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The effects of activated carbon adsorption and ozonation on trihalomethane speciation

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The University of Arizona, 1989

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THE EFFECTS OF ACTIVATED CARBON ADSORPTION AND

OZONATION ON TRIHALOMETHANE SPECIATION

by

Lo Tan

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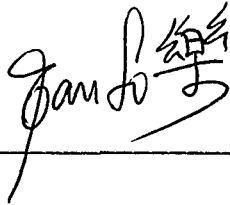
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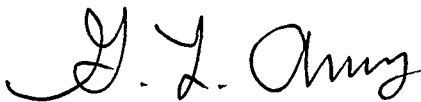
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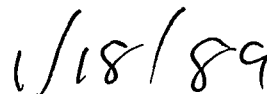
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ABSTRACT

Two surface water sources in the southwestern United States, Colorado River Water (CRW) and California State Project Water (SPW), were studied in bench-scale experiments examining two Trihalomethane (THM) precursor removal processes, activated carbon adsorption and ozone oxidation. Both source water contained bromide (Br$^-$) ion leading to brominated THMs upon chlorination. Activated carbon removed THM precursors, as measured by dissolved organic carbon (DOC), while having little effect on bromide. The net result was an increase in the ratio of Br$^-$/DOC and an increase in the relative abundance of brominated THMs. Ozone oxidized higher molecular weight precursor molecules into lower molecular weight by-products which were less reactive with chlorine. Moreover, ozonation transformed Br$^-$ to hypobromous acid (an "in-situ" oxidant), leading to an increase in the percentage of brominated THMs.

CHAPTER 1

INTRODUCTION

In natural waters, aquatic humic substances, comprised of humic and fulvic acids, are the predominant organic compounds and account for approximately 50% of the dissolved organic carbon (DOC). The fulvic acid fraction constitutes the main component of "yellow color" associated with humic substances present in groundwaters and surface waters [1,2]. Upon water disinfection, naturally occurring humic substances have been recognized as precursors to the formation of chlorination by-products such as trihalomethanes (THMs) and other chlorinated organic compounds [3,4,5,6,7].

In bromide-containing waters, chlorination will lead to the formation of brominated THMs and other brominated organic compounds.

Most fresh water systems contain bromide ion (Br⁻) at concentrations in the range of approximately 10 to 500 ug/l. Water systems affected by sea water intrusion or weathering of bromide-rich minerals, that is, by anthropogenic processes [8,9,10] may exhibit bromide levels in excess of 1,000 ug/l. Sea water itself contains 65,000 ug/l of bromide [9].

Currently, there are no treatment techniques which are economically feasible to remove Br^- [10,11].

The ubiquity of occurrence of THM compounds has been widely reported by the National Cancer Institute [12], the National Organics Reconnaissance and the National Organics Monitoring Survey [13]. Among the four THMs of concern in this research, chloroform has been proven to be an animal carcinogen and is a potential suspected human carcinogen [14,15], while bromoform may have mutagenic and genetic effects [9,16].

Based on health effects associated with organic chemicals, the United States Environmental Protection Agency (U.S.E.P.A.) proposed a regulation establishing a maximum contaminant level (M.C.L.) of 100 ug/l of total THMs [15,17,18,19,20,21] in potable drinking water.

While the present primary drinking water standards regulate THMs at a level of 100 ug/l, there are strong indications that the U.S.E.P.A. will promulgate an even more stringent standard in the foreseeable future. Hagar [20] indicated that the future THM standard may first be lowered the range of 25 to 50 ug/l of total THMs (TTHM), with an ultimate goal of 20 ug/l of TTHM containing 5 ug/l of each of the four THM species. This last standard will eventually require an equal distribution of THM compounds provided bromide is present in the natural water source.

Therefore, in this research, knowledge and understanding of the aquatic chemistry of bromide and its effects on water chlorination combined with activated carbon adsorption or ozonation will provide an important treatment approach to meet the future stringent THM primary standards.

CHAPTER 2

OBJECTIVES

The research objectives were to investigate the effects of two physicochemical processes (activated carbon adsorption and ozonation) on the speciation of four THM compounds that are formed during water chlorination of CRW and SPW sources.

The carbon-related research reported herein focused on two potentially interrelated issues: (i) the removal of different apparent molecular weight (AMW) fractions of the dissolved organic matter (DOM) by activated carbon, and (ii) the effects of bromide ion (Br^-) on THM speciation. These two topics are interrelated in that activated carbon treatment changes the Br^-/DOC ratio, and thus increases the formation of brominated THM species. A key concern in this research relates to the fate of bromide through activated carbon treatment and subsequent chlorination.

The ozone-related research also focused on the same two interrelated issues: (i) the effects of ozonation on the AMW distribution of the DOM present in two source waters (Colorado River Water and California State Project Water), and (ii) the effects of ozone on THM speciation during water chlorination in the presence of bromide ion. A key concern is the fate of bromide through the ozonation process.

CHAPTER 3

LITERATURE REVIEW

The disinfection efficiency of chlorine (Cl_2) depends on its chemical form in water. When chlorine gas is dissolved in water, it undergoes hydrolysis to produce hydrochloric acid (HCl) and hypochlorous acid (HOCl).

Being a weak acid, the hypochlorous acid generated can dissociate to hypochlorite ion (OCl^-) and hydronium ion (H_3O^+). The pH parameter can thus affect the relative amounts of HOCl and OCl^-; that is, the distribution of various chlorine species (Cl_2, OCl^- and HOCl) over a pH range [22]. In general, the disinfection capabilities of HOCl are much greater than those of OCl^- [22].

Chlorine can act as either an oxidizing agent or a substituting agent in the presence of natural organic matter (NOM). In the absence of bromide ion, chlorine reacts with NOM constituents to form chloroform as the only THM. The presence of bromide leads to the formation of brominated THM species ($CHCl_2Br$, $CHClBr_2$ and $CHBr_3$) during water chlorination.

Chlorine in the dissociated form of $HOCl/OCl^-$ oxidizes Br^- to hypobromous acid/hypobromite ion ($HOBr/OBr^-$) [23,24,25,26,27]. Hypobromous acid is a second disinfectant which is generated "in-situ" upon chlorination. Then, a

mixture of HOCl/HOBr leads to the potential formation of the four THM species ranging from chloroform to bromoform.

In the THM formation reaction, chlorine acts as a better oxidant, whereas bromine is more active as a halogen-substituting agent [24,25].

In terms of oxidizing power, chlorine is more efficient than chlorine dioxide, for instance, which is a common and alternative chlorine-containing disinfectant used in water treatment. Specifically, chlorine can oxidize Br^-, but ClO_2 is incapable of oxidizing Br^- [8,28].

A sorbent such as activated carbon removes THM precursors "intact", thus resulting in a net reduction in DOC. While activated carbon adsorbs THM precursors, it is ineffective in removing bromide ion. However, bromine can be readily adsorbed by activated carbon [29].

Once some THM precursors are adsorbed by activated carbon, a higher ratio of Br^-/DOC will be observed in a carbon-treated effluent compared to the corresponding influent. The net result is the promotion of a higher proportion of brominated THM species in the effluent upon chlorination.

Ozone (O_3) alone can lead to the formation of bromoform ($CHBr_3$) [18,30] provided bromide ion is present in the natural water sources. Thus, pre-ozonation prior to post-chlorination can affect THM speciation.

Ozone oxidizes bromide ion (Br^-) to bromine consisting of hypobromous acid (HOBr) and hypobromite ion (OBr^-) under water treatment conditions [27,31,32]. Hypobromite ion derived from the ionization of the weak acid, HOBr, further reacts to form bromate ion (BrO_3^-). It should be noted that the undissociated hypobromous acid (HOBr) cannot be directly oxidized by ozone [31,32]. Eventually, all of the bromide originally present in the natural waters may be converted quantitatively to bromate ion. Thus, $HOBr/OBr^-$ serves as an important intermediate in the conversion of bromide to bromate. The maximum transient concentration of this intermediate specie occurs under lower pH conditions due to slower bromate formation kinetics [31]. The maximum $HOBr/OBr^-$ concentration is reached typically within 20 minutes under water treatment conditions [31].

A proposed detailed schematic of chemical reactions of ozone with Br^- and OBr^- in aqueous solution [31,32] is shown in Figure 1. Several important observations can be made with respect to Figure 1. If a great excess of bromide is present in the natural water source as a result of sea-intrusion or weathering of bromide-rich minerals [8,9,10], ozone will be consumed to form mainly OBr^-. If that is the case, the cycle of O_3 with Br^- and OBr^- cannot be completed [32]. Once OBr^- is formed, it can further react with ozone to form Br^- and BrO_3^- under the respective reaction rate constants k_2
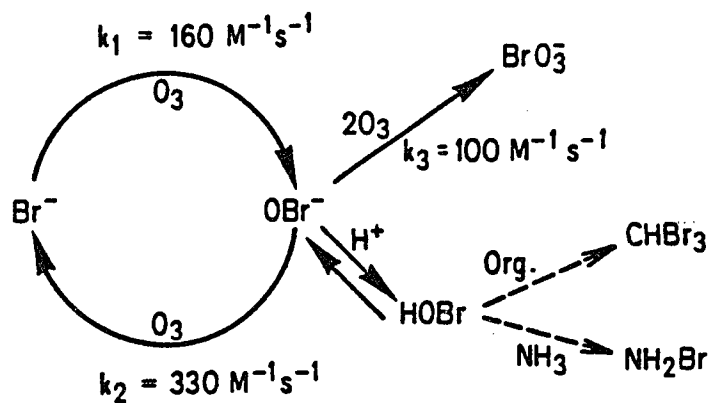
Figure 1. Detailed Schematic of Chemical Reactions of O_3 With Br^- and OBr^- in Aqueous Solution [31,32].

and k_3.

It is interesting to note that the cyclic oxidation reactions of Br^- with O_3 (with rate constant k_1) and OBr^- with O_3 (with rate constant k_2) constitute a "chain reaction". Therefore, it can be stated that Br^- serves as a catalyst in the consumption and destruction of O_3.

When the reaction of OBr^- with O_3 takes place, bromate (BrO_3^-) is the final end product, and it is unreactive towards THM formation potential (THMFP).

Upon protonation, OBr^- forms HOBr which in turn can react with any ammonia (NH_3) present in natural water to form bromamine (NH_2Br) and/or with the organic matter to form bromoform $(CHBr_3)$. As a result of the presence of H^+ and ammonia, and/or organic matter, the OBr^- will be drawn out from the cycle, and the Br^- and BrO_3^- formation will be discontinued and suppressed [32].

Based on the above explanation, bromide cannot be quantitatively recovered as THMs in the ozonated water because:

1. the intermediate OBr^- can be further oxidized to BrO_3^-,

2. the intermediate HOBr can react with NH_3, if there is any, to form bromamine, and finally

3. some bromide may be complexed as higher molecular weight organobromine compounds [8].

According to the Latimer Diagram [33], bromate ion

will not undergo spontaneous disproportionation under either acidic or basic solution condition. This observation can be supported by a thermodynamic calculation of change in Gibb's free energy. A positive value of Gibb's free energy change for bromate disproportionation is a clear indication of bromate stability as the final end product of a sequence of ozone oxidation reactions.

Also, based on the Latimer Diagram [33], OBr^- will not disproportionate in basic solution, but HOBr will disproportionate to Br_2 under acidic condition (i.e., in the presence of H^+).

In the presence of both bromide ion and humic substances, the intermediate HOBr, which is essentially a disinfectant generated "in-situ" by O_3, can react to form organo-brominated compounds such as bromoform.

Ozonation also oxidizes THM precursors to partial oxidation by-products that are generally less reactive with chlorine as a substituting agent. While little overall reduction in dissolved organic carbon (DOC) is observed (that is, little complete oxidation of organic-C to CO_2), partial oxidation by-products comprising the DOC generally exhibit a lower reactivity with chlorine, as reflected by the ratio of THM/DOC.

CHAPTER 4

MATERIALS AND METHODS

Sample Processing and Storage

Both CRW and SPW were evaluated as sources of natural organic matter (NOM) during this research. Water samples were collected in acid washed nalgene containers and sent to the University of Arizona by the Metropolitan Water District (MWD) of Southern California.

Upon receipt, the raw water samples were filtered through a prewashed 0.45 um membrane filter to isolate the dissolved organic matter (DOM). The filtered water samples were then stored at $4^{o}C$ refrigerator for future chemical characterization and treatment processes.

Ultrafiltration

The ultrafiltration (UF) procedure involved parallel processing of identical aliquots of DOM associated with the CRW and SPW sources through each of Amicon's YM series UF membranes, yielding permeates with the following apparent molecular weight (AMW) ranges: <500, <1000, <5000 and <10000 [34].

Before the beginning of UF processing, each AMW membrane was soaked skin (glossy) side down in a beaker containing milli-Q water for approximately one hour to

remove glycerin, which was added by Amicon Corporation in order to prevent drying [34,35]. Each rinsed AMW membrane was then stored in a jar containing a solution of 1 part ethanol and 9 parts of milli-Q water and refrigerated at 4°C. Prior to its use, each stored membrane was rinsed with milli-Q water to remove ethanol.

The UF was accomplished using an Amicon 8200 stirred cell with a volume capacity of 200 ml.

The UF membrane was placed in the cell and stirred by a magnetic stirring device. The UF cell was operated at a gauge pressure of 60 psig with nitrogen gas to drive the sample through the membrane, producing a permeate (filtrate) and retentate (reject).

The stirred cell was first filled with 80 ml of milli-Q water, and UF was performed obtaining 50 ml of filtrate and 30 ml of retentate. This was done to flush the connection system and the collection tubes of the stirred cell and to evaluate the performance of the membrane. Once this was done, 180 ml of a water sample were placed in the stirred cell. The first 5 ml of filtrate were discarded, and the final 150 ml of filtrate were collected in a 250 ml Erlenmeyer flask covered with plastic parafilm to avoid any contamination from the research laboratory.

After its use, the membrane was soaked in a 10 M sodium chloride (NaCl) solution for 45 minutes. Then, it was

rinsed thoroughly with milli-Q water to eliminate any excess NaCl and stored in the ethanol solution for future use.

In order to assure and maintain maximum performance, each membrane was used for a maximum of 10 times provided no problems of membrane properties arose and then discarded.

It should be noted that the UF procedure did not provide "discrete" AMW fractions but instead it generated a series of "cumulative" fractions. In this research, UF was used to separate NOM/DOM from surface waters (CRW and SPW) according to different AMW cutoffs. In general, UF has been used for separating the dissolved and colloidal organic matter present in sea water, soil and sediments, brackish water, wastewater and leachates of sanitary landfills [36,37].

Dissolved Organic Carbon

The dissolved organic carbon (DOC) analysis was used to measure the content of DOM present in the raw water and the cumulative UF permeate fractions of both untreated and treated CRW and SPW.

This test was performed using a Dohrmann Total Organic Carbon Analyzer, model DC-80. Prior to sample analysis, the instrument was calibrated using a daily standard curve of 10.0, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0 and 0.5 ppm.

Water samples for DOC analysis were first acidified at room temperature with 3 drops of nitric acid (70% by volume)

until acidic pH (2 to 3) was obtained. The acidified sample was then purged with nitrogen gas for 4 minutes. This step was done to strip off the CO_2 from inorganic carbon sources such .. as alkalinity, bicarbonate and carbonate. The acidification step can also increase the stripping efficiency of CO_2 allowing its complete removal.

For all water samples prepared according to the above steps, one ml was injected into the DOC instrument which was set in the lowest-range channel. The displayed readouts of DOC in ppm were recorded and compared directly to the daily standard calibration curve in order to determine the actual DOC concentration.

For statistical purposes, the DOC results of all water samples were run in triplicate, and the final value was the average of all three runs.

Ultraviolet Absorbance Measurement

Ultraviolet (UV) absorbance was measured with a double beam Perkin-Elmer 200 UV-Visible Spectrophotometer at a fixed wavelength of 254 nm and a path length of one cm. The instrument was first calibrated with blank distilled water placed in the reference cell. Water samples were all adjusted to neutral pH (pH = 7) prior to UV absorbance measurement in the sample cell.

The double beam spectrophotometer offers the advantage of correcting any drift in intensity of light source. This

correction is effectively done because the ratio of sample and reference intensities is measured each time. Therefore, a drift in light intensity will affect both the reference and the sample, thus leading to the cancelation of systematic errors from light source.

Bromide Ion Measurement

Bromide ion (Br$^-$) was determined by an Orion Model 94-35 ion specific electrode. A standard curve was prepared from a bromide stock solution.

For both standard solutions and water samples, 100 ml were placed in a stirred beaker. One ml of ionic strength adjuster (ISA) was added to the content of beaker [38], and the milli-volt readout was recorded and compared to the calibration curve.

Activated Carbon Adsorption Isotherms

Batch-mode experiments were employed to evaluate water samples of CRW and SPW. Samples of these sources were first filtered through a 0.45 um membrane to isolate DOM.

The candidate powdered activated carbon (PAC) used in this research was pulverized Filtrasorb 400 with a particle size of <325 mesh from Calgon Corporation. This material is widely used as a granular activated carbon (GAC) and thus provides insight into both GAC treatment as well as PAC treatment.

The equilibrium adsorption isotherm experiments took

the form of "bottle-point" [18] experiments and were conducted at room temperature (23°C) and under ambient pH conditions. Preliminary kinetic experiments were performed to identify an appropriate contact time for establishing "pseudo-equilibrium" conditions. Results of these experiments suggested a contact time of 4 hours.

An overall "bottle-point" experiment encompassed the following range of activated carbon doses: 0, 50, 100, 200, 300 and 500 mg/l of sample. The zero mg/l dose served as a blank control for the adsorption process, while the highest dose gave insight into the non-adsorbable fraction of the DOM.

After the required contact time of 4 hours on a gyrotory table, the contents of each bottle or flask were filtered through a prewashed 0.45 um membrane filter to remove carbon fines.

Ozonation

Water samples of CRW and SPW were evaluated by bench-scale ozonation. Sample aliquots were first filtered through 0.45 um filter membrane to isolate the DOM.

Approximate applied ozone doses were 0, 0.5, 1.0 and 1.5 mg O_3/mg DOC. The net utilized or the actual transferred doses of ozone were determined by the difference between applied ozone and off-gas ozone. The ozone consumed through autodecomposition and the dissolved ozone were not measured

in this experiment.

Ozone in the exit gas was captured in two potassium iodide (KI) traps in series and subsequently titrated according to Standard Methods [39]. A semi-batch mode, bench-scale ozonator was used (OREC Model O3B1-O with 2-L capacity virtis reactor with an impeller operated at 500 rpm and a # 316 stainless steel ozone sparger). All ozonation experiments were conducted at room temperature ($23^{\circ}C$) and under ambient pH conditions. The pH values of water samples before and after ozonation were also measured in order to determine the pathway of ozone oxidation.

pH Measurements

The pH measurements were made using an Orion 811 pH/millivolt meter at room temperature conditions. Prior to sample analysis, the pH meter was first calibrated with three buffer solutions having pH values of 4.0, 7.0 and 10.0 to assure reliable response from the instrument.

Trihalomethane Formation Potential

The trihalomethane formation potential (THMFP) was based on THM species analyzed with a Hewlett-Packard 5790 Gas Chromatograph (GC) equipped with an Electron Capture (EC) detector and a large bore capillary column (DB-5). Helium was used as the carrier gas, and nitrogen as the make-up gas. The EC detector signal was sent and measured by a Hewlett-Packard 3390A integrator.

Trihalomethanes were recovered from the aqueous solution of 120 ml "headspace free" serum vials by using a simplified liquid/liquid extraction method with pesticide grade pentane. Five ml of pentane solvent were injected to the "headspace free" serum vial (by double syringe technique, as shown in Figure 2) for extraction allowing maximum recovery of THMs from water [13].

The pH of water samples was adjusted to 7.0 before chlorination. For most water sources, a Cl_2/DOC mass ratio of 3 to 1 was adequate for maintaining a positive chlorine residual over the time frame of the experiment. Collins, Amy and King [5] found that a ratio of 3 to 1 was adequate for a series of CRW. The same mass ratio was also found valid for SPW in this research.

Chlorine doses were based on DOC values of water samples and on an applied Cl_2/DOC mass ratio of 3 to 1. Chlorine solution was added to the serum vial by double-syringe technique (Figure 2).

The serum vials containing chlorinated water samples were incubated for 168 hours at 20°C. At the end of incubation time, the THM reaction was terminated by injecting 1.5 ml of 0.1 N sodium thiosulfate ($Na_2S_2O_3$) solution to the serum vial via double-syringe technique. The amount of $Na_2S_2O_3$ injected for dechlorination purpose was in great excess of the stoichiometric requirements.
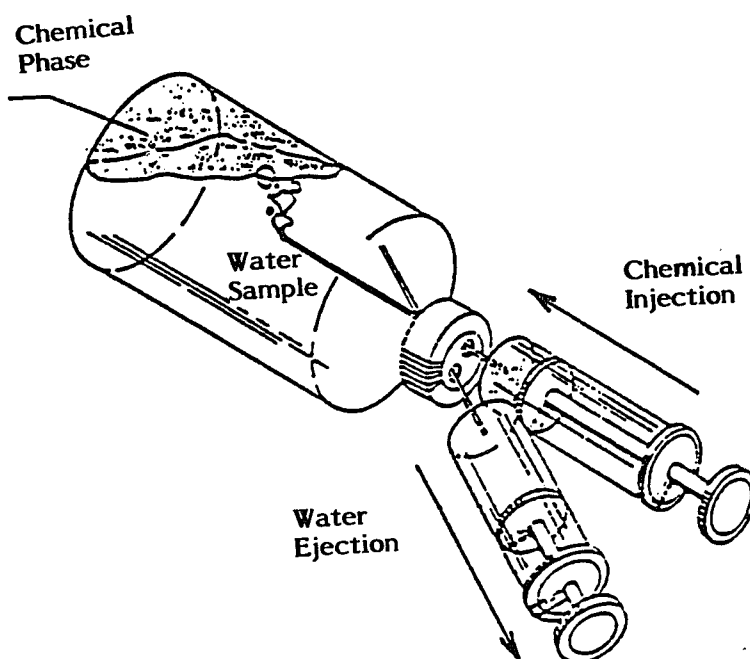
Figure 2. Double-Syringe Technique.

The amount of chlorinated water sample (1.5 ml) displaced from the serum vial by $Na_2S_2O_3$ was used for a qualitative determination of free chlorine residual. This determination was done by transferring the above volume to a test tube containing 1.5 ml of phosphate buffer and 1.5 ml of N,N-diethyl-p-phenylenediamine (DPD) indicator [39]. The presence of positive free chlorine residual was indicated by a pink color, and the absence of chlorine residual was indicated by other color.

It should be recognized that an important stipulation of the THMFP test is the need to maintain a positive chlorine residual over the 168-hour time frame. In this research, all water samples were found to maintain a positive free chlorine residual at the end of 168 hours of incubation time using the applied Cl_2/DOC mass ratio of 3 to 1.

Experimental Protocol of Chemical Characterization

The use of pre-washed 0.45 um membrane filters provided an operational definition of DOM, and UF further fractionated the DOM into AMW fractions, with particular emphasis on the <1000 fraction. The total DOM (<0.45 um) as well as the lower AMW DOM fraction (<1000 AMW) were analyzed for DOC, UV absorbance (at 254 nm) and Br^-. In addition, each of the fractions (total and <1000 AMW) was chlorinated as part of an analysis for THMFP, with values of THM-Br and

THM-Cl calculated. Based on results derived from the two measured fractions (total and <1000 AMW), corresponding values for the >1000 AMW DOM fraction were calculated by difference.

After activated carbon adsorption or ozonation treatment, treated waters were analyzed for DOC, UV absorbance and Br^- (Figure 3). All untreated and treated waters were subjected to formation potential experiments based on a Cl_2/DOC mass ratio of 3 to 1.

In addition to equilibrium adsorption and ozonation experiments involving the overall DOM, parallel experiments were conducted to evaluate the carbon adsorption and ozone oxidation capabilities of the <1000 fraction "alone". In this endeavor, UF was used to pre-isolate the <1000 AMW material from the overall DOM of the source water. The pre-isolated <1000 AMW DOM was then contacted with activated carbon or ozonated.

```
                              Sample
                               ||
                               \/
                             0.45 um
                               ||
                               \/
                              DOM
                               ||
                               \/
        Ozone<=========\/=====>Activated Carbon
           ||           ||            ||
           ||           ||            ||
           \/==========>||<=========\/
                        ||
                        ||
                        \/
   _____
        ||                ||                    ||
        ||                ||                    ||
   UF (<1000 AMW)         ||                    ||
        ||                ||                    ||
        \/                \/                    \/
   ====================>||           Calculated Values
                        ||           for >1000 AMW
                        ||
                        ||
                        \/
                       DOC
                       UV Abs
                       Br⁻
                        ||
                        ||
                        \/
                      Cl₂/DOC =3
                        ||
                        ||
                        \/
                      THMFP
                      THM-Br
                      THM-Cl
```

Figure 3. Overall Experimental Protocol of Chemical
        Characterization.

CHAPTER 5

RESULTS AND DISCUSSION

A detailed summary of all experimental results is presented in Tables 1 and 2 for the CRW source, and Tables 3 and 4 for the SPW source.

Untreated Water Characterization

The apparent molecular weight fingerprints of the DOM found in untreated CRW and SPW sources are presented in Figures 4 and 5. Using these distributions, the average molecular weights, based on DOC, were estimated to be 1,320 and 2,050 for the CRW and SPW sources, respectively. From data of Tables 1 and 3, it can be observed that the <1000 AMW fractions of both CRW and SPW are the most reactive fractions as indicated by their reactivity towards THMFP (i.e., THM/DOC).

Activated Carbon Adsorption

Preliminary experiments were conducted to define equilibrium adsorption isotherms for each water source. A first series of isotherms involved the evaluation of the entire "DOC pool" (i.e., the heterogeneous mixture of DOM comprising of hydrophobic and hydrophilic components) with post-treatment measurement of the equilibrium concentrations of total DOC and <1000 AMW DOC. A second set of experiments involved the evaluation of a <1000 AMW pre-isolated fraction

Table 1. THM Precursors in Untreated and Treated Waters: CRW Source.

(Date: 1/13/88)

Sample/ Fraction	DOC (mg/L)	UV Abs. (cm⁻¹)	UV/DOC	pH	THMFP (ug/L)	THMFP (umol/L)	THM/DOC (ug/mg)
Untreated:							
< 0.45 um	3.11	.0510	.016	8.29	113	0.87	36
< 10000 AMW	2.96	.0470	.016	---	91.7	0.71	31
< 5000 AMW	2.42	.0420	.017	---	82.4	0.59	34
< 1000 AMW	1.48	.0170	.012	---	67.5	0.49	46
< 500 AMW	0.98	.0080	.008	---	42.9	0.31	44
Ozone-Treated (Transferred O_3 = 1.46 mg/L = 0.47 mg O_3/mg DOC):							
< 0.45 um	3.05	.0410	.013	8.41	101	0.73	33
< 1000 AMW	1.45	.0170	.012		66.4	0.48	46
Ozone-Treated (Transferred O_3 = 3.05 mg/L = 0.98 mg O_3/mg DOC):							
< 0.45 um	2.93	.0375	.013	8.43	100	0.72	34
< 1000 AMW	1.40	.0155	.011		67.2	0.48	48
Carbon-Treated (PAC Dose = 100 mg/L):							
< 0.45 um	1.85	.0230	.012	---	58.8	0.37	32
< 1000 AMW	1.25	.0180	.014		33.5	0.25	27
Carbon-Treated/Pre-Isolated <1000 AMW Material (PAC Dose = 100 mg/L):							
< 1000 AMW	1.12	.0130	.012	---	33.2	0.25	30

Table 2. THM Speciation in Untreated and Treated Waters: CRW Source.

(Date: 1/13/88)

Sample/ Fraction	THMFP (ug/L)	Br⁻ (ug/L)	THM-Cl (ug/L)	THM-Br (ug/L)	THM-Br THM-X (%)	THM-Br Br⁻ (%)	Br⁻ DOC (ug/mg)
Untreated:							
< 0.45 um	113	61	95.7	14.8	13	25	20
< 10000 AMW	91.7	61	77.7	12.5	14	21	21
< 5000 AMW	82.4	61	57.5	22.0	28	36	25
< 1000 AMW	67.5	61	50.2	15.3	23	25	41
< 500 AMW	42.9	61	31.8	9.9	24	16	62
Ozone-Treated (Transferred O_3 = 1.46 mg/L = 0.47 mg O_3/mg DOC):							
< 0.45 um	101	57	73.0	24.0	25	42	19
< 1000 AMW	66.4	57	49.0	15.5	24	27	40
Ozone-Treated (Transferred O_3 = 3.05 mg/L = 0.98 mg O_3/mg DOC):							
< 0.45 um	100	55	70.9	26.3	27	47	19
< 1000 AMW	67.2	55	48.3	16.9	26	31	39
Carbon-Treated (PAC Dose = 100 mg/L):							
< 0.45 um	50.8	61	37.5	12.0	24	20	33
< 1000 AMW	33.5	61	26.9	5.8	18	10	48
Carbon-Treated/Pre-Isolated <1000 AMW Material (PAC Dose = 100 mg/L):							
< 1000 AMW	33.2	61	25.7	6.8	21	11	54

Table 3. THM Precursors in Untreated and Treated Waters: SPW Source.

(Date: 3/9/88)

Sample/ Fraction	DOC (mg/L)	UV Abs. (cm^{-1})	UV/DOC	pH	THMFP (ug/L)	THMFP (umol/L)	THM/DOC (ug/mg)
Untreated:							
< 0.45 um	3.87	.0860	.022	8.40	187	1.25	48
< 10000 AMW	3.75	.0810	.022	---	163	1.05	43
< 5000 AMW	3.08	.0580	.019	---	159	1.00	52
< 1000 AMW	1.53	.0210	.014	---	87.5	0.56	57
< 500 AMW	1.11	.0085	.008	---	29.3	0.15	26
Ozone-Treated (Transferred O$_3$ = 3.73 mg/L = 0.96 mg O$_3$/mg DOC):							
< 0.45 um	3.78	.0500	.013	8.31	181	1.18	48
< 1000 AMW	1.49	.0160	.011		85.4	0.54	57
Ozone-Treated (Transferred O$_3$ = 6.51 mg/L = 1.68 mg O$_3$/mg DOC):							
< 0.45 um	3.70	.0370	.010	8.24	180	1.16	49
< 1000 AMW	1.42	.0115	.008		77.0	0.43	54
Ozone-Treated/Pre-Isolated <1000 AMW DOM (O$_3$ = 1.48 mg/L = 0.97 mg/mg DOC):							
< 1000 AMW	1.32	.0120	.009	8.32	57.6	0.35	44
Ozone-Treated/Pre-Isolated <1000 AMW DOM (O$_3$ = 2.15 mg/L = 1.40 mg/mg DOC):							
< 1000 AMW	1.21	.0085	.007	8.34	50.1	0.31	41
Carbon-Treated (PAC Dose = 50 mg/L):							
< 0.45 um	2.30	.0370	.016	8.38	108	0.67	47
< 1000 AMW	1.42	.0150	.011		66.7	0.45	47
Carbon-Treated/Pre-Isolated <1000 AMW Material (PAC Dose = 50 mg/L):							
< 1000 AMW	1.32	.0100	.008	---	22.2	0.11	17
Untreated/Bromide-Spiked:							
+ 0 ug/L Br$^-$	3.87	.0860	.022	---	187	1.25	48
+ 42 ug/L Br$^-$	"	"	"		215	1.23	56
+100 ug/L Br$^-$	"	"	"		214	1.15	55
+170 ug/L Br$^-$	"	"	"		217	1.13	56

Table 4. THM Speciation in Untreated and Treated Waters: SPW Source.

(Date: 3/9/88)

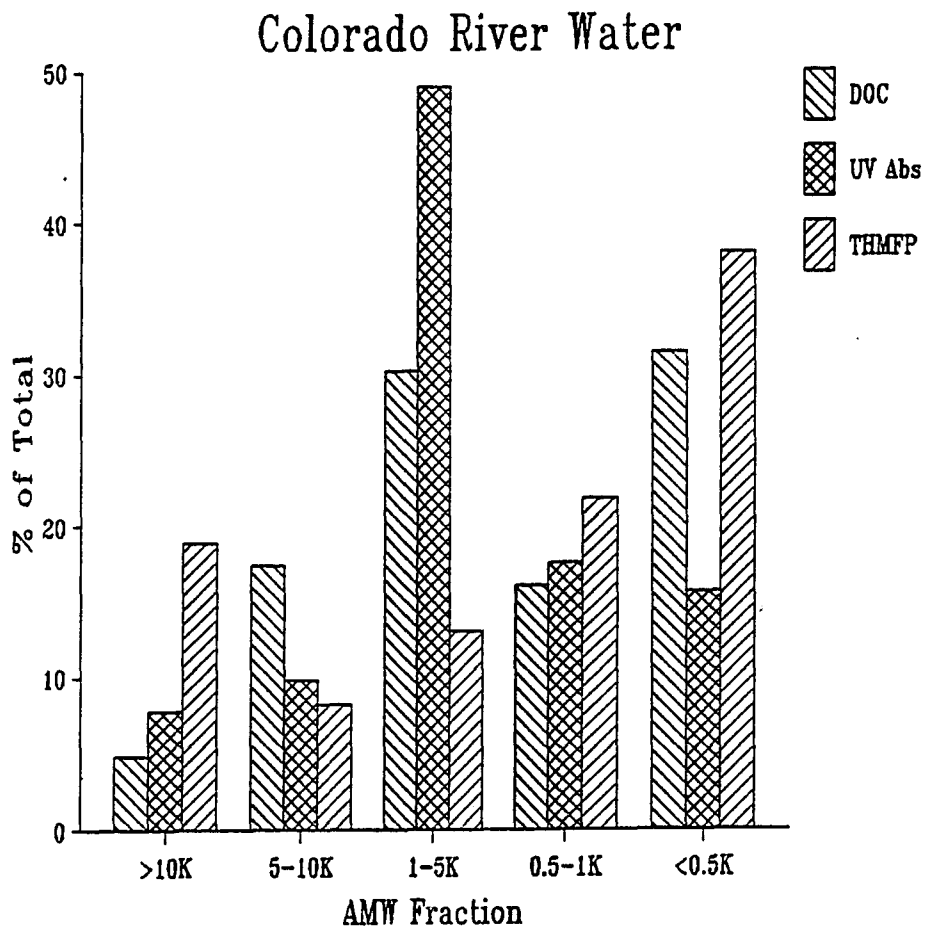| Sample/ Fraction	THMFP (ug/L)	Br⁻ (ug/L)	THM-Cl (ug/L)	THM-Br (ug/L)	THM-Br/THM-X (%)	THM-Br/Br⁻ (%)	Br=/DOC (ug/mg)
Untreated:							
< 0.45 um	187	143	112	53.5	32	37	37
< 10000 AMW	163	143	88.4	68.9	44	48	38
< 5000 AMW	159	143	80.5	72.8	48	51	46
< 1000 AMW	87.5	143	47.0	37.5	44	26	93
< 500 AMW	29.3	143	6.3	21.4	77	15	129
Ozone-Treated (Transferred O_3 = 3.73 mg/L = 0.96 mg O_3/mg DOC):							
< 0.45 um	181	135	102	73.0	42	54	36
< 1000 AMW	85.4	135	44.2	38.2	46	28	91
Ozone-Treated (Transferred O_3 = 6.51 mg/L = 1.68 mg O_3/mg DOC):							
< 0.45 um	180	129	96.9	76.5	44	59	35
< 1000 AMW	77.0	129	27.0	37.4	58	29	91
Ozone-Treated/Pre-Isolated <1000 AMW DOM (O_3 = 1.48 mg/L = 0.97 mg/mg DOC):							
< 1000 AMW	57.6	137	29.3	24.4	45	18	104
Ozone-Treated/Pre-Isolated <1000 AMW DOM (O_3 = 2.15 mg/L = 1.40 mg/mg DOC):							
< 1000 AMW	50.1	129	25.1	23.1	48	18	106
Carbon-Treated (PAC Dose = 50 mg/L):							
< 0.45 um	108	143	54.0	50.0	48	35	62
< 1000 AMW	66.7	143	40.0	25.0	38	17	101
Carbon-Treated/Pre-Isolated <1000 AMW Material (PAC Dose = 50 mg/L):							
< 1000 AMW	22.2	143	5.0	16.0	77	11	109
Untreated/Bromide-Spiked:							
< 0.45 um	187	143	112	54.0	32	37	37
"	215	185	81.0	127	61	69	48
"	214	243	65.0	142	69	59	63
"	217	313	57.0	153	73	49	81

Colorado River Water

Figure 4. AMW Fingerprints for Untreated CRW Source.
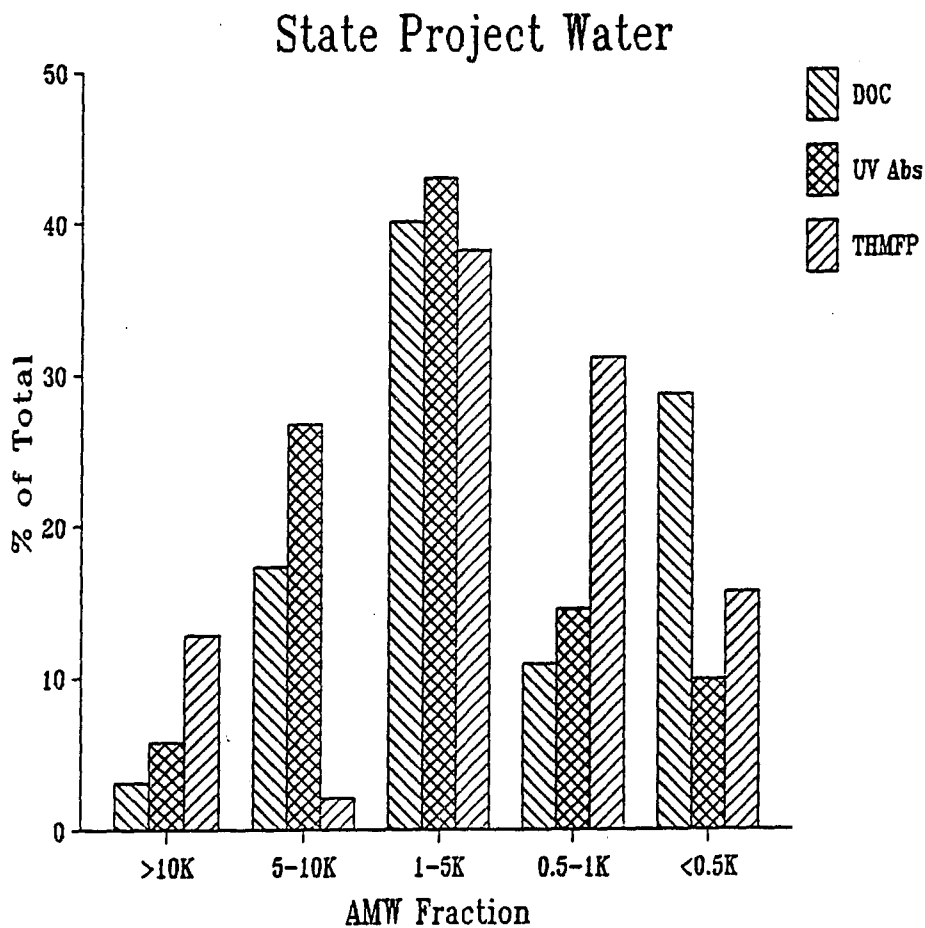
State Project Water

Figure 5. AMW Fingerprints for Untreated SPW Source.

of the DOC whereby UF was used to first isolate <1000 AMW
material that was subsequently contacted with activated
carbon.

Equilibrium adsorption isotherms for CRW and SPW
sources are presented in Figures 6 and 7, respectively. It
can be seen that the higher molecular weight material (i.e.,
>1000 AMW) is more adsorbable than lower AMW material (i.e.,
<1000 AMW). The greater adsorption of the "more hydrophobic"
material (>1000 AMW) on activated carbon is indicated
graphically by the "favorable shape" of its corresponding
adsorption isotherm towards the solid phase DOC
concentration, Q (Figures 6 and 7). These results are also
consistent with the heterogeneous nature of humic substances
and suggest that there is competitive adsorption between the
various AMW fractions. In comparing the <1000 AMW data
observed for the entire "DOC pool" with results derived from
the pre-isolated <1000 AMW material for both CRW and SPW
(Tables 1 and 3), it can be seen that the lower AMW material
is more adsorbable when in the absence of higher AMW
material. In terms of kinetics of adsorption process, the
higher molecular weight material (>1000 AMW) shows slower
kinetics than the lower molecular weight material (<1000
AMW).

The equilibrium isotherm data were analyzed according
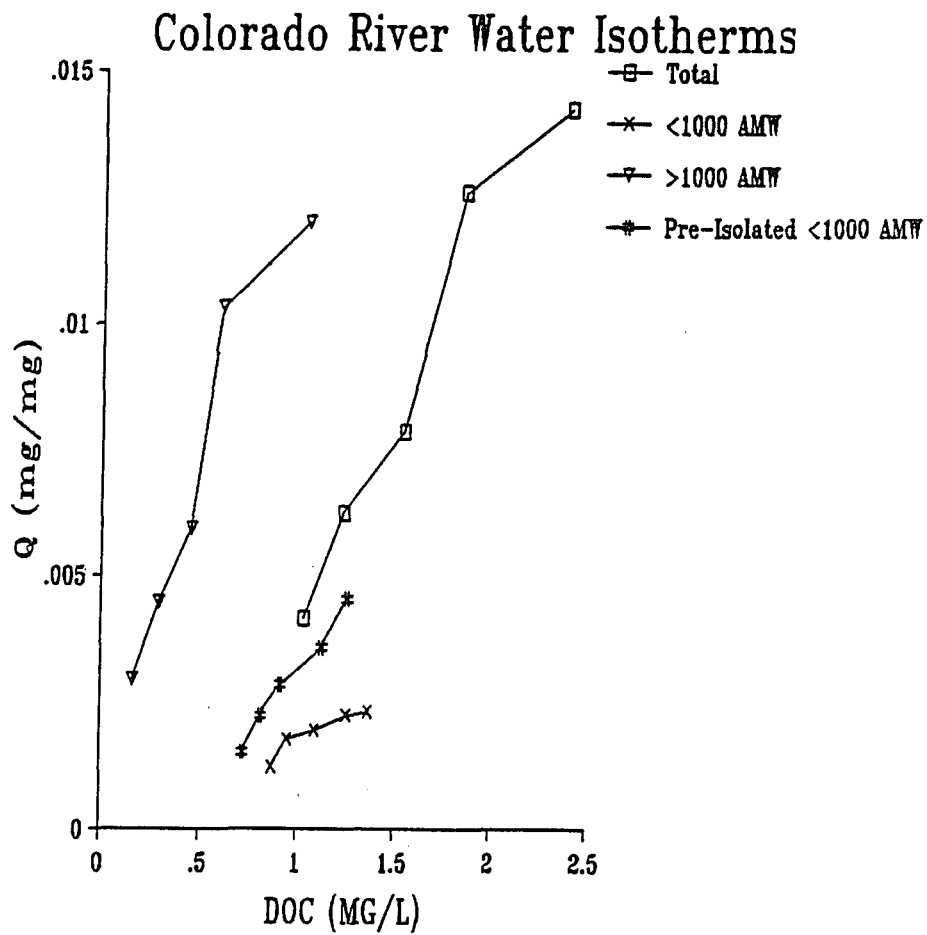to the Freundlich equation [22,37,40,41,42]. The arithmetic

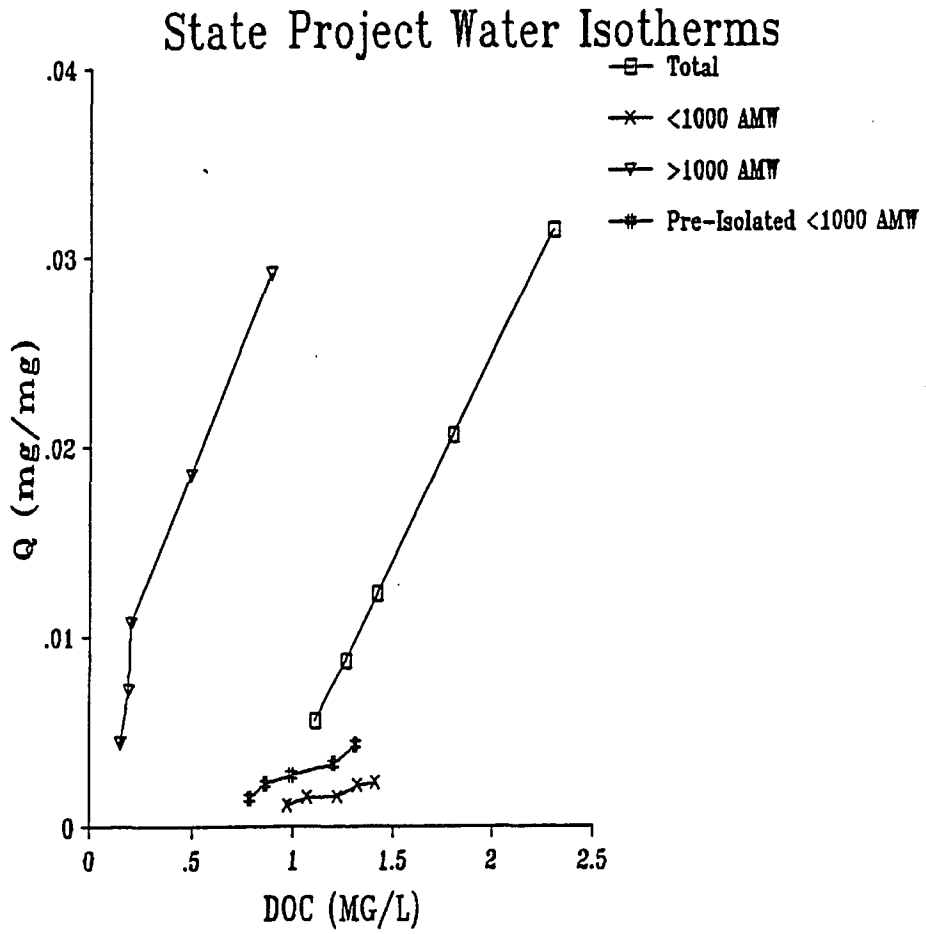**Figure 6.** Activated Carbon Equilibrium Isotherms for CRW Source.

State Project Water Isotherms

Figure 7. Activated Carbon Equilibrium Isotherms for SPW Source.

form of the Freundlich equation is shown below:

$$Q = K \ (C)^{1/n}$$

where,

   Q = solid phase DOC concentration, in mg DOC/mg PAC

   K = sorption capacity, an empirical constant

   C = equilibrium liquid or aqueous phase DOC

      concentration, in mg/l

   1/n = adsorbent intensity, an empirical constant

The linear form of Freundlich equation can be obtained by applying logarithmic functions:

$$\log Q = 1/n \ \log C + \log K$$

where the slope of this straight line is 1/n, and the Y-intercept is log K.

A summary of empirical constants log K and 1/n appears in Table 5. The non-adsorbable fractions were determined from the application of a very high PAC dose of 500 mg/l. Of the 3.11 mg/l of total DOC and 1.48 mg/l of <1000 AMW DOC present in the CRW source, the non-adsorbable fractions were estimated to be 1.03 and 0.87 mg/l, respectively. This same trend was observed for the SPW source: an estimated 1.11 mg/l of the total DOC of 3.87 mg/l and 0.97 mg/l of the <1000 AMW DOC of 1.53 mg/l were observed to be non-adsorbable materials. It is evident that the lower molecular weight material is more hydrophilic and less adsorbable. Pore size distribution and different

Table 5. Summary of Freundlich Equation Parameters.

Sample/ Fraction	log K	1/n	r^2 (# of cases)	Q @ C = 3.5 mg/L
Colorado River Water:				
Total	-2.37	1.49	0.96 (5)	.028
<1000 AMW	-2.78	1.26	0.85 (5)	---
>1000 AMW	-1.90	0.80	0.95 (5)	---
Pre-Isolated <1K	-2.51	1.83	0.96 (5)	---
State Project Water:				
Total	-2.32	2.36	0.98 (5)	.092
<1000 AMW	-2.91	1.78	0.90 (5)	---
>1000 AMW	-1.45	0.95	0.92 (5)	---
Pre-Isolated <1K	-2.59	1.75	0.93 (5)	---

equilibrium contact times are also problems associated with the adsorption of hydrophilic material. Also shown in Table 5 are the estimates of solid phase loadings, Q, corresponding to an equilibrium aqueous phase DOC concentration of 3.50 mg/l, approximating the untreated water concentration of both the CRW and SPW sources. These estimates provide insight into anticipated GAC loadings. Comparing Q values of Table 5, it is apparent that SPW source enables a higher loading rate of activated carbon than CRW source.

A modified arithmetic form of the Freundlich equation [42] appears below:

$$Q = K \ (C - C_{na})^{1/n}$$

where,

C_{na} = non-adsorbable equilibrium liquid or aqueous

   phase DOC concentration, in mg/l

and the other terms are as defined previously.

Similarly, the linear form of the modified Freundlich equation can be obtained by applying logarithmic fuctions:

$$\log Q = 1/n \ \log \ (C - C_{na}) + \log K$$

where the slope of this straight line is $1/n$, and the Y-intercept is $\log K$.

It is noteworthy to point out that the term $C - C_{na}$ represents the "actual" or "true" adsorbable fraction of DOM present in CRW and SPW sources. The experimental importance

of this term is to reflect and emphasize the effectiveness of PAC treatment. A detailed summary of empirical constants log K, 1/n and solid phase loadings, Q in the modified Freundlich linearized equation is shown in Table 6.

Based on the isotherm results, an "optimum" PAC dose was selected to produce a larger batch of treated water for a more detailed characterization. The PAC dose was chosen on the basis of an arbitrary criterion of a targeted 40% reduction of overall DOC. This level of reduction provides insight into both PAC and GAC treatment. The selected doses were 100 mg/l and 50 mg/l for the CRW and SPW sources, respectively.

Ozone treatment

Large batches of ozone-treated waters were produced for detailed characterization. Targeted transferred ozone doses of approximately 0.5, 1.0 and 1.5 mg O_3/mg DOC were specified for this research. Generally, lower ozone doses (e.g., < 0.5 mg O_3/ mg DOC) are employed for induced enhancement of microflocculation [43,44,45,46] while higher doses (e.g., > 1.0 mg O_3/ mg DOC) are used for the oxidative destruction of DOM. The emphasis of this research was on the latter phenomenon.

Effects of Bromide on THM Speciation

As the concentration of bromide ions increases, there is a shift toward brominated THM species over chloroform,

Table 6. Summary of Modified Freundlich Equation Parameters.

Sample/Fraction	log K	1/n	r^2 (# of cases)	Q @ C = 3.5 mg/L
Colorado River Water:				
Total	-1.91	0.47	0.93 (4)	.019
<1000 AMW	-2.59	0.15	0.95 (4)	---
>1000 AMW	-1.87	0.55	0.91 (4)	---
Pre-Isolated <1K	-2.27	0.37	0.96 (4)	---
State Project Water:				
Total	-1.56	0.62	0.99 (4)	.047
<1000 AMW	-2.58	0.26	0.69 (4)	---
>1000 AMW	-1.50	0.44	0.93 (4)	---
Pre-Isolated <1K	-2.34	0.29	0.87 (4)	---

with all other experimental factors held constant. This behavior is reflected by the relevant "bromide-spike" data that appear in Table 4 and that are plotted in Figure 8.

It can be seen from Figure 8 that the chloroform concentration decreases nonlinearly with respect to initial bromide concentration. Bromodichloromethane increases to a maximum concentration with increasing bromide ion and thereafter levels off. Dibromochloromethane passes through a maximum concentration which occurs at a higher bromide concentration and thereafter levels off. Bromoform increases significantly with increasing bromide concentration. This same kind of "bromide-spike" trend was observed and discussed by several other researchers [24,25,47,48].

From the bromide-spike data of Tables 3 and 4, it is interesting to note that the total THM concentration also increases until reaching a plateau at a concentration of approximately 215 ug/1 of TTHM.

In relation to these results, an influential key factor is the ratio of Br⁻/DOC.

Activated Carbon Effects on Speciation

Activated carbon removes THM precursors "intact" while having very little effect on bromide ion. The net result is an increase in the ratio of Br⁻/DOC in treated water versus the corresponding untreated water. As a general rule, an increase in this ratio for the overall "DOC pool"
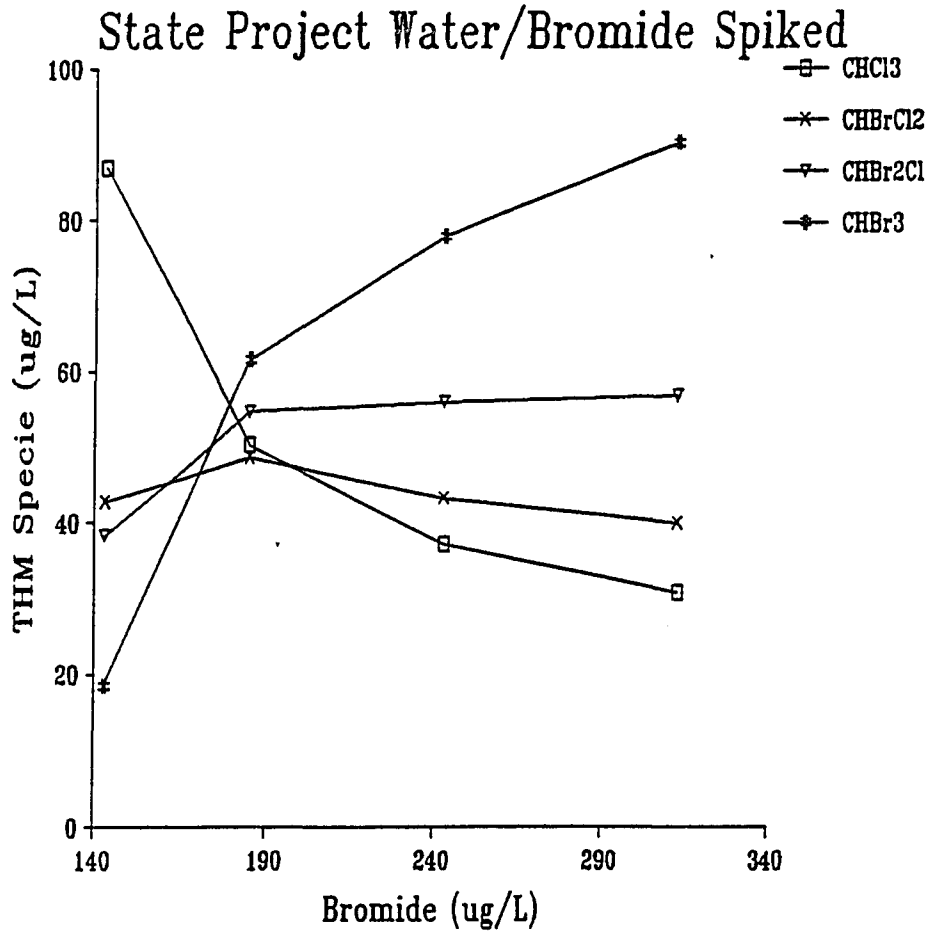
State Project Water/Bromide Spiked

Legend:
- CHCl3
- CHBrCl2
- CHBr2Cl
- CHBr3

Y-axis: THM Specie (ug/L)
X-axis: Bromide (ug/L)

Figure 8. Effects of Added Bromide on THM Speciation in SPW Source.

(i.e., <0.45 um) led to an increase in the relative amount of brominated THMs, as reflected by the parameter THM-Br/THM-X. The greater amount of bromide available in treated water for the THMFP reaction with the "reduced DOC pool" is a predominant factor in the increase of brominated THM species. This trend is observed for both CRW and SPW and is exemplified by the data shown in Figure 9.

Ozone Effects on Speciation

In general, as the ratio of O_3/DOC increased, the concentration of THM-Cl decreased while values of THM-Br increased. The explanation for these trends is that ozone opens and cleaves the conjugated bonds of aromatic rings of humic substances into smaller fragments such as aldehydes, ketones or acids depending on the substituting group(s) present in the humic substance. By doing so, ozone actually enhances the incorporation of bromide during the THMFP reaction. The above trends are graphically portrayed in Figures 10 and 11. While ozonation produced only slight reduction in THMs, it caused a discernable shift from chloroform to brominated THMs.

The percentage of the original bromide incorporated into THM species (as defined by the parameter THM-Br/Br⁻) varied from about 25 to 60%. The values of bromide incorporation increased as a function of the ratio of O_3/DOC, as illustrated in Figure 12.
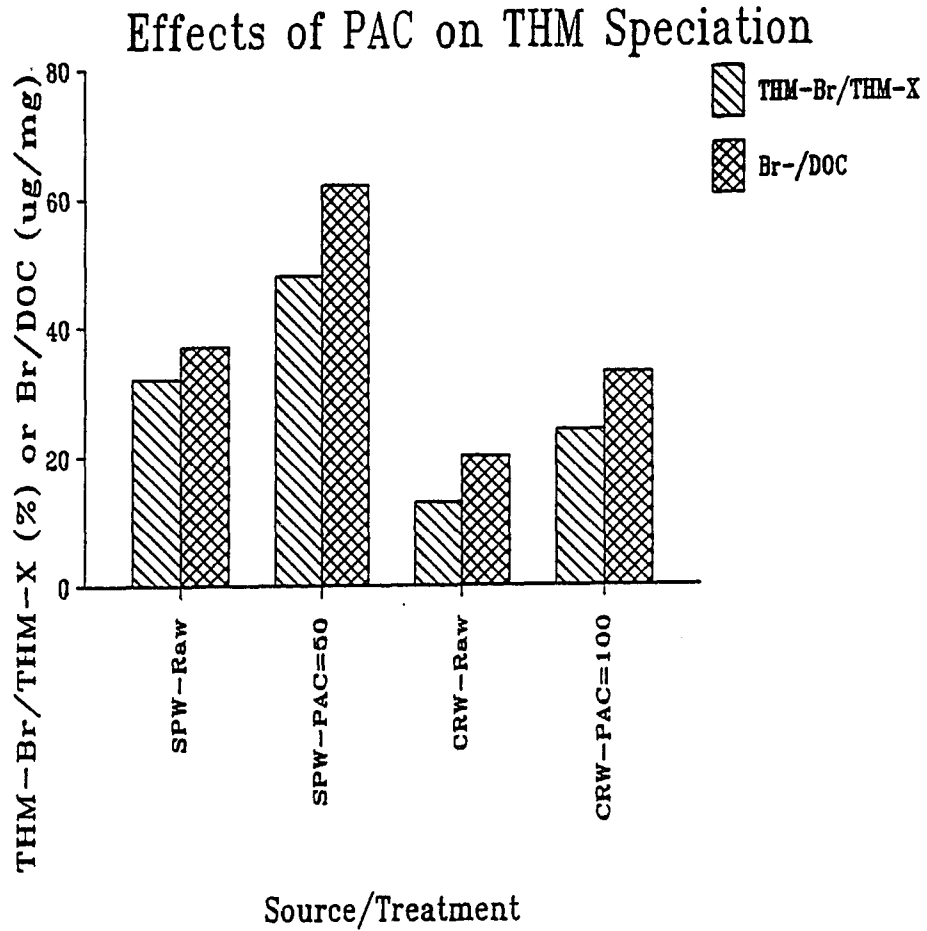
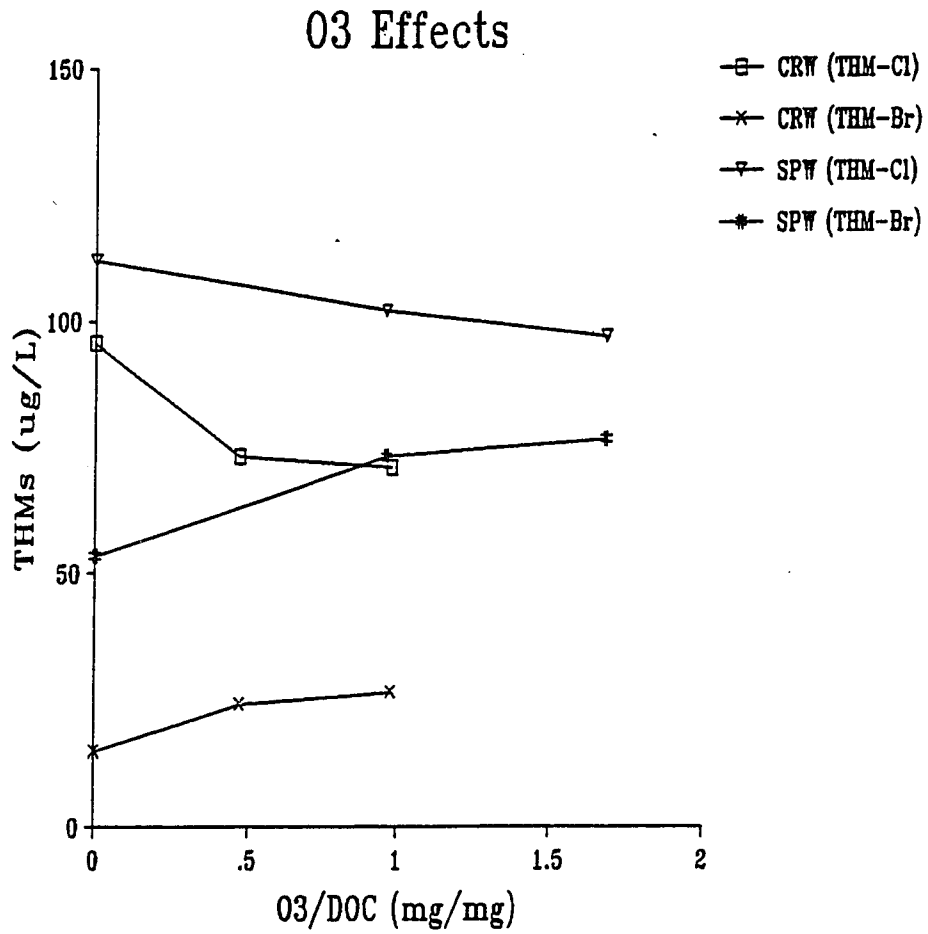Figure 9. Effects of Activated Carbon on THM Speciation.

O3 Effects

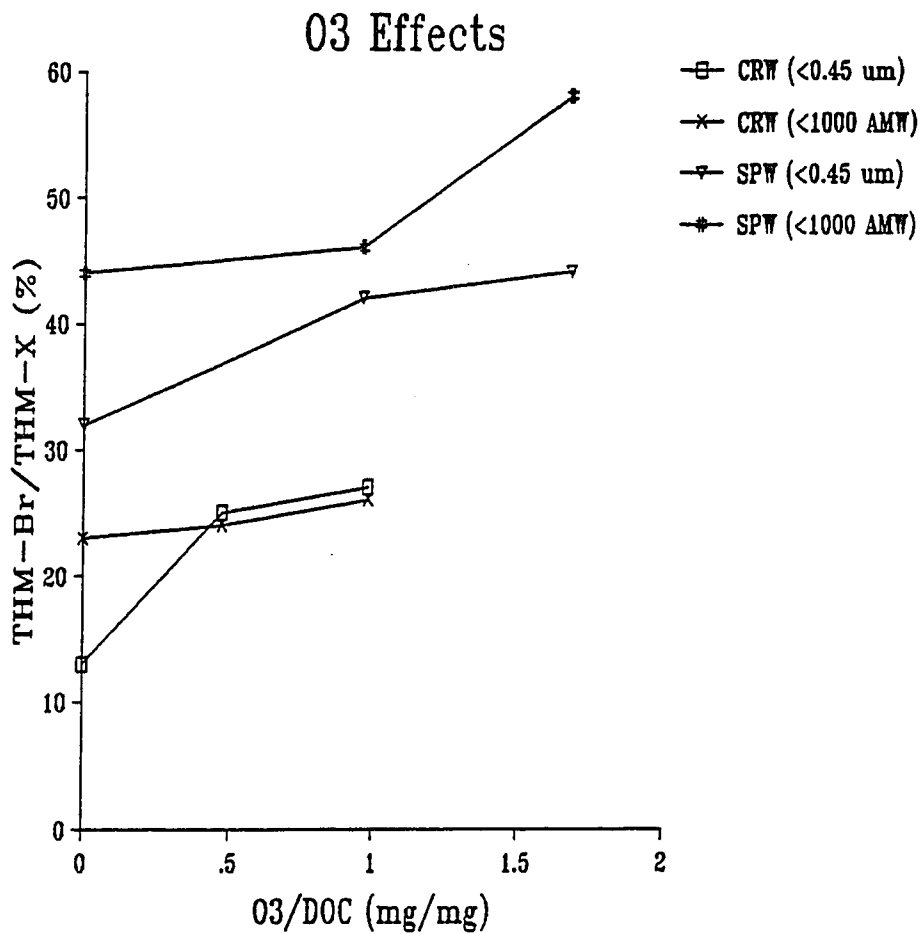**Figure 10.** Ozone Effects on THM-Cl versus THM-Br Formation.

Figure 11. Ozone Effects on Relative Formation of THM-Br.
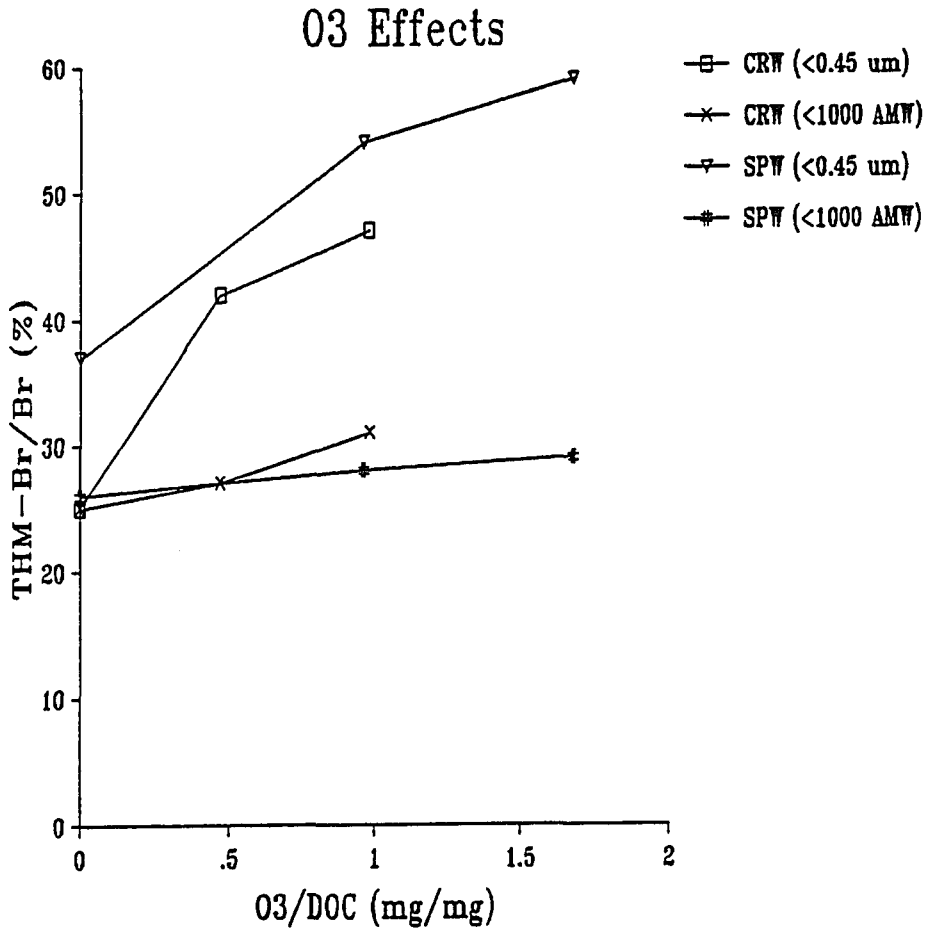
O3 Effects

Figure 12. Ozone Effects on Bromide Conversion to THM-Br.

Effects of Activated Carbon and Ozone

Treatment on AMW Distributions

The two treatments evaluated in this research, activated carbon adsorption and ozone oxidation, affected the AMW distributions of both the CRW and SPW sources. It is important to recognize the fundamental difference between "removals" by adsorption versus oxidation. Adsorption process removes humic and fulvic acid molecules "intact". Generally, higher AMW, hydrophobic molecules are more effectively adsorbed than lower AMW hydrophilic molecules. In spite of their great adsorption capacity, pore size exclusion phenomena of activated carbon may interfere with adsorption of very large molecular size molecules [18,37].

While moderate ozone doses (e.g., approximately 1.0 mg O_3/mg DOC) resulted in little overall reduction in DOC (Tables 1 and 3), there was a discernable shift from higher AMW to lower AMW material, presumably reflecting the creation of partial oxidation by-products. Based only on simple stoichiometric considerations, it would take 8 mg O_3/mg DOC to completely oxidize DOC to CO_2 [18,37].

Important THM precursor and THM speciation characteristics of carbon-treated and ozone-treated waters are summarized in Tables 1 through 4. Overall reductions in DOC, UV absorbance and THMFP provided by the various treatments appear in Figures 13 and 14 for CRW and SPW
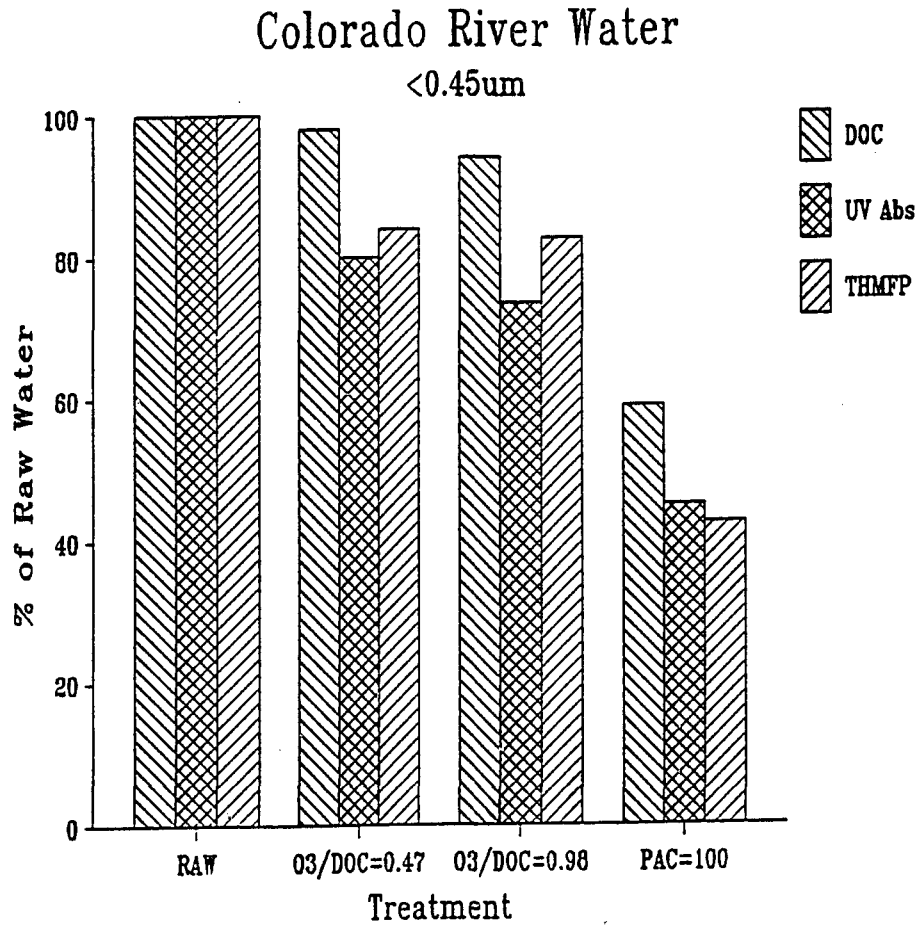
Colorado River Water
<0.45um

Figure 13. DOM Removal by Ozone and Activated Carbon: CRW Source.

State Project Water
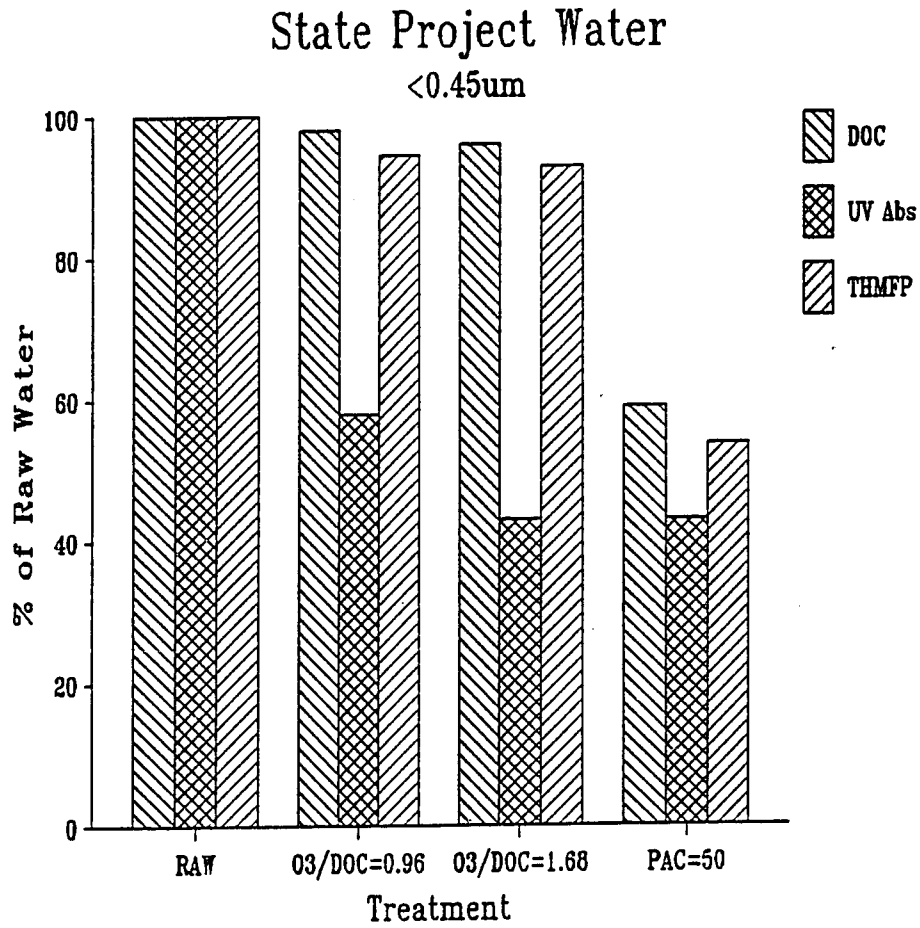## <0.45um

Figure 14. DOM Removal by Ozone and Activated Carbon:
        SPW Source.

sources, respectively.

Ozone provided little reduction in DOC (2 to 5%) while only slightly better reductions in THMFP (5 to 15%) were observed. The DOC and THMFP reductions by ozone discussed above are consistent with those observed by other researchers [49,50,51]. As explained previously, cleavage and destruction of conjugate bonds by ozone results in partial oxidation products that are less reactive towards THMFP. Also notice the alkaline pH of treated waters from data of Tables 1 and 3. This is a strong indication of ozonation by free radical pathway, a "non-selective mechanism" [22,37,52]. Eventhough the free radical induced pathway is faster than the direct oxidation at acidic pH, the radicals may "self-extinguish" and/or react with scavengers such as alkalinity (HCO_3^-) and NOM, a problem at high pH [22,37,52].

The most effective role of ozone was in reducing the UV absorbance, indicative of the color imparted by humic substances [1,2,44]. The effect of UV absorbance reduction caused by ozone agrees with that observed by other researchers in ozonation work [49,51].

The activated carbon adsorption treatment proved more effective than ozone treatment, under the limited range of experimental conditions studied in this research.

The effects of the two treatments on AMW distributions

are shown in Figures 15 and 16 for CRW and SPW sources, respectively. In relation to THMFP results presented for the CRW source, ozone was modestly capable of removing higher AMW material. Although the experimental data suggest little effect on lower AMW material, the conversion of >1000 AMW to <1000 AMW material may be approximately equivalent to the destruction of originally present <1000 AMW material. The DOC data presented for the SPW source reflect the same general trend.

Experimental results derived from treatment of pre-isolated <1000 AMW material are shown in Figures 17 and 18 for CRW and SPW sources, respectively. A comparison of the "pre-isolated fraction" DOC and THMFP results with the corresponding results derived from treatment of the overall DOM associated with each water source indicates that both adsorption and oxidation were more effective in removing lower AMW material when in the absence of higher AMW material.
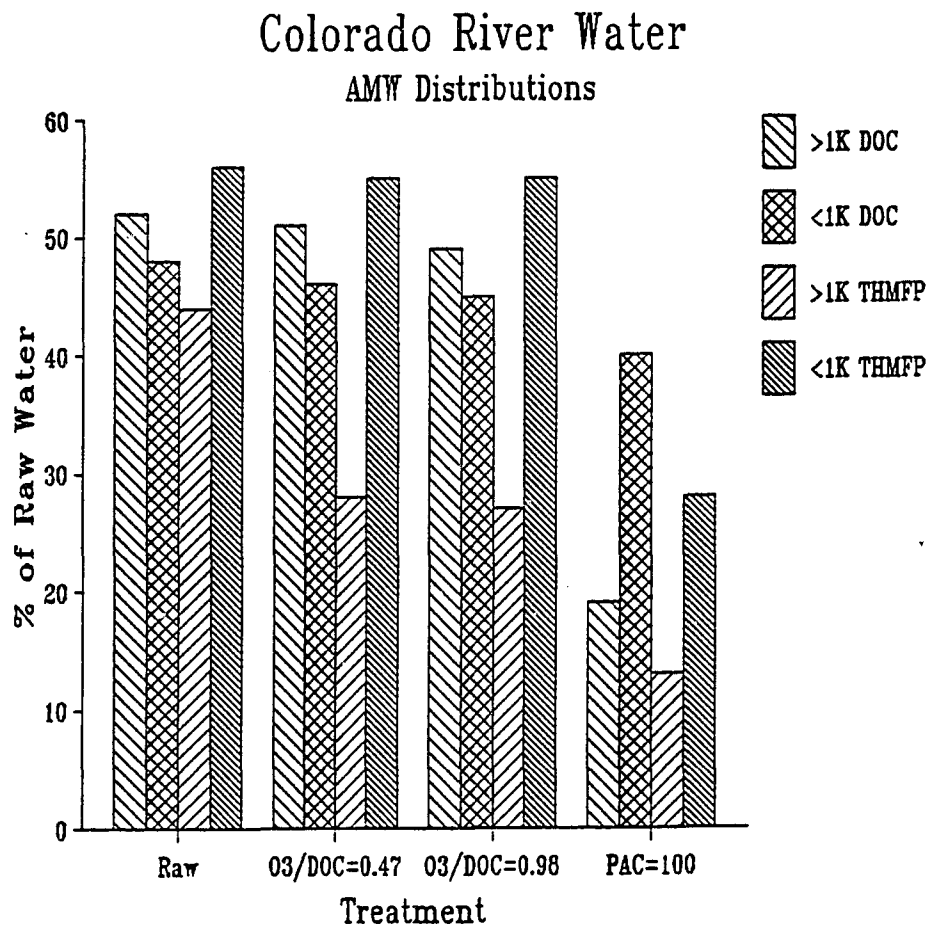
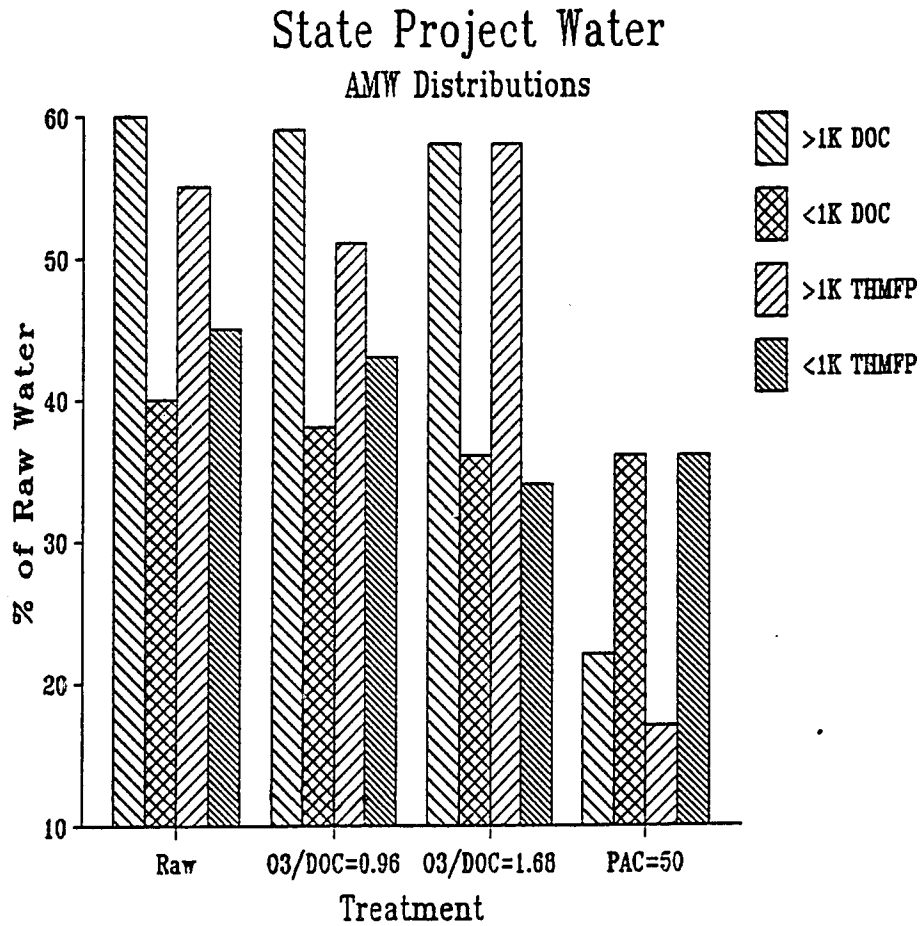**Figure 15.** Treatment Effects on AMW Distributions: CRW Source.

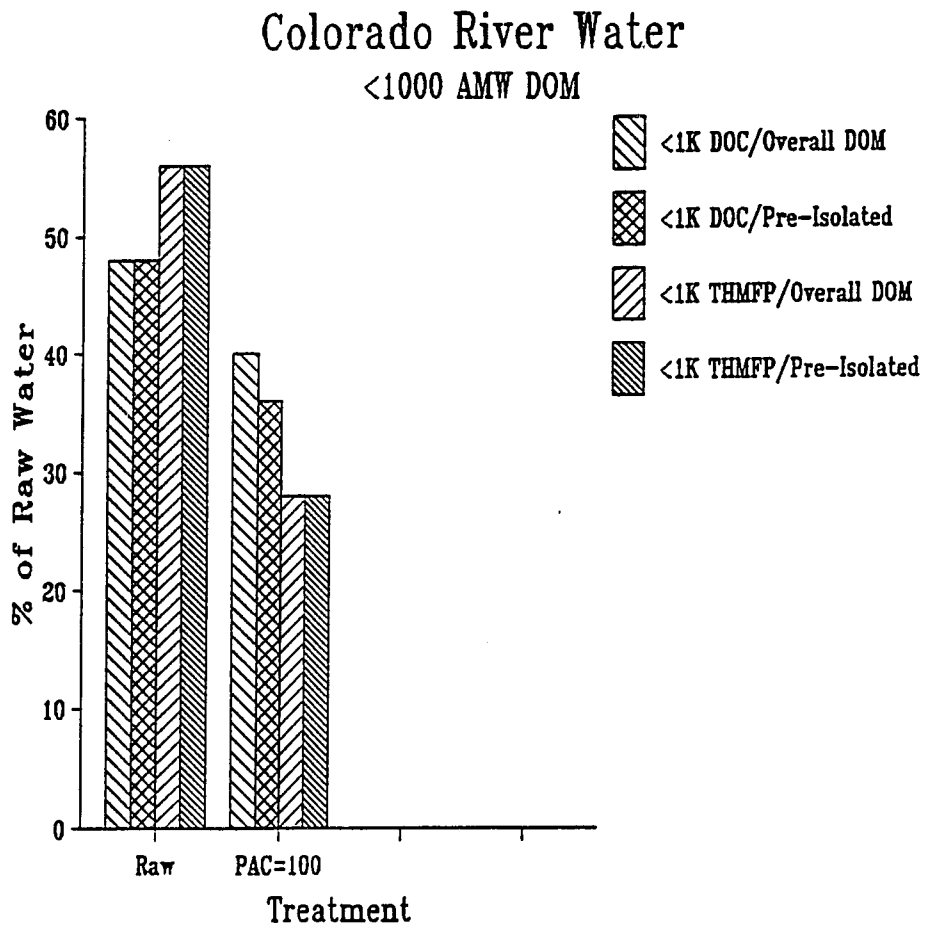**Figure 16.** Treatment Effects on AMW Distributions: SPW
Source.

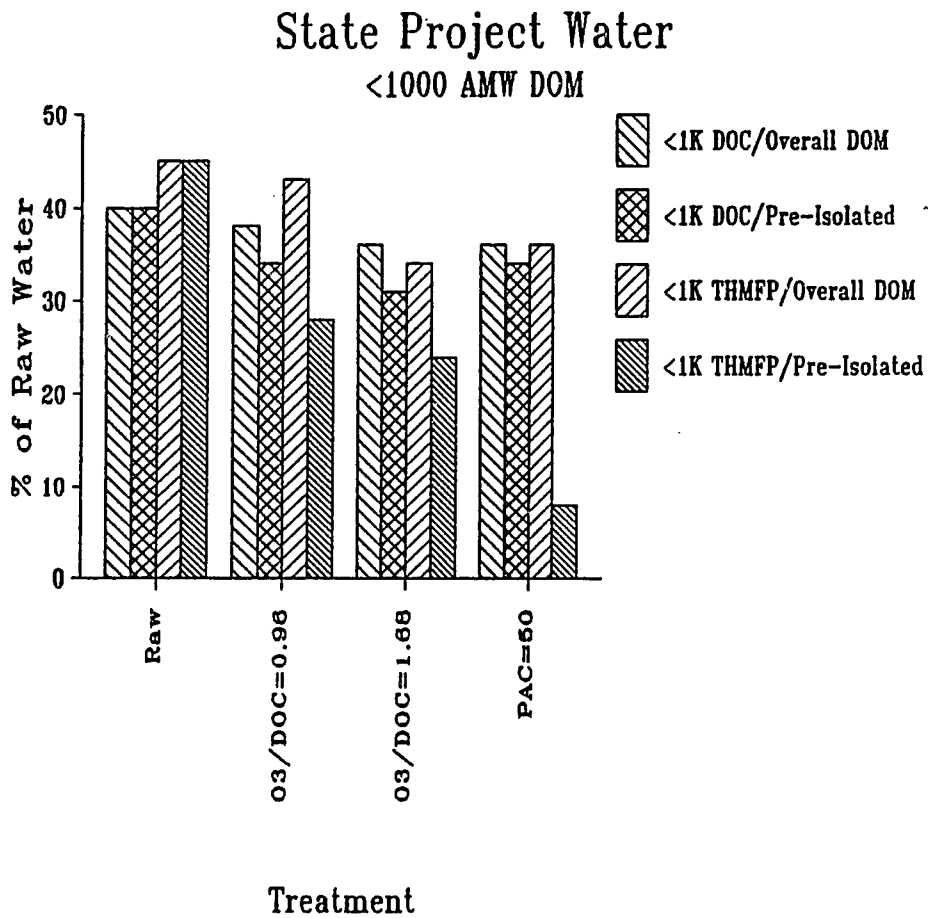Figure 17. Treatment Effects on <1000 AMW DOM: CRW Source.

Figure 18. Treatment Effects on <1000 AMW DOM: SPW Source.

CHAPTER 6

CONCLUSIONS

Bromide ion played an important role in the quantitative formation and speciation of THM compounds in CRW and SPW sources. In the absence of bromide, chlorine reacted with THM-precursors (i.e., humic substances) to form chloroform, the most ubiquitous THM species. In the presence of bromide, brominated THMs were formed, including bromodichloromethane, dibromochloromethane and bromoform. These species result as a consequence of the oxidation of bromide to bromine (HOBr) by chlorine. Comparing these two halogens, HOCl functions as a more effective oxidant while HOBr behaves as a more efficient halogen-substituting agent.

Generally, less than 10% of the applied chlorine becomes incorporated into THM-Cl (i.e., organo-Cl associated with either of the three chlorine-containing THM species). In contrast, as much as 50% or greater of the original bromide present becomes incorporated into THM-Br.

While the present primary standard is 100 ug/l for total THMs, it is important to note that the higher molecular weight of bromine exerts a strong influence on the mass yield of THMs. For example, a 1.0 umol/l concentration of chloroform corresponds to a weight-basis concentration of 120 ug/l while a 1.0 umol/l concentration of bromoform is

equivalent to a weight-basis concentration of 253 ug/l. This factor coupled with the greater halogenation efficiency of bromine makes it more difficult to meet the present standard if the source water contains significant amounts of both bromide and precursor material. Another concern is that THMs are not the only brominated organic by-products formed; significant amounts of ill-defined bromohumics and bromo/chlorohumics are also formed, as well as other brominated disinfection by-products (DBPs).

"Bromide-spike" studies indicate that the presence of bromide affects the THM species yield, distribution and rate of formation. An increase in bromide ion concentration will result in an increased yield (on both a weight and a molar basis) of total THMs. The THM species distribution is due to the fast oxidation of bromide to bromine by chlorine which is in turn faster than the reaction of chlorine with THM-precursors to form chloroform. The effects of bromide on THM formation kinetics are less clear. It appears that, at high Br^-/DOC ratios, bromoform formation is kinetically preferred to chloroform formation. The shift to brominated THM species can presumably be attributed to the independent roles of chlorine and bromide in the chlorination and bromination reaction series.

Activated carbon adsorption, either in a GAC or PAC mode of treatment, increases the Br^-/DOC ratio and also

causes a shift in THM species toward more brominated species. Even if THM-precursors are significantly removed by adsorption, bromide ion can still interact with subsequent oxidants (e.g., chlorine) with any resultant bromine (an "in-situ" disinfectant generated from chlorine) able to react with residual THM-precursor.

Ozone even without post-chlorination can lead to the formation of bromoform in waters containing bromide. The bromoform formation is due to bromine (HOBr) which is essentially an "in-situ" disinfectant and an important intermediate generated from ozone oxidation. If post-chlorination is practiced, pre-ozonation of water containing humic substances and bromide can cause a shift in THM species from chloroform to brominated THM species. In this case, the "in-situ" bromine disinfectant is generated from both ozone and chlorine. Obviously, the concentration of brominated THMs, in particular that of bromoform, depends on the extent of ozone oxidation (i.e., O_3 concentration), applied chlorine dose, the pathway of ozone oxidation (i.e., pH), the concentration of bromide ion and the nature of THM-precursors present in natural aquatic systems.

The main application of this research is to achieve a better quantitative understanding of THM formation and speciation in order to meet future, more stringent federal primary standards.

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