for the largest

portion of the TOC, followed by organics under 0.5 kd. Likewise, Manka and Rebhun (1982) found a bimodal distribution when they studied organics in tertiary wastewater effluent; compounds over 20 kd and under 0.5 kd were the largest fractions. In Lake Mary, Hall and Lee (1974) found molecular weights ranging above 50 kd with only 4% of the DOC under 0.7 kd. While in Mississippi River water, nearly 50% of the DOC was under 1 kd (Anderson and Maier 1979). Obviously, the weight distribution of organic carbon in surface waters varies widely. The major determinant is probably the abundance and source of allochthonous humic material. As reviewed in the Introduction, these molecules vary extensively in structure and molecular weight and are considered to be the largest source of organic halide precursors in surface waters.

Molecular Size as a Factor in DOC Removal

The molecular size distribution of DOC was identified as the largest determinant of DOC removability by coagulation. Compared to Harwood's Mill, increased removability of DOC from Occoquan water can largely be attributed to its higher median molecular weight. Statistical analysis established that the size effect was real, not a consequence of correlation between size and any other measured variable. A size effect has been reported for other types of adsorbent processes. Manka and Rebhun (1982) found that lime addition preferentially removed

heavier organics; Davis and Gloor (1981) found similar results for aluminum oxide adsorption. Sorption of organics by powdered activated carbon is also biased toward heavy molecules (El-Dib and Badaway 1979). This size effect does not appear to be related to solubility, at least in this study. For the present, the reason for the size discrimination is unknown.

While DOC removal varied with molecular size, rarely was all the DOC in a particular size range eliminated by coagulation. For DOC heavier than 10 kd, removal efficiencies of 90% were readily effected at moderate coagulant doses, but even large dose increments only slightly enhanced removal from those size ranges that had been most affected at lower doses. This result is consistent with previous reports that up to 90% of humic material can be removed by coagulation (Hall and Packham 1965, Narkis and Rebhun 1975).

The primary effect of dose increments was enhanced DOC removal in progressively smaller size ranges. At times, DOC removal appeared to proceed sequentially from one size range to the next smaller as coagulant dose was incremented, but this trend did not extend to the smallest size ranges. Organic compounds under 1.0 kd could be marginally affected at high coagulant doses, but molecules under 0.5 kd were unaffected by ferric coagulant. As dose increased, a point was reached where no additional DOC was removed in any size

range, indicating that factors other than molecular size influence the removal process. The apparent ineffectiveness of coagulation in removing organics under 0.5 kd partly explains why THM, dichloroacetate, trichloroacetate, and chlorinated acetones, the major halide substituted products of the reaction between chlorine and DOC, are poorly removed by coagulation. A further implication is that so-called VOCs (volatile organic compounds), which are scheduled for regulation by the USEPA, may also be unremovable by coagulation.

Charge as a Factor in DOC Removal

The charge distributions of DOC in both Harwood's Mill and Occoquan Reservoir waters were dominated by acidic and neutral compounds. Organic bases were only a small component. Similar results were reported by Leenheer and Huffman (1976) for groundwaters from Colorado and Wyoming. But in a subsequent study, Leenheer (1981) found that 27% of the DOC in South Platte River water was basic. The distribution of basic compounds was inversely related to molecular weight suggesting they were produced autochthonously by microbial activity rather than transported into the reservoirs with humic material.

Statistical analyses of DOC removal data established that charge was second only to molecular size as a factor influencing removability of organic molecules. Both anionic (acidic) and cationic (basic) molecules were selectively

removed, while neutral compounds remained in solution. Within a specified size range, removal efficiencies for acids and bases were usually similar. Despite this similarity, basic compounds were not an important component in precipitated DOC because they were relatively abundant only below 1 kd where they could not be readily removed by coagulation. Most of the organic matter above 1 kd was acidic. Size, charge, uv absorbance, and the observation that no precipitates were formed upon acidification classified these compounds as fulvic acids. In the 1-10 kd range, Occoquan water contained twice as much acidic DOC as Harwood's Mill water. Increased abundance of acidic compounds in the Occoquan Reservoir sample was the secondary reason for the enhanced removability of organics compared to Harwood's Mill samples.

Some authors have noted that humic acids are preferentially precipitated over fulvic acids. This selection has been attributed to the higher charge density of fulvic acids (Babcock and Singer 1979, Amy and King 1980). My data suggest that higher charge density should favor fulvic acid removal. A more probable explanation for selection of humic acids is their larger molecular size.

The dominant iron hydrolysis species at pH 5 are cationic. Anionic molecules, like fulvic acids, can react directly with dissolved iron to form insoluble complexes or can bind to cationic sites on floc particles. Evidence for

direct precipitation is based on reports that the precipitation of humic material by cationic coagulants is stoichiometric (Black and Christman 1963, Black *et al.* 1963, Hall and Packham 1965, Edzwald *et al.* 1977, Narkis and Rebhun 1977, Glazer and Edzwald 1979). At the same time, Semmens and Field (1980) and Davis and Gloor (1981) have shown that organics can adsorb onto aluminum hydroxide particles. In a comprehensive study of fulvic acid precipitation by alum, Dempsey *et al.* (1984) found both mechanisms operative. Direct reaction with dissolved aluminum was favored at low Al concentrations and pH values near 5, while adsorption to aluminum hydroxide dominated at higher pH and higher Al concentrations.

Coagulation of Harwood's Mill and Occoquan water precipitated basic compounds nearly as well as acidic ones. Apparently bases also complex with acidic molecules and iron through charge neutralization. Removal of neutral compounds is related to their polarity, but the most likely mechanism is sorption unto less polar organic domains of floc.

Solubility as a Factor in DOC Removal

In both Harwood's Mill and Occoquan reservoirs, the solubility distribution of DOC approximated a normal distribution. About 2/3 of the organics in the 1-10 kd range were classified as mesic in terms of solubility with the residual divided between the philic and phobic fractions. Other investigators, using XAD resins, have

partitioned naturally occurring DOC into hydrophobic and hydrophilic categories. Hoehn *et al.* (1984) sampled water from Claytor Lake in southwest Virginia over a one year period and found approximately 2/3 of the DOC was hydrophobic in character. Leenheer (1981) analyzed water from the South Platte River and reported more than half the DOC was hydrophobic. Because of methodological differences, these results cannot be directly compared to mine. But assuming that their hydrophobic fractions would include my phobic and most of my mesic fractions, then there is similarity.

The general trend toward decreasing solubility of organic compounds as their molecular weight increases was not observed in the size ranges examined. In the Harwood's Mill sample, the highest levels of phobic compounds were found below 1 kd. Charge appeared to be unrelated to solubility also. Though ionized compounds are expected to be more soluble than neutral ones, acidic, basic, and neutral compounds were broadly distributed over all solubility classes.

Solubility significantly influenced DOC removal in samples from both reservoirs. ANOVA results from both reservoirs showed that philic and phobic compounds were removed at similar levels while mesic compounds, the largest solubility class, were precipitated only about half as effectively. I hypothesize this pattern is the consequence

of two distinct processes. The first accounts for selection of philic compounds. Because solubility in aqueous solution is related to polarity, the philic fraction should include the most polar molecules. Polar molecules interact with hydrolyzed iron in the same way that ionized molecules do, with the degree of interaction proportional to the polarity. According to this model, philic compounds would be more removable than mesic ones with phobics the least affected. Interestingly, even fulvic acid removal by alum coagulation at pH 5 has been shown to follow this pattern (Dempsey et al. 1984). The selection of phobic compounds may be due to the affinity of hydrophobic molecules for one another. As organic molecules condense with hydrolyzed iron to form floc, hydrophobic molecules in solution should be attracted to the less polar organic domains created there. In this model, phobic molecules would be selectively removed over mesic compounds, leaving philic compounds as the least affected. This removal pattern has been found for activated carbon adsorption (El-Dib and Badaway 1979). The conjunction of the two models accounts for selective removal of both philic and phobic compounds over mesic ones.

Effect of Coagulation on Organic Halide Formation

Except for anomalously high 1-day/7-day TOXFP ratios in the Occoquan 5-10 kd range, the formation rates of TOX and THM in untreated water were similar in both reservoirs, indicating that the same types of precursors were present.

But, the reservoir samples did differ in their THM and TOX specific yields. The specific yields for bulk Occoquan water were 40% greater than corresponding values for bulk Harwood's Mill water. This difference was due to the higher proportion of fulvic acids in Occoquan water. The THM and TOX specific yields from organic compounds between 1 and 10 kd in Harwood's Mill Reservoir water were 88 and 274 ug/mg, respectively, and from those in the Occoquan Reservoir 142 and 389 ug/mg, respectively. Compared to Harwood's Mill water, the THM and TOX specific yields were 61% and 42% higher, respectively, in the Occoquan water. In this same range, fulvic acids accounted for 54% of the DOC in the Harwood's Mill sample and 81% in the Occoquan sample, a 50% higher abundance. Since the only significant difference in DOC composition was the higher proportion of fulvic acids, and the higher specific yields closely corresponded to the higher fulvic acid concentration, it appears that fulvic acids were the main group of organic halide precursors in untreated water. In addition, the correlation between selective reductions in THM and TOX formation potentials and selective removal of fulvic acids also indicates that fulvic acids accounted for a disproportionate share of organic halide precursors. Finally, selective fulvic acid removal also corresponded to reductions in formation rates of organic halide compounds. To summarize, in both reservoirs fulvic acids were the dominant group of organic halide

precursors because of their abundance, their high specific yields, and their rapid OX formation rates. Other studies have also concluded that humic compounds are the largest precursor group in untreated waters (Stevens *et al.* 1976, Rook 1977, Babcock and Singer 1979, Oliver and Lawrence 1979, Oliver and Visser 1980, Christman *et al.* 1983, Kringstad *et al.* 1983, Reckhow and Singer 1984). In particular, Oliver and Visser (1980), Veenstra and Schnoor (1980), and Joyce *et al.* (1984) have specified fulvic acids between 1 and 10 kd as the largest source of OHP. This result is consistent with the Harwood's Mill data. Organics between 1 and 10 kd had high specific yields and accounted for about half the DOC. In Occoquan Reservoir water, specific yields were also high but only a third of the DOC was between 1 and 10 kd in size.

Though fulvic acids were the dominant source of OX precursors in untreated waters, they were not necessarily the largest or most important precursor group in coagulated waters. Despite the fact that nearly all fulvic acids could be precipitated with a sufficiently high coagulant dose, their removal did not eliminate the formation of organic halide compounds. After stripping away fulvic acids by coagulation, some patterns recognizable in raw water data became enhanced. In both Harwood's Mill and Occoquan Reservoir samples, THM and TOX specific yields for organic compounds under 1 kd were markedly lower (except in the

final Harwood's Mill sample). Similar results have been reported by Joyce *et al.* (1984). Also, the formation of THM and TOX was slower for DOC under 1 kd, at least in Harwood's Mill Reservoir samples. No similar data are available from the Occoquan Reservoir sample, though the trend was toward slower reaction rates with decreasing molecular size. These shifts imply that many of the smaller precursors are different from the fulvic acids that dominate the larger size ranges. The same pattern can be seen in the heavier size ranges after the fulvic acids have been largely eliminated. The specific yields and OX formation rates of the residual organics were reduced compared to those in untreated water. Some characteristics of this refractory precursor group can be identified. First, they were almost entirely neutral compounds. Second, they were largely classified in the less polar mesic and phobic fractions. These two factors explain the lower specific yields. Formation of THM and many TOX compounds requires carbonyl or hydroxyl moieties which are undoubtedly less abundant among compounds characterized as nonpolar neutrals than among fulvic acids. It was also evident that these compounds reacted with chlorine to generate organic substituted products at a slower rate than fulvic acids. The reason for this unclear, but may be related to the types of reaction sites available.

The reaction rate of organic halide precursors varies

widely. Some molecules react immediately while others are still contributing THM after as long as 300 h (Young and Singer 1979). For example, methyl ketones are known to generate THM more slowly than dihydroxyl phenolic compounds (Rook 1977, Dore *et al.* 1982), which are common among humic material. The rate limiting step is enolization of the ketone which is favored by high pH. Below 1 kd, the abundance of fulvic acids declines, while that of neutral aliphatic compounds increases. This factor may explain why slower reaction rates occurred not only in the small size classes, but also among heavier residual organics after the fulvic acids had been eliminated by coagulation.

The precipitation of DOC by coagulation and settling minimized the formation of organic halide compounds for at least three reasons. First, organic halide precursors were precipitated more effectively than DOC in general. Second, heavier organics, which included more faster reacting precursors, were selectively precipitated. Third, the faster reacting precursors in every size range tended to be preferentially precipitated. All three of these observations can be explained by selective removal of fulvic acids. Despite these trends, finished waters from both reservoirs could generate THM in excess of the 0.10 mg/L MCL. The problem is that even though fulvic acids can be precipitated quite effectively at elevated coagulant doses, the residual, low molecular weight, nonpolar, neutral

organics are present in sufficient concentration to produce more than 0.10 mg/L THM over a several day period. The concentration of this type of precursor, not the fulvic acids, determined whether coagulation would control THM formation sufficiently for regulatory compliance. In waters like these, the most effective treatment sequence may be coagulation, at sufficient dosage to remove fulvic acids, followed by some type of activated carbon process to reduce the concentration of smaller neutral organics. If activated carbon proves ineffective or uneconomical, chloramines may be required for disinfection.

Effect of Coagulant Dose on DOC Removal

The effect of coagulant dose on DOC removal was presented in Figure 10 for both Occoquan and Harwood's Mill Reservoirs. These DOC removal curves can be arbitrarily divided into three sections with breakpoints at Fe/OC ratios of 0.2-0.3 and 0.5. The coagulant doses used to generate treated water for chromatographic analyses were chosen to be near those breakpoints. Occoquan Reservoir water was treated at Fe/OC ratios of 0.3 and 0.5, and Harwood's Mill Reservoir water was treated at ratios of 0.2 and 0.5. By comparing the DOC composition at the first breakpoint with the composition at the second, the DOC removal trends in each portion of the curve can be ascertained. Initially, removal increased very rapidly with dose up to ratios of 0.2-0.3. In this region, over 80% of the organics above 5

kd were removed. These compounds consisted largely of fulvic acids. At ratios between 0.2 and 0.5, removal continued to increase but at a much slower rate. In this region, the smaller (<5 kd) bases and fulvic acids were also removed along with many of the heavier neutral compounds. At ratios above 0.5, little additional removal occurred, leaving a residual DOC pool dominated by low molecular weight, nonpolar, neutral compounds. The limiting factor in DOC removal by coagulation was the concentration of these types of compounds, not any property of the coagulant such as availability of sorption sites. Alum sludge can be recycled up to four times and still adsorb additional organics (Semmens and Field 1980). This explains why sequential coagulation does not remove any more organic matter than coagulating once with the same cumulative dose. If sorption or reaction sites associated with the coagulant were limiting, a constant fraction of the residual DOC would be removed each time the water was coagulated.

Understanding the organic matter removal process also clarifies the role of oxidants in DOC removal by coagulation. Oxidant addition prior to coagulation has two effects on DOC. Oxidative cleavage of organic molecules lowers the median molecular weight, and increases the polarity and acidity of the dissolved compounds. The first effect should diminish DOC removal; the second should enhance it. The net result should depend upon the initial

composition of the water. If the DOC pool contains a high concentration of nonpolar molecules and relatively few acidic ones, preozonation may improve DOC removal. Conversely, DOC removal from waters dominated by heavy fulvic or humic acids may be more difficult after preozonation because of a lighter weight distribution.

SUMMARY

The molecular size, charge, and solubility characteristics of DOC in raw and treated waters from two Virginia reservoirs were investigated to determine what types of organic compounds were effectively removed by the conventional treatment sequence of coagulation, settling, and filtration. The most important factor was found to be the molecular weight distribution of the DOC. DOC precipitation by Fe(III) coagulation was size dependent with bias toward larger molecules. Charge was the secondary factor in DOC removal, with ionic compounds (acids and bases) selectively removed over neutral ones. Removal of ionic compounds was attributed to their capacity to form insoluble complexes with positively charged iron species; neutral compounds were probably removed by enmeshment and/or sorption unto organic domains of floc. The final, but still significant, factor affecting DOC removal was solubility. It was proposed that hydrophilic compounds were selectively removed because their polarity permitted interaction with hydrolyzed iron. Selective removal of hydrophobic compounds was attributed to sorption onto less polar organic domains created by concentrating DOC in floc. Compounds of intermediate solubility were poorly removed.

The dominant precursors of THM and TOX in untreated waters were fulvic acids because of their abundance, high specific yields, and fast reaction rates. These compounds

were readily removable by coagulation. The dominant precursors in treated waters were low molecular weight neutral compounds of intermediate to low solubility. These compounds could not be precipitated by coagulation. Compared to fulvic acids, this precursor group had lower specific yields and slower reaction rates.

CONCLUSIONS

1. The molecular weight distribution of DOC was the most important factor in determining the extent of DOC removal by coagulation. Larger molecules were precipitated more effectively than smaller ones.

2. The charge distribution of DOC was the secondary factor in determining the extent of DOC removal. Ionized molecules were removed more effectively than neutral ones.

3. The solubility distribution of DOC also affected DOC removal by coagulation. Both hydrophilic and hydrophobic compounds were selectively removed compared to compounds of intermediate solubility.

4. Maximum DOC removal was achieved with coagulant doses corresponding to molar Fe(III)/TOC ratios of 0.5. Little or no additional DOC removal was realized by using doses beyond this level.

5. Because of their abundance, high organic halide yields, and fast reaction rates with chlorine, fulvic acids were the dominant organic halide precursors in untreated waters. However, these compounds were readily removed by coagulation.

6. In coagulated waters, the residual DOC consisted largely of low molecular weight neutral compounds of intermediate to low solubility. Compared to fulvic acids, these molecules had lower organic halide yields and slower reaction rates with chlorine. It was the concentration of

these molecules that determined whether regulatory compliance with the THM standard was attainable by conventional treatment.

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REMOVAL OF DISSOLVED ORGANIC MATTER FROM SURFACE WATERS
BY COAGULATION WITH TRIVALENT IRON

by

Robert L. Sinsabaugh III

(ABSTRACT)

The molecular size, charge, and solubility, distributions of natural DOC in raw and treated surface waters were investigated to determine the types of organic compounds removed by coagulation and settling. The distribution of organic precursors that react with chlorine to form organic halide compounds was also determined, along with the reaction rates. DOC removal by coagulation was size dependent. Compounds over 5,000 d were readily removed while compounds under 1,000 d were largely unaffected. Acidic and basic molecules were precipitated much more effectively than neutral ones. Both hydrophilic and hydrophobic molecules were selectively removed compared to compounds of intermediate solubility. Two groups of organic halide precursors were identified. Fulvic acids had high specific organic halide yields, and fast reaction rates with chlorine, but could be effectively removed by coagulation. Nonpolar neutral compounds were lower in molecular weight, slower to react with chlorine, and produced less organic halide, but could not be precipitated by coagulation.