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**EVALUATION OF TREATMENT ALTERNATIVES  
FOR THM-PRECURSOR REMOVAL FROM THE  
PO RIVER AND NI RIVER, VIRGINIA**

by

**Siroos Mostaghimi**

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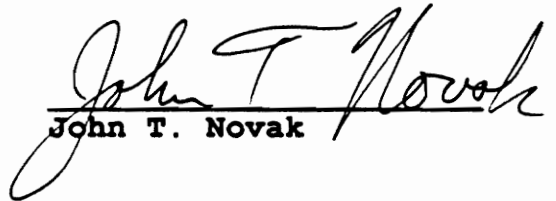
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**IN**

**ENVIRONMENTAL SCIENCE AND ENGINEERING**

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Environmental Engineering

(ABSTRACT)

A study was undertaken to evaluate the effectiveness of alum coagulation, permanganate and chlorine dioxide preoxidation, and powdered activated carbon pretreatment for the removal of trihalomethane (THM) precursors from the Po River, the Ni River and the Ni River Reservoir waters in eastern Virginia. The effects of temperature and storage were also studied. Samples were collected on two occasions and were analyzed for total organic carbon (TOC), THM-formation potential (THMFP), color, UV-absorbance and pH. Samples were then treated in a manner similar to that in a typical water treatment plant by bench-scale jar tests and reanalyzed for TOC, THMFP, color and UV-absorbance.

The results indicate that the THMFPs of both Po and Ni River waters were high. Alum coagulation at pH 6.0 reduced TOC by as much as 48 percent while THMFP reductions averaged 63 percent. Permanganate preoxidation at dosages as high as 2.0 mg/L reduced THM precursors by less than 14 percent. Powdered activated carbon at 10 to 20 mg/L reduced THM precursors by less than four percent. Application of 2

mg/L chlorine dioxide reduced THM-precursors by eight percent over what could be achieved by alum coagulation alone. A major conclusion was that treatment of the Po River by conventional measures to meet existing and future drinking water standards for THMs would be difficult, if not impossible.

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# CHAPTER I

## INTRODUCTION

The disinfection of water supplies has been used to prevent transmission of waterborne diseases throughout the world. Chlorine has been the principal disinfectant because of its low cost and its persistence at levels necessary for destroying bacteria throughout the distribution system. This method of disinfection, however, became suspect when Rook (1974) in the Netherlands and Bellar et al. (1974) in the United States reported the presence of trihalomethanes (THMs) and other halogenated organics in finished waters. The National Cancer Institute (1976) reported that chloroform, a by-product of chlorination, produced an increased incidence of tumors in laboratory experiments with mice and rats.

In 1975, the National Organics Reconnaissance Survey (Symons et al., 1975) investigated the quality of 80 city water supplies throughout the United States. Four THMs were found to be common in chlorinated drinking waters, although they were either absent or present in low concentrations in the raw waters. In 1979 the United States Environmental Protection Agency (USEPA, 1979) promulgated a maximum

contaminant level (MCL) of 0.10 mg/L of total trihalomethanes (TTHMs) at the consumer's tap.

The methods used for controlling the concentrations of THMs can be categorized as :

- 1) prevention of THM formation by removing precursors before chlorination.
- 2) removal of THMs after their formation.
- 3) use of a disinfectant other than chlorine.

The objectives of this study were to :

1. evaluate the relative effectiveness of THM-precursor reduction in surface waters by : a) preoxidation with chlorine dioxide and potassium permanganate, b) adsorption by powdered activated carbon, and c) alum coagulation.

2. compare the characteristics and treatability of the Ni River and Ni River reservoir so that inferences regarding the effects of impounding the Po River could be made.

3. evaluate the effects of long-term laboratory storage and temperature on TOC reduction and THM formation in surface waters.

The study focused on the Po River, which was under consideration at the time as a potential water supply for Spotsylvania County. A major consideration in determining the suitability of this river was its THM formation potential after optimum treatment. The research was

intended also to provide data that Hayes, Seay, Mattern and Mattern, consulting Engineers for Spotsylvania County, could use in selecting treatment procedures at new treatment plant.

## CHAPTER II

### LITERATURE REVIEW

The research detailed in this thesis concerned effective treatment of a surface water supply for the prevention of trihalomethane (THM) formation in water. Trihalomethanes are chlorinated organic compounds that are formed during the disinfection of drinking water with chlorine, the major disinfectant in the United States today. There are many aspects of the subject of THMs in water supplies, and these are reviewed in this chapter.

#### Trihalomethanes

##### Occurrence

Rook (1974) in the Netherlands and Bellar et al. (1974) in the United States reported the presence in finished drinking water of THMs and other halogenated organic compounds. Symons et al. (1975) initiated the National Organics Reconnaissance Survey (NORS) to determine to what extent organics were present in drinking water nationwide. Several THMs were discovered in the drinking waters and were suspected of being formed by chlorination. Rook (1974) and Stevens et al. (1976) suggested that organic

precursors responsible for the formation of THMs during chlorination were naturally occurring humic substances in the water. Trihalomethanes are formed when chlorine is added to water containing organic precursors. The predominant volatile, chlorinated organics formed are : chloroform ( $\text{CHCl}_3$ ); bromodichloromethane ( $\text{CHBrCl}_2$ ); dibromochloromethane ( $\text{CHBr}_2\text{Cl}$ ), and bromoform ( $\text{CHBr}_3$ ). Of these four, chloroform appears most frequently and in the highest concentration (Symons et al., 1975; Duke et al., 1980; Johnson and Jenson, 1986; Batchelor et al, 1987).

Brett and Calverly (1979) surveyed the THM concentration changes in a distribution system. They reported that THM concentrations increased by 75 percent when the water was stored for seven days at a temperature of 20 °C.

Singer et al. (1980) conducted a survey of THM concentrations in several North Carolina drinking water supplies. They studied the THM formation in the raw water, settled water, and finished water. They reported that the instantaneous THM concentrations in finished water ranged from 9 to 257 ug/L, while the instantaneous, raw-water THM concentrations were less than 5 ug/L. The seven-day total THM (TTHM) concentrations at pH 6.7 ranged from 40 to 427 ug/L. The instantaneous THM concentrations were higher in the summer and lower in the winter. They suggested that



this variation was because of the temperature effect on the kinetics of reactions.

Glaze and Rawley (1979) conducted a survey of THM concentrations in 25 raw-and-treated water supplies in east Texas. They reported that the total trihalomethane (TTHM) concentrations in the raw waters were very small, averaging less than 1 ug/L. The TTHM concentrations in the finished water samples, which were chlorinated with 15 mg/L of chlorine and incubated for 5 days at 26 °C, were significantly higher and ranged from 6 ug/L to 905 ug/L. Veenstra and Schnoor (1980) studied TTHM levels in an Iowa River water supply and reported that TTHM concentrations varied seasonally from 50 to 335 ug/L with a mean of 173. They attributed the seasonal changes in TTHM concentrations to the nature of the organic precursors and not to environmental conditions. They suggested that apparent molecular weight and the presence of humic or fulvic acids (to be discussed later) were among the properties of the naturally occurring organic matter that may be responsible for the seasonal patterns in the TTHM levels in the Iowa River.

#### Health Effects of THM

The risks associated with exposure to the variety of

organic contaminants that may be present in drinking water supplies are difficult to quantify. The National Cancer Institute (1976) reported that chloroform, a by-product of chlorination, produced an increased incidence of tumors in laboratory mice and rats. Levin et al. (1987) emphasized that although THMs may not be the only harmful by-product of water chlorination, they may indicate the presence of other chlorinated organic contaminants. Issacson et al. (1983) conducted a study to identify potential correlation of THMs in groundwater and surface water supplies serving communities of 1000 to 10000 people. They reported that THMs were detected in 94 percent of the surface water supplies included in the study.

As a result of widespread reports of hazardous health effects of THMs, the USEPA, in 1979, began to regulate the concentration of THMs in public water supplies serving more than 10,000 people. The maximum contaminant level (MCL) currently allowed is 0.10 mg/L TTHM (EPA, 1979).

### **Formation of Trihalomethanes in Natural Waters**

#### **Humic Substances**

Many surface waters have a characteristic brown color that is caused by the presence of complex organic compounds

of natural origin derived from the water-soluble compounds of soil and humus and peat (Hall and Packham, 1965). These substances are generally referred to as "humic substances". Aquatic humic substances are important from the water treatment perspective for several reasons, including their role as precursors in the formation of chlorinated byproducts, such as THMs and other organochlorine compounds. Rook (1974, 1976) reported that chloroform is formed from the reaction of chlorine with humic substances in natural waters. These substances originate from vegetative decay and make up a significant portion of total organic carbon (TOC) content of natural waters (Thurman, 1985).

Humic substances can be divided into three categories based on their solubility differences (Oliver and Visser, 1980; Collins and Amy, 1985) : 1) fulvic acids (FA), which are soluble under both acidic and basic conditions; 2) humic acids (HA), which are soluble under basic conditions but precipitate under acidic conditions; and 3) humins, which are insoluble.

Humic acids and fulvic acids, constitute over 80 percent by weight of natural organic materials (Veenstra and Schnoor, 1980). The humic acids have a higher molecular weight and more readily coagulate than the fulvic acids (Babcock and Singer, 1979). The three humic fractions have

similar structures but differ in functional group content, elemental analysis, and molecular-weight distribution. A summary of the major elements typically found in humic and fulvic acids is presented in Table 1 (Schnitzer and Khan, 1972). The data in this table indicate that fulvic acids differ from humic acids in that they contain more oxygen but less carbon and hydrogen and have a higher content of oxygen containing functional groups (COOH, OH, C=O) per unit weight.

Schnoor et al. (1979) separated naturally occurring organic matter in the Iowa River and found that 90 percent of the organics (as organic carbon) were associated with organics having a molecular weight of <3000. Seventy-five percent of the THMs were derived from that fraction. They also reported that seven percent of the organics and 20 percent of the THMs were derived from compounds of <1000 molecular weight. In a related study, Veenstra and Schnoor (1980) reported that the greatest THM yield per unit of organic carbon occurred in coagulation with molecular weight with an apparent molecular weight of <1000.

Joyce et al. (1984) found that the lowest molecular weight fraction (<1000) of humic substances collected from three separate sources in Massachusetts were characterized by the lowest chloroform yield. They also reported that

Table 1. Elemental analysis of humic and fulvic acids  
(Schnitzer and Khan, 1972).

---

Element	<u>Percentage, ash-free dry weight</u>	
	Humic acid	Fulvic acid
Carbon	50-60	40-50
Hydrogen	4-6	4-6
Oxygen	30-35	44-50
Nitrogen	2-6	< 1-3
Sulfur	0-2	0-2

---

removal of the highest molecular weight fraction can achieve the greatest reduction in THMs. Collins and Amy (1985) reported that the reactivity of aquatic organic matter, including humic substances, in forming THMs varies as a function of molecular weight, and, with few exceptions, THMs increased with increasing molecular weight. Babcock and Singer (1979) reported that both humic and fulvic acids are precursors of chloroform. The chlorination of humic acid results in a greater yield of chloroform than the chlorination of an equivalent amount of fulvic acid.

#### Factors Affecting THM Formation

Factors influencing THM formation include the nature and concentration of precursors, pH, temperature, chlorine to TOC ratio, concentration of bromide ion, and chlorine dose and contact time (Stevens et al., 1976; Stevens and Symons, 1977; Trussel and Umphers, 1978).

#### Nature and Concentration of Precursors

Although humic substances in natural waters are the most significant THM precursor compounds (Rook, 1974; Stevens et al., 1976), a wide variety of organic substances can act as THM precursors. Morris and Baum (1978) reported that naturally occurring soluble organics other than humics are also THM precursors. Rook (1976) investigated the effect of

varying precursor concentrations on the production of chloroform and reported that a linear relationship exists between chloroform production and organic matter up to 250 mg/L TOC.

### pH

In general, THM formation increases with increasing pH, probably because the final step in the haloform reaction in which requires basic conditions (Stevens *et al.*, 1976; Oliver and Lawrence, 1979; Oliver, 1979; Berger, 1987). Morris and Baum (1978) reported that THM formation can continue after the free chlorine has been quenched if the pH is raised. Stevens and Symons (1977) showed that chloroform yield of humic substances at pH 9.2 was twice that at pH 6.7.

### Temperature

Seasonal variations in temperature will influence THM formation. In general, THM formation increases with increasing temperature (Stevens *et al.*, 1976; Oliver, 1979). Stevens and Symons (1977), using water samples from the Ohio River, reported that approximately twice as much chloroform was produced at 25 °C as at 3 °C. Knocke *et al.* (1986) reported that the THM concentration in finished water

that had been treated at 2 °C was significantly lower than in water treated at 22 °C. Kavanaugh et al. (1979) determined a third-order kinetic rate constant for THM formation in which the rate constant doubles for every 10 degree increase in temperature between 0 °C and 30 °C .

### Chlorine to TOC Ratio

Babcock and Singer (1979) studied the effect of varying chlorine dose to TOC ratio. They reported that a chlorine-to-TOC ratio of less than one resulted in complete chlorine consumption in less than five hours. They also concluded that a chlorine-to-TOC ratio greater than five resulted in free chlorine residual and continuous chloroform formation after four days of chlorine contact time.

### Bromide Ion

The presence of bromide ion in natural waters not only affects the distribution of the individual THMs but also influences the total THM concentrations (Berger, 1987). Oliver (1979) reported an increase in brominated THMs with increasing bromide ion concentration. He concluded that the increase in THM concentrations was caused by the rapid reaction of bromide ion with chlorine in water to produce hypobromous acid and hypobromide ion. He also reported that



the total concentration of THMs increases markedly with increasing bromide ion to three times the initial concentration in the absence of bromide at  $\text{Br}^- : \text{Cl}_2$  ratios greater than one.

#### Chlorine Dose and Contact Time

Production of THMs will continue as long as there is chlorine residual and excess TOC available. Since there is a chlorine residual requirement at the consumer's water tap, therefore THM production will be increasing with increasing contact time. Several investigators have reported the effects of chlorine dose and contact time ( Rook, 1977; Stevens et al., 1976; Trussel and Umphres, 1978). Rook (1976), using a synthetic water containing fulvic acid reported that as the chlorine dose increased, The TTHM concentration increased but at a decreasing rate.

#### Controlling THM Formation

Since early 1900s, chlorine has been the principal disinfectant because it is an effective germicide and it is relatively inexpensive (White, 1986). The safety of chlorine as a disinfectant for drinking water was first questioned in 1974 when it was found that chlorination of drinking water will result in the formation of THMs (Rook,

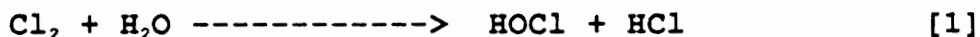
1974; Bellar et al., 1974). Additional concerns were raised when the National Cancer Institute (1976) reported that chloroform produced an increase incidence of cancerous tumors in mice and rats. The initial response to these observations was to examine alternative disinfectants that would not produce THMs. An overview of the alternative disinfectants is presented in this section.

## Alternative Disinfectants

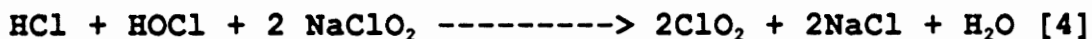
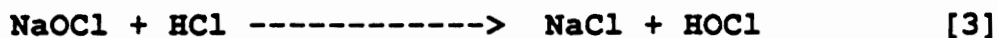
### Chlorine Dioxide

Chlorine dioxide is a powerful disinfectant and oxidant. It is available in two forms : 1) gas, and 2) aqueous solution. Chlorine dioxide in the gaseous form is almost never used commercially, because of its explosiveness (White, 1986). Two methods are commonly used to generate chlorine dioxide for water treatment (Katz, 1980) :

a) from chlorine and sodium chlorite



b) from sodium hypochlorite and sodium chlorite



In either method , the addition of a mineral acid can be used to control the reaction stoichiometry and thus

eliminate an excess of either free chlorine or chlorite to prevent THM formation or chlorite toxicity.

Chlorine dioxide has been suggested as one of the best alternatives to chlorine gas (Katz, 1980), but the use of chlorine dioxide has been limited by its cost (three times of that chlorine) and the absence of a clear understanding of the chemistry of biological impact (Calabrese et al., 1978). Tiffet et al. (1977) and Cronier et al. (1977) reported that chlorine dioxide is a more efficient vermicide and bactericide than chlorine and is effective in over a wide pH range. Chlorine dioxide that is chlorine-free, in reaction with humic substances does not form THMs (Aieta and Berg, 1986). Chlorine dioxide can be used to remove iron and manganese from the water supply. Both Fe and Mn compounds are oxidized more efficiently by chlorine dioxide at pH 7 or above (Katz, 1980). The dosage of chlorine dioxide used depends on whether it is used to pretreat the influent water, the plant water or to treat the effluent water. The approximate range of chlorine dioxide added is 0.1 to 1.5 mg/L (Gall, 1978).

### Ozone

Ozone ( $O_3$ ) is an unstable gas which is slightly soluble in water. It is the most powerful oxidizing agent/

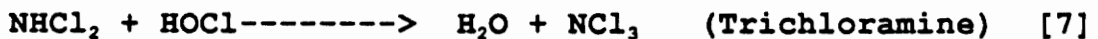
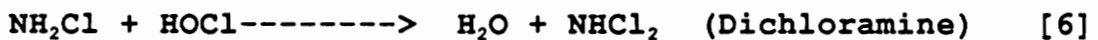
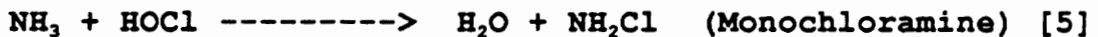
disinfectant readily available for water and wastewater treatment (White, 1986). Ozone is applied to water for the following purposes (Rice et al., 1986): a) oxidation of natural organics as an aid to floc formation, b) destruction of THMs precursors prior to chlorination, c) destruction of THMs and other toxic organic molecules, and d) preoxidation in preparation for biological treatment.

Ozone must be generated on site because it rapidly decomposes and reverts back to oxygen. It usually is generated by an electric discharge process in a flowing air or oxygen stream (White, 1986). The beneficial effects of ozone as a disinfectant and oxidant have been reported by several researchers (McBride, 1978; Kimes and Taylor, 1980; Tate and Trussel, 1980). Most significant are the advantages of preozonation in direct filtration systems where improved flocculation is accompanied by lower THM levels when the water chlorinated (Cheremisinioff et al., 1981). Kuhn et al. (1978) summarized the advantages and disadvantages of ozone oxidation of drinking water. Among other things, they reported rapid disinfection and virus inactivation as advantages and high investment and operating costs as disadvantages of using ozone in water treatment. Knight and Tuckwell (1985), using a River water from Bristol in England, reported that preozonation of filtered water

improved the quality of water by reducing color, TOC, absorbance due to aromatic organic compounds, chlorine demand, and THM formation after chlorination.

### Chloramines

Chloramines are formed when water containing ammonia is chlorinated or when ammonia is added to water containing chlorine. Chloramination can be accomplished by application of chlorine at a chlorine-to-ammonia nitrogen ratio of 5:1 or less (White, 1986). Three chloramine compounds can be produced depending upon the ratios of chlorine and ammonia :



Chloramines are less effective as disinfectants than free chlorine; however, their residual is more persistent than chlorine (Black and Willems, 1961). Chloramines do not form chlorinated organics (Stevens et al., 1976; Norman et al., 1980; Houck et al., 1985). Chloramines offer a relatively inexpensive means for reducing THM formation by providing an alternative disinfection process to the use of free chlorine residual (White, 1986). Norman et al. (1980) reported an average reduction of 75 percent in formation of THMs at the consumer's tap by introducing chloramines

instead of free chlorine for disinfection. They also reported improvement in the taste and odor of the water.

### Permanganate

Little work has been done on the control of organics by permanganate treatment. Usually, permanganate application is limited to taste-and-odor control and, in some cases, for reducing iron, manganese, sulfide and phenols (Voss et al., 1980). Singer et al. (1980) studied reduction in THM formation potential (THMFP) by treatment of raw water and settled water with permanganate. Neither was chlorinated before treatment with potassium permanganate. They reported THMFP reductions from 20 to 40 percent, but doses of 10 mg/L permanganate were required to give the best results. The effect was greater at pH 10.3 than at 6.5. Voss et al. (1980) using an unrealistic dose of permanganate (48 mg/L), and 3.5 hours contact time at pH 10.3, reported 83 percent reduction in chloroform formation levels.

### Ultraviolet (UV)

Ultraviolet radiation is effective against all waterborne pathogens. the electromagnetic waves of ultraviolet rays provide disinfection by direct contact with microorganisms (White, 1986). Ultraviolet can be generated

by passage of an electric discharge through a low-pressure mercury vapor enclosed in a special glass tube known commercially as germicide lamp (Oliver and Gray, 1976). The disadvantages with UV are that there are no long-term residual germicidal effects. Color, turbidity and iron salts can reduce the disinfectant potential of UV radiation. Generation and use of UV is generally more costly than other disinfectants (Cheremisinoff et al., 1981).

### THM Precursor Removal

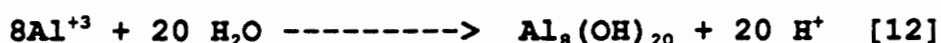
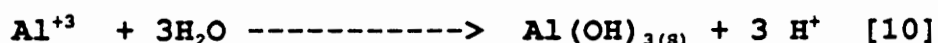
#### Coagulation and Sedimentation

The type, size and concentration of particles affect their behavior in water treatment systems. The coagulation process involves both the chemical destabilization of particles and physical transport of destabilized particles resulting in particle collisions to form larger aggregates called floc (Edzwald, 1979). Particle destabilization may be accomplished by four mechanisms (O'Melia, 1972) :

1) compression of the electrical double layer by addition of electrolyte, 2) adsorption/charge neutralization, 3) interparticle bridging, and 4) enmeshment of colloids in a precipitate of metal hydroxide.

Salts of aluminum, [Al(III)] and iron, [Fe(III)] are widely used as coagulants. Alum ( $\text{Al}(\text{SO}_4)_3 \cdot 14 \text{H}_2\text{O}$ )

dissolves readily in water, releasing ions to solution. Some of the hydrolysis reactions are as follows (O'Melia, 1979) :



The aluminum species that is formed depends on the pH of the water and the alum dosage.

The extent of coagulation of humic substances or color with aluminum and iron salts varies with the concentration of humic material in the raw water, coagulant dosage, pH and turbidity of water ( Black and Willems, 1961; Hall and Packham, 1965; Mangravite et al., 1975 ). Edzwald (1979) studied the effect of pH on humic acid removal and reported that higher alum dosages were required as the pH increased above 5. He concluded that at pH 4 to 6, destabilization is accomplished by charge neutralization and, as alum dosage increased or if the pH is raised above 6, precipitation is the mechanism for removal of humic substances.

Semmens and Field (1980) reported that organic removal increased with increasing alum dose, and alum doses higher



than those normally used for turbidity removal (5-20 mg/L) are needed to obtain the best organic removal. They also reported that the optimum pH for organic removal was pH 5 in the rapid mix, which corresponded to a final pH of 5.6 to 5.8.

Knocke et al. (1986) reported that water temperature did not appear to effect the removal of total organic carbon (TOC) during coagulation with metal ion salts, but color removal was slightly reduced at low temperatures. They also found out that the efficiency of coagulation for removing TOC, color and THMFP improved when the water was treated at pH 5 rather than pH 7, regardless of temperature.

Hoehn et al. (1984) reported that alum coagulation of a lake water reduced THM precursors by about 50 percent, and its effectiveness did not appear to be altered by variation in algal or bacterial densities in the lake.

#### Powdered Activated Carbon (PAC)

Powdered activated carbon (PAC) is most frequently used for taste and odor control, and it can be added either through a dry feed or as carbon slurry (Blank, 1979). Application of PAC can increase the removal of THM precursors, as well remove THMs after they are formed (McGuire and Suffet, 1980). The Environmental Protection

Agency has suggested a 10 mg/L limit on PAC dosage, based upon the average annual dosage (Culp, 1984). Environmental Science and Engineering (1986) citing Seegar et al. (1978) reported a removal of 20 percent carbon tetrachloride from the raw Ohio River water by using 30 mg/L of PAC. Factors that must be evaluated in application of PAC are : 1) contact time, 2) proper mixing, and 3) effects of chlorine and other chemicals (ESE, 1986).

## CHAPTER III

### MATERIALS AND METHODS

#### Sample Collection

Water samples were collected from Po River, Ni River, and Ni Reservoir. The Po River was sampled on two occasions: June 14, 1989 and January 10, 1990. The Po River is approximately three miles south of Spotsylvania Courthouse, where it flows under the bridge on Route 208 in eastern Virginia. The Ni River was sampled on one occasion (August 14, 1989) in the National Forest near Katherine's Furnace along Jackson Trail, which is approximately 18 miles upstream of the confluence on the Ni River and Cattail Branch and 20 miles above the backwater of Ni River Reservoir. The Ni River Reservoir was also sampled on August 14 at the raw-water intake of the Spotsylvania County water treatment plant.

The samples were collected from the surface water in a five-gallon, plastic bucket and put in prewashed, polyethylene carboys for transport to the Virginia Tech Environmental Laboratories. For metal analyses, separate

samples from each collection site were collected in amber, 200-mL, glass bottles and acidified to pH<2 with nitric acid. The samples were refrigerated at 6 °C upon arrival in the laboratory. Approximately one gallon of each sample was incubated at laboratory temperature in an amber glass jar, and changes in total organic carbon (TOC) and trihalomethane formation potential (THMFP) were monitored for several months.

### Laboratory Analysis

#### Chemical Analysis

##### pH

The pH was measured with a Fisher (Pittsburgh, PA) Accumet Model 230 pH/Ion Meter, which was calibrated before each use with standard buffer (pH 4, and 10) solutions.

##### Alkalinity

Alkalinity was determined according to the method described in Standard Methods for the Examination of Water and wastewater, 16th Edition (1985).

##### Color

The color of raw and treated water was determined by

measuring light absorbance at 420 nm with a Beckman Spectrophotometer Model DU-6 using 1 cm light path. Sample absorbance was compared to that of standard solutions of cobaltous-platinum chloride according to the spectrophotometric method (Sec. 204 B) of Standard Methods for the Examination of Water and Wastewater, 16th Edition (1985).

### TOC

Total organic carbon was determined with a Dohrmann/Envirotech (Santa Clara, California) Model 54 Total Organic Carbon Analyzer, operating in the ultralow mode. All glassware used for TOC determination was washed with soap and tap water, soaked in a chromic acid bath for 24 hours, then rinsed first with tap water and finally with distilled water. They were dried at 105 °C and sealed with aluminum foil caps until used. Water samples were placed into the clean bottles, five drops of 85 percent phosphoric acid were added, and the sample was air bubbled for five minutes before analysis. The TOC analyzer was standardized with a 10 mg/L standard carbon solution of potassium hydrogen phthalate each day on which analyses were performed. Each sample was analyzed three times, and the results were averaged.

### Iron and Manganese Determinations

Samples that were preserved with nitric acid to pH 2.0, were analyzed for Fe and Mn concentrations by flame ionization spectroscopy with a Perkin-Elmer (Norwalk, Connecticut) Model 703 Atomic Absorption Spectrophotometer equipped with a flame atomizer.

### Turbidity

Turbidity was measured with a Hach 2700 Model Turbidimeter (Ames, Iowa). The turbidimeter was calibrated prior to use with standards provided by manufacturer.

### Ultraviolet Absorption

The absorbance of ultraviolet light at 254 nm was determined with a Beckman Spectrophotometer, Model Du-6 with a cuvette path length of one centimeter.

### Jar Test Procedures

#### Basic Procedure

A conventional, six-place paddle mixer (Phipps and Bird, Richmond, VA) was used to conduct the jar tests. Alum solution was prepared by dissolving aluminum sulfate crystals,  $\text{Al}_2(\text{SO}_4)_3 \cdot 14.3 \text{H}_2\text{O}$ , in water. One-liter samples were placed in rectangular jars and were held to equilibrate

to laboratory temperature for two hours before alum treatment. Prior to alum addition 50 mg/L (milligrams per liter) of alkalinity in the form of sodium bicarbonate ( $\text{NaHCO}_3$ ) was added to buffer the water and ensure a good floc. Alum dosages of 20, 40, 60, 80, and 100 mg/L were added to the samples and rapid-mixed for one minute at a paddle speed of 100 rpm. The pH was adjusted to 6.0 by addition of either 0.5 N HCl or 0.5 N NaOH during the rapid mix phase. The paddle speed was then reduced to 15 rpm, and samples were flocculated for 30 minutes. The paddles were then removed from the water, and the suspended alum floc was allowed to settle for one hour. The supernatant was filtered through Whatman #42 filter paper that had been previously washed with deionized, distilled water to remove extraneous organic carbon. The treated water samples were collected in 1-L, prewashed, glass jars with tight seals and were refrigerated to await further analysis.

The basic procedure described above was common to all the studies involving the evaluations of oxidants and powdered activated carbon (PAC). The following describe those evaluations :

#### Powdered Activated Carbon (PAC) Treatment

Dosages of 10, 20, 40, 50 and 60 mg/L of CECA brand PAC

(CECA 20-C) were used to evaluate its effectiveness for removing THM precursors from samples of Po River, Ni River and Ni River Reservoir waters. The samples were slowly-mixed for 30 minutes prior to alum coagulation (60 mg/L alum), flocculation and settling by the jar-test procedure just described. This particular PAC was selected because previous unpublished studies had shown that it was a superior carbon for removing humic materials (Hoehn, personal communication).

#### Permanganate Treatment

The pH of the samples was adjusted to 7.0 or 10.5 and treated with varying doses of permanganate (0.25, 0.50, 1.0, 1.50, and 2.0 mg/L). The permanganate solution was prepared from reagent grade potassium permanganate. The samples were slowly mixed (40 rpm) for 30 minutes to allow the permanganate to react with substances in the water. After 30 minutes, the samples were treated by the jartest procedure described earlier.

#### Chlorine Dioxide Treatment

Chlorine dioxide was generated from sodium chlorite and acid by procedures described in the Standard Methods for the Examination of Water and Wastewater, 16th edition (Section



410 A, 1985). The strength of the stock solution was determined by titration with 0.0056 N phenylarsine oxide (PAO) with a Fisher Scientific Automated Titrimeter. The procedure was one described by Aieta et al. (1984). The stock solution was refrigerated at 5-7 °C.

Raw water samples were dosed with chlorine dioxide (2, 4, 6, and 8 mg/L) and slowly mixed for 30 minutes. After the preoxidation period, the samples were treated by the jar-test procedure described previously.

#### Trihalomethane Analysis

The TOC of the samples was determined after each treatment described earlier. Chlorine was added to 40-mL samples in glass vials in the ratio of three parts chlorine for each part TOC (weight basis). A standard calcium hypochlorite solution was used as chlorine source. The pH of the sample was adjusted to 7.0 by addition of a phosphate buffer solution, and the vials were sealed with caps lined with Teflon-coated septa. The chlorinated samples were maintained at ambient room temperature (22-24 °C) in the dark, for seven days (The THMFP were defined as the THM concentration that developed after seven days. Rates of THM formation were determined by daily analysis of samples incubated for seven days). Chlorine remaining after the

incubation period was quenched by addition of 100 uL sodium sulfite, and the samples were acidified with nitric acid to prevent hydrolysis, which causes higher THM concentrations. The samples were stored in the refrigerator until analyzed, which usually was not for more than one week.

The THM analyses was the purge-and-trap technique outlined by the Environmental Protection Agency (EPA, 1979). A Tracor (Austin, Texas) Model 560 Gas Chromatograph equipped with a Tekmar LSC-2 purge and Trap concentrator accessory was used for THM analyses. The Tracor instrument was equipped with a Hall electrolytic conductivity detector. The conditions were as follows:

Tekmar LSC-2 (Conductor)

Purge 8 minutes, trap at 30 °C

Desorb 4 minutes, trap at 180 °C

Bake 6 minutes, trap at 225 °C

Tracor 560 Gas Chromatographer

Column- 8 ft. by 0.1 inch ID glass

Packing 0.2 percent carbonax 1500 on Carbonpack-c  
(80/100 mesh)

Carrier gas Helium at 30 ml/min.

A 5-ml sample was introduced into the concentrator.

Areas under each peak were registered automatically by an integrator (Hewlett Packard Model 3390 A) and compared with the peaks obtained from analysis of standard solutions of chloroform ( $\text{CHCl}_3$ ), bromodichloromethane ( $\text{CHCl}_2\text{Br}$ ), dibromochloromethane ( $\text{CHClBr}_2$ ), and bromoform ( $\text{CHBr}_3$ ).

### Quality Control

Samples of the standard solution were analyzed periodically during the THM analysis, to check the instrument calibration. After every six analysis a THM standard was analyzed and variations more than 5 percent were not acceptable. If the variation was greater than five percent, the instrument was recalibrated. Other quality control procedures included analysis of standards prepared by the laboratory supervisor. Also dihydroxybenzoic acid (DHBA) solution was chlorinated, and the chloroform produced was analyzed. The method for using DHBA for quality control is described in Standard Methods for Examination of Water and Wastewater. 17th edition (Section 5710 B, 1989). To make sure that there was enough chlorine in the sample after incubation period, a larger sample of water (100 mL) was chlorinated at the same time the samples were chlorinated. Usually between 0.5-1.0 mg/L chlorine was present at the end of the incubation period.

### Stock Solution and Reagents

The chlorine stock solution was prepared from reagent grade  $\text{Ca}(\text{OCl})_2$  and maintained at 5 °C. Sodium sulfite was used as the dechlorination agent. A solution was made by dissolving 10 grams of reagent grade sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) in 100 mL of distilled water. One tenth mL of this solution will destroy about 5 mg of residual chlorine. A fresh solution was used to quench chlorine in the samples.

Phosphate buffer used to buffer the sample pH to 7.0 was prepared by dissolving 6.81 grams of reagent grade potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ) and 1.17 grams of reagent grade sodium hydroxide ( $\text{NaOH}$ ) in 100 mL of organic-free water. This solution was made fresh every week.

### Effects of Incubation and Temperature

#### on TOC and THMFP

A series of experiments was conducted to evaluate the effects of time and temperature on the TOC and THMFP of Po and Ni River waters. Raw water from both rivers was stored in sealed, amber, glass containers at ambient laboratory temperature (22-24 °C), and in the refrigerator at 5-7 °C. One sample stored at room temperature was shaken three times daily. Analysis of TOC and THM were performed periodically by procedures described previously.

## CHAPTER VI

### RESULTS AND DISCUSSION

#### Raw Water Characteristics

The water-quality characteristics of the Po River, the Ni River, and the Ni River Reservoir are presented in Table 1. The alkalinities of the three samples were low, and ranged from 13 to 16 mg/L. The pH of both the Po and Ni Rivers were in the acidic range (6.3), while the pH of the Ni River Reservoir was neutral (pH 7.0). Both the Po River and Ni River waters were intensely yellow colored ( 222 and 242 pcu, respectively). Humic substances are the cause of the yellow or brown color in waters with high organic content (Edwards and Amirtharajah, 1985). The Ni River Reservoir was also highly colored but much less than the rivers.

Organic compounds which are aromatic or have conjugated double bonds absorb light in the ultraviolet (UV) wavelength region. UV-absorbance can be used to measure the presence of naturally occurring organic compounds, such as humic substances because they contain aromatic moieties and absorb light (Edzwald et al., 1985). The highest UV-absorbance at

Table 2. Water-quality characteristics of the Po River, Ni River, and Ni River Reservoir used in this study

Water Quality Characteristics	Po River*	Ni River	Ni River Reservoir
Alkalinity, as CaCO <sub>3</sub> , mg/L	16.0	13.0	14.0
pH	6.3	6.3	7.0
Color, pcu	222.0	242.0	102.0
UV-Absorb., 254 nm, 1cm	0.418	0.472	0.238
TOC, mg/L	7.28	8.35	8.45
7-Day THMFP**, ug/L	707.0	1068.0	1061.0
Turbidity, ntu	5.8	6.3	2.3
Total Iron, mg/L	2.88	4.10	0.45
Total Manganese, mg/L	0.07	0.39	0.24

\* Po River was sampled in June 14, 1989. Ni River and Ni River Reservoir were sampled in August 14, 1989.

\*\* THMFP = Trihalomethane formation potential

254 nm was measured in the Ni River water sample (0.472), though that of the Po River water was also quite high (0.418). The UV-absorbance of the Ni Reservoir water was nearly half the level as the rivers. The total organic carbon (TOC) concentrations in the Ni River and the Ni Reservoir (8.35 and 8.45 mg/L, respectively) were higher than that in the Po River (7.28 mg/L).

Note from Table 1 that while the TOC concentrations in the Ni River and the Ni River Reservoir were only slightly greater than that of the Po River, the THM formation potentials (THMFP) were markedly greater. Part of these differences in THM precursors concentrations may be explained by seasonal changes in the types of organic compounds which enter into these waters from different runoff sources in the watershed. Also the Po River was at a very low stage and water was moving slowly at the time of sample collection. The THM yields from the TOC in the Ni River and the Ni River Reservoir were approximately 128 and 126 ug/L, respectively. These values are among the highest values for yield in surface waters reported in the literature. Edzwald (1987) surveyed the literature and reported yields ranging from 70 to 140 ug/mg for different surface waters containing different THM-precursor types. The THM yield from the TOC in the Po River contrasts

markedly with those of the Ni River and the Ni River Reservoir and was relatively lower (97 ug/L). Although more data are needed to evaluate the effects of impoundment, the data in Table 1 indicate that impoundment of the Ni River did not improve the water quality.

Part of the high THMFP of the Ni River Reservoir might be the results of biological activity in the impounded water. Algae produce a variety of organics during photosynthesis and upon death and decay, and some are high-yielding THM precursors (Hoehn et al., 1980). Although the impoundment of water in the reservoir may allow for agglomeration and settling of organic matter, at the same time biological activity would produce soluble organic compounds, thus offsetting any improvement in the water quality afforded by agglomeration and settling. Therefore, biological activity likely has a great effect on water quality in the reservoir and should be monitored periodically.

The turbidities of the Po and Ni River samples were quite low and in the same range ( 5.8 and 6.3 ntu, respectively). As expected, because of stagnation, the turbidity of the Ni River Reservoir water was lower (2.3 ntu).

Iron (Fe) concentrations in the Ni River were quite



high (4.10 mg/L), much more so than in the Po River (2.88 mg/L). Manganese concentrations also differed markedly (0.39 vs. 0.07 mg/L). The impoundment of water in the Ni River Reservoir markedly reduced the concentration of iron (89 percent), while manganese was reduced only slightly (38 percent). Generally, it is more difficult to oxidize Mn than Fe, which, perhaps accounts for the modest reduction in Mn in the impoundment.

### Effectiveness of Alum Coagulation

#### TOC and THM-Precursor Removal

The effects of alum coagulation on TOC and THMFP of the water from the Po River, the Ni River, and the Ni River Reservoir are presented in Figures 1, and 2 ( Tables B1, and B2 in Appendix B). Alum coagulation was carried out at pH 6.0. As expected, the TOC concentration was reduced with increasing alum dosage up to about 60-80 mg/L. Note that the magnitudes of TOC reductions were similar in all three samples, with the largest reduction obtained at 100 mg/L alum for all three samples; however, little additional reduction was evident after 60 mg/L alum. Figure 2 shows the effects of alum coagulation on THM reduction in the three water samples. As can be seen, a greater percentage of the THM-precursors was removed from the Po River water

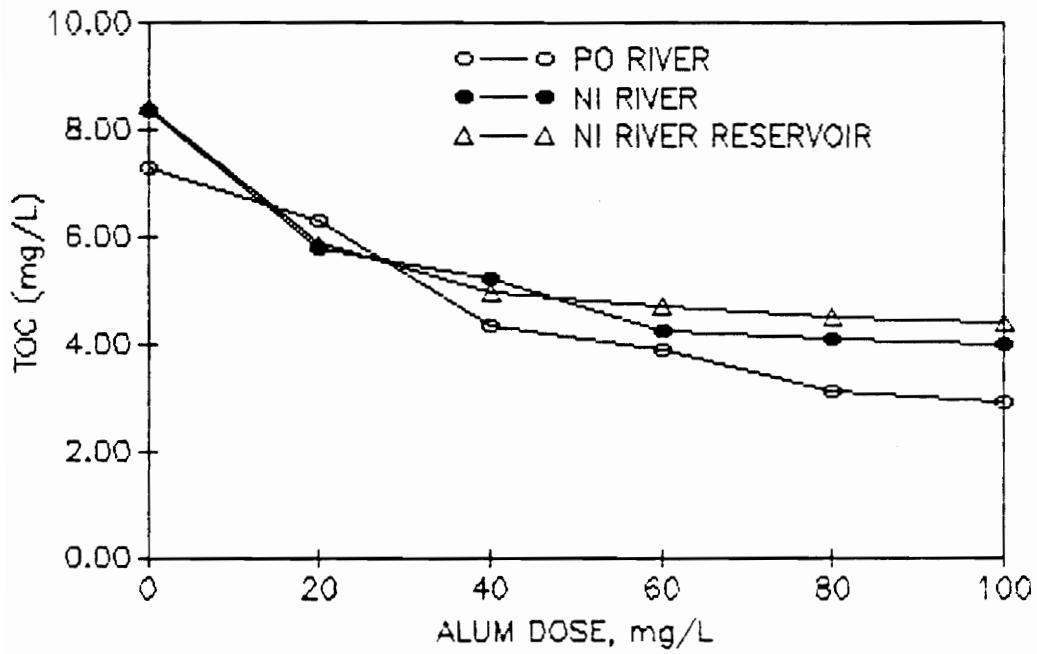


FIGURE 1. EFFECT OF INCREASING ALUM DOSE (mg/L) ON TOC OF THE PO RIVER, NI RIVER AND NI RIVER RESERVOIR WATERS

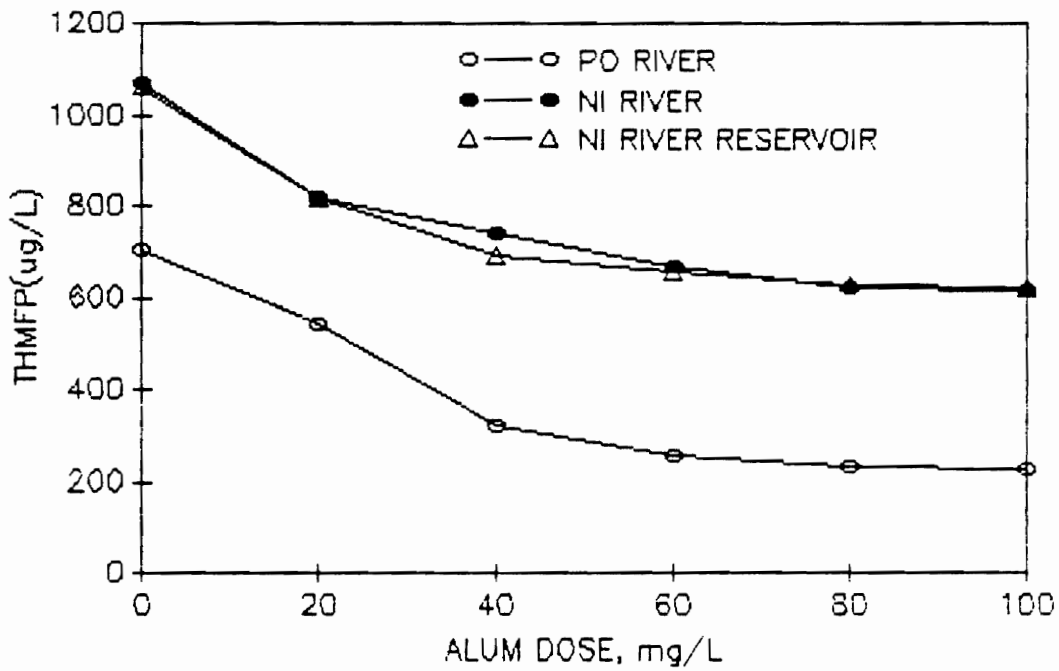


FIGURE 2. EFFECT OF INCREASING ALUM DOSE (mg/L) ON THMFP OF THE PO RIVER, NI RIVER AND NI RIVER RESERVOIR WATERS

than from the Ni River and the Ni River Reservoir waters. One of the reasons for differences in rate of THM-precursor removal in these samples may be the molecular-weight distributions. If the majority of the soluble organics were compounds with small molecular weight, alum coagulation would not be as effective in removing them as it would if they were more colloidal and larger (Veenstra and Schnoor, 1980).

The similarity of THM-precursor removals from the Ni River and the Ni River Reservoir samples suggest that the organic matter in these two sources were very similar and that impoundment of the river did not affect the nature of the organics insofar as their removability by alum coagulation. Note that alum treatment removed a greater percentage of the TOC than THM precursors from the Ni River and The Ni River Reservoir waters. Generally the reverse is true. The molecular-size distribution may be implicated here in that the smaller, more soluble organic molecules were poorly removed by coagulation from these waters, and, therefore remained in solution after the floc settled and were available to react with chlorine to form THMs.

#### Color Removal

The color removals from all samples by alum coagulation

were excellent (Figures 3 and 4, and Table B3 in Appendix B). Almost 99 percent of the color in the Po River was removed with 100 mg/L alum coagulation, while the removals from the Ni River and the Ni River Reservoir water samples were 90 and 86 percent, respectively. Most of the color in surface waters is typically caused by the higher-molecular-weight organics, which can be easily removed by alum coagulation.

### Rates of THM Formation

#### Raw Water

Figure 5 shows the rates of THM formation in chlorinated raw water samples from the Po River, the Ni River and the Ni River Reservoir ( See also Table 4 in Appendix B). The THM rate study on the Ni River and the Ni River Reservoir were conducted 3 weeks after sampling, and visual observations indicated that although the samples were refrigerated, some of the larger molecular-size materials had settled to the bottom of the container. This fact explains the discrepancy in the seven-day THM concentration indicated in Figure 5 and the one listed in Table 1. Almost 78 percent of the THM's in the Po River sample and 85 percent of THM's in the Ni River and the Ni River Reservoir samples were formed during the first three days of chlorine-

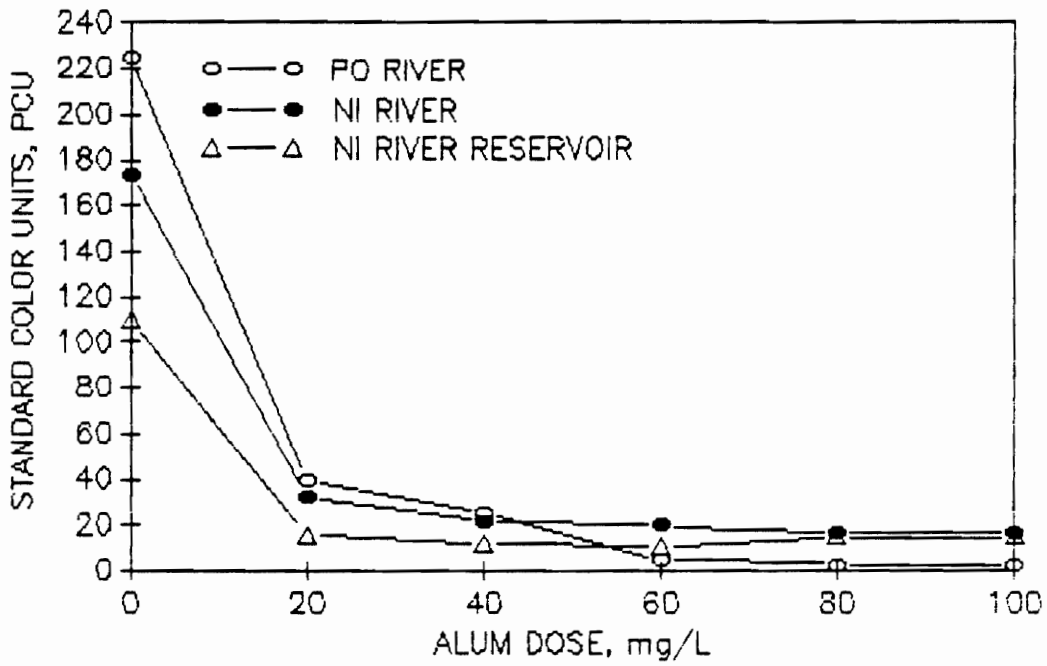


FIGURE 3. EFFECT OF INCREASING ALUM DOSE (mg/L) ON COLOR (PCU) OF THE PO RIVER, NI RIVER AND NI RIVER RESERVOIR WATERS

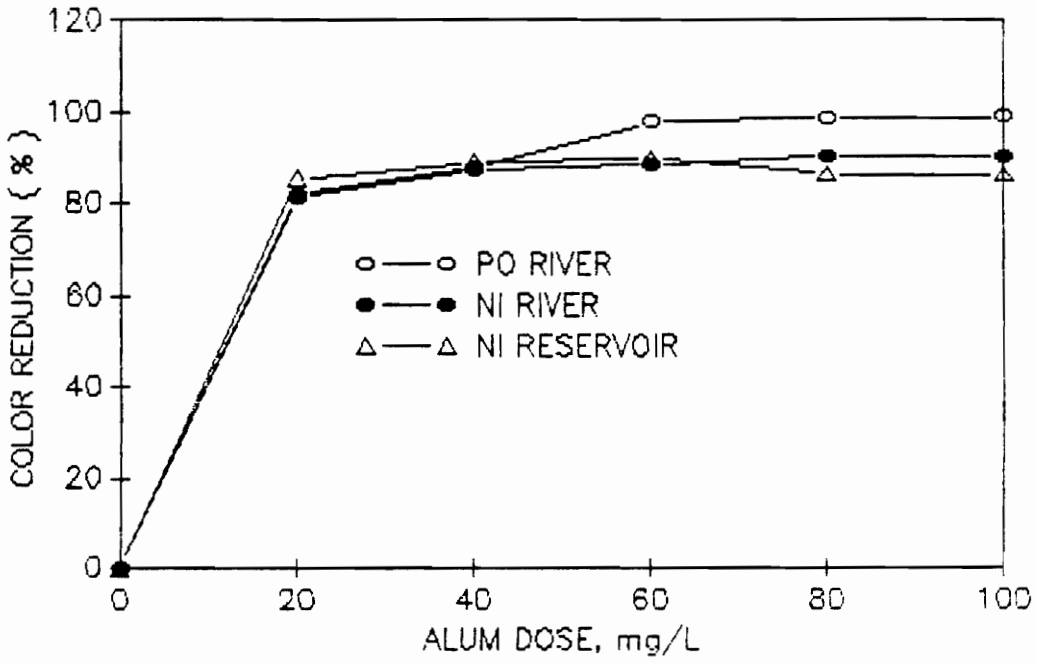


FIGURE 4. EFFECTS OF ALUM COAGULATION ON COLOR REDUCTION (%) OF THE PO RIVER, NI RIVER AND NI RIVER RESERVOIR WATERS

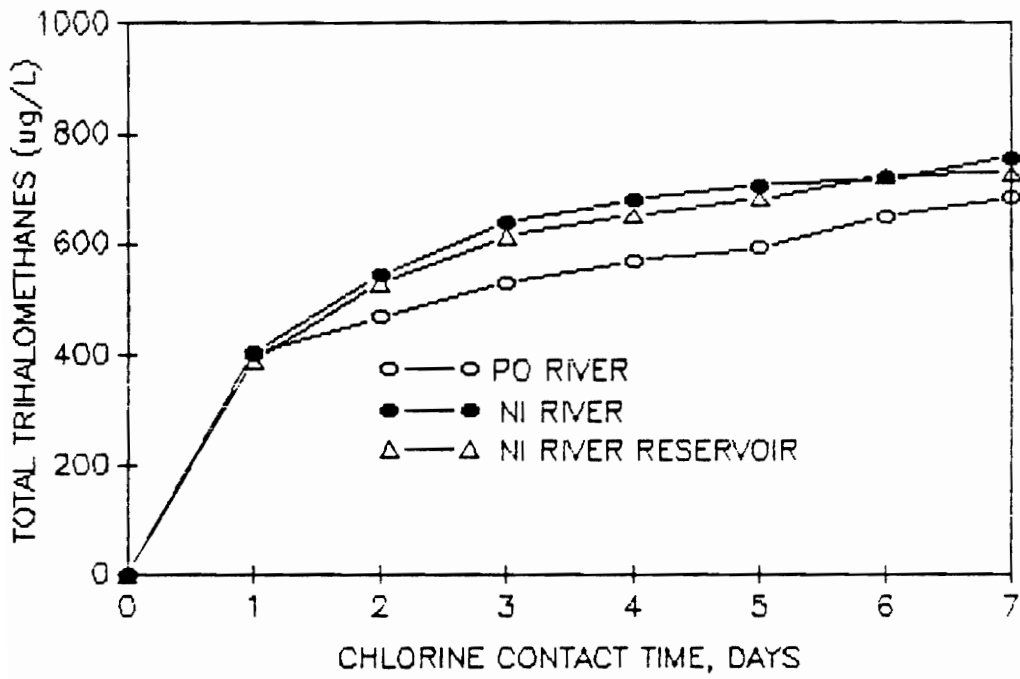


FIGURE 5. EFFECT OF CHLORINE CONTACT TIME (DAYS) ON TOTAL TRIHALOMETHANE FORMATION ( $\mu\text{g}/\text{L}$ ) OF PO RIVER, NI RIVER AND NI RIVER RESERVOIR WATERS



contact time. These data indicate the presence of fast-reacting THM-precursor organics in these samples. Also note that the final THM levels were almost the same for the Ni River and the Ni River Reservoir samples, indicating again the similarity of these two waters and the lack of water quality improvement in the Ni River Reservoir by impoundment. Only  $\text{CHCl}_3$  and  $\text{CHBrCl}_2$  were detected in these samples, and none of the more highly brominated compounds of  $\text{CHBr}_2\text{Cl}$  and  $\text{CHBr}_3$  were found. Dichlorobromo methane accounted for less than two percent of the total THMFP in any of the samples. The relative proportions of brominated compounds were the same in all samples.

Reduction in TOC and THMFP by  
Preoxidation and Alum Coagulation

Permanganate

Figures 6, 7, 8 and 9 (Tables B5, B6, B7, B8 in Appendix B) show the combined effects of permanganate preoxidation and alum coagulation on TOC and THMFP in the Po River, the Ni River and the Ni River Reservoir waters. Permanganate was applied 30 minutes prior to coagulation with 60 mg/L alum. Generally, TOC was reduced with increasing permanganate dose; however, the change in TOC was in a very small range. Note that permanganate preoxidation

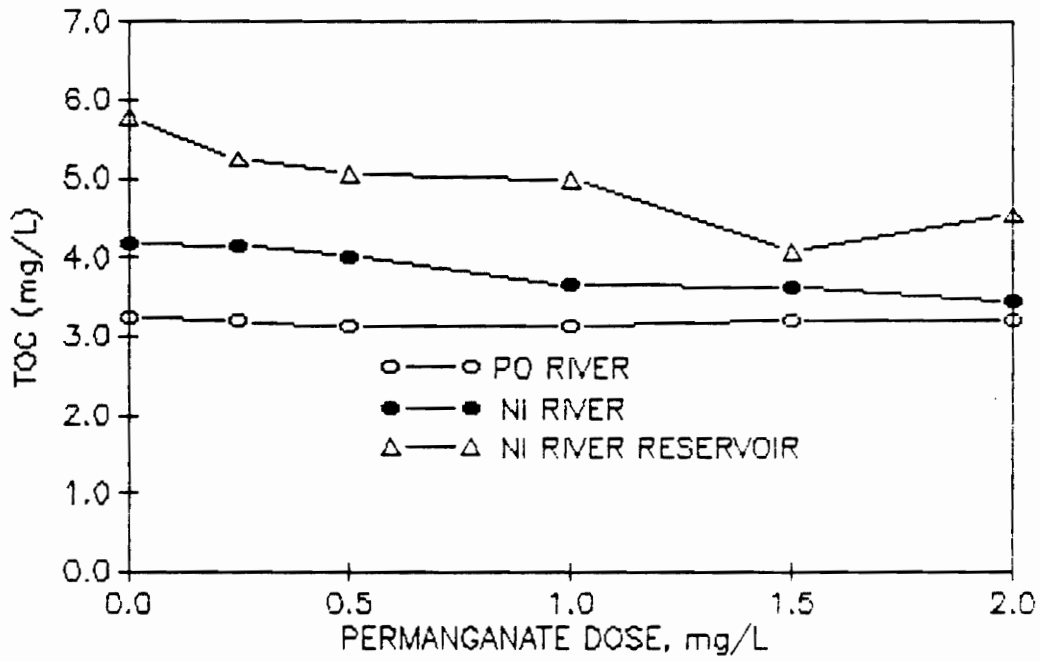


FIGURE 6. EFFECTS OF PREOXIDATION WITH PERMANGANATE (pH=7.0), FOLLOWED BY ALUM COAGULATION AT pH 6 ON TOC OF THE PO RIVER, NI RIVER AND NI RIVER RESERVOIR WATERS

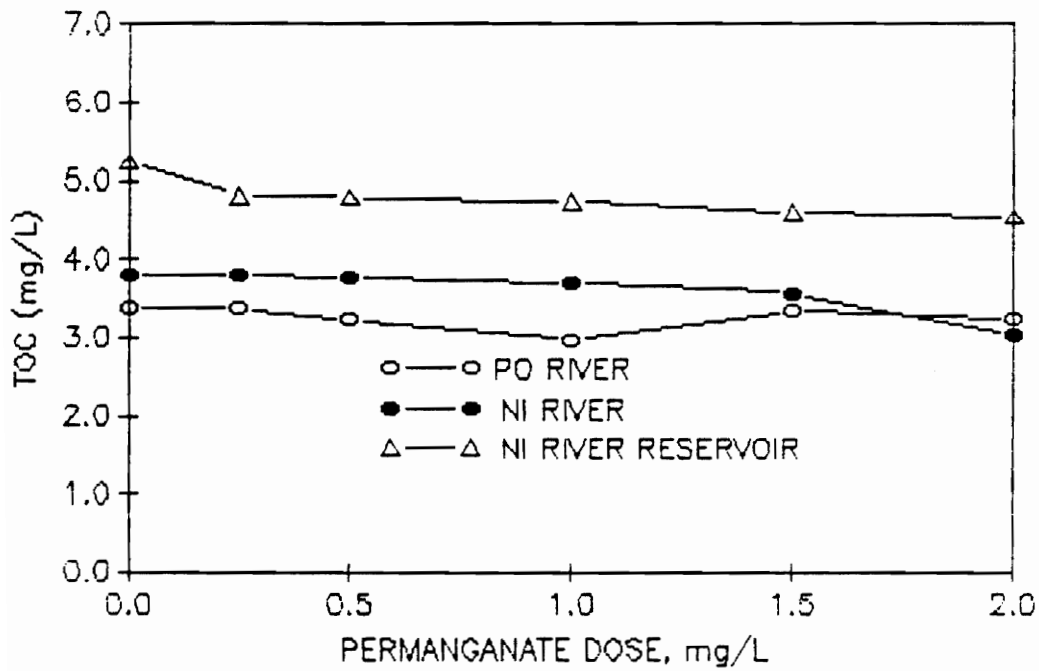


FIGURE 7. EFFECTS OF PREOXIDATION WITH PERMANGANATE (pH=10.5), FOLLOWED BY ALUM COAGULATION AT pH 6 ON TOC OF THE PO RIVER, NI RIVER AND NI RIVER RESERVOIR WATERS

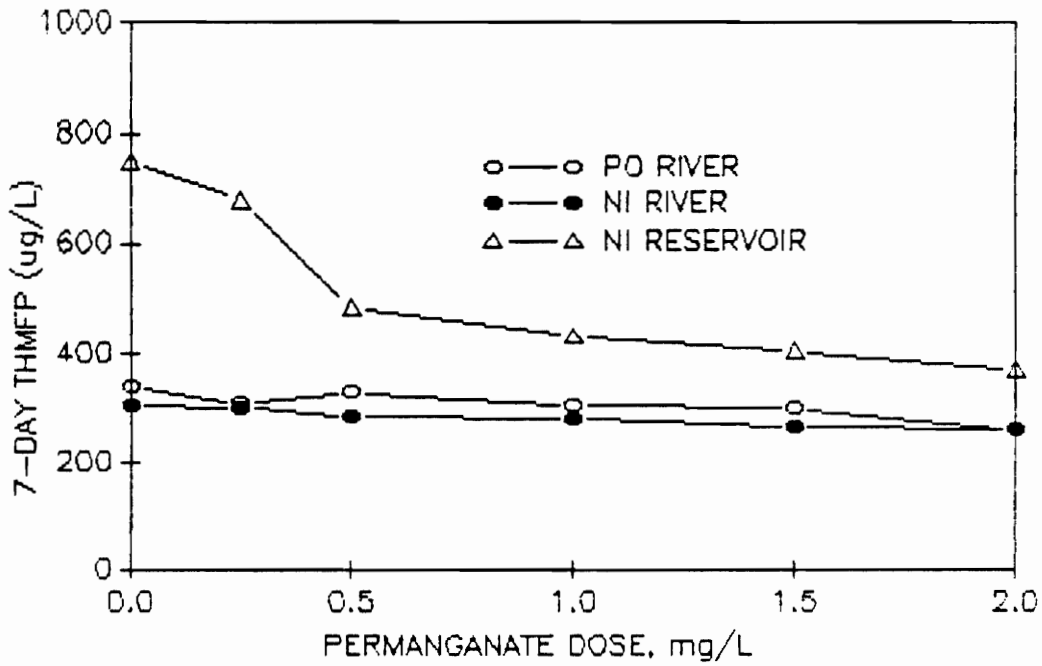


FIGURE 8. EFFECTS OF PREOXIDATION WITH PERMANGANATE (pH=7.0), FOLLOWED BY ALUM COAGULATION AT pH 6 ON THMFP OF THE PO RIVER, NI RIVER AND NI RIVER RESERVOIR WATERS

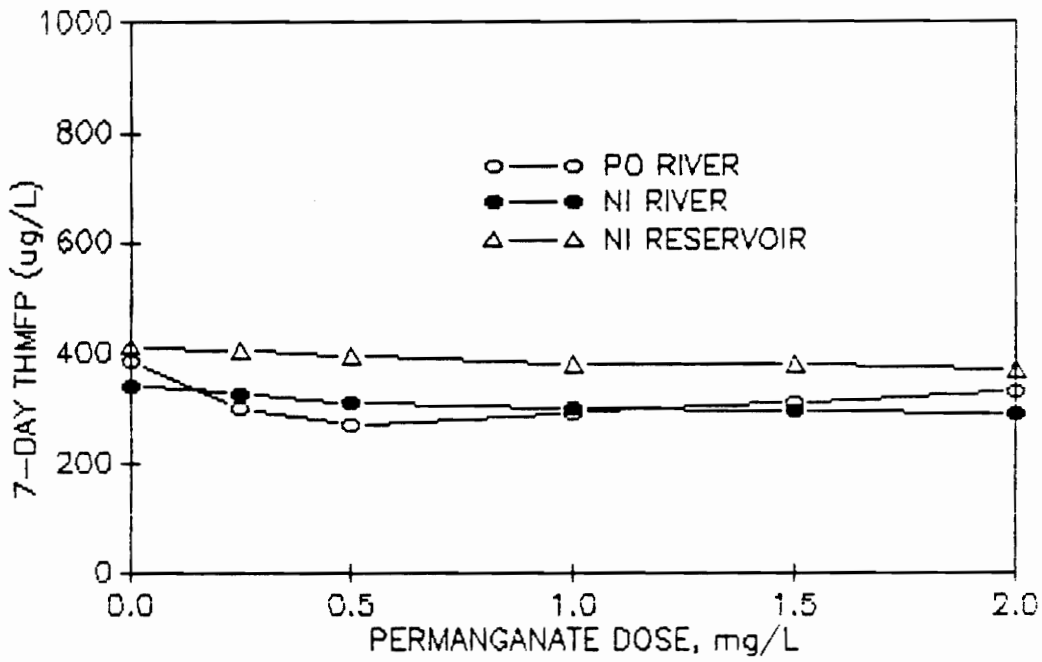


FIGURE 9. EFFECTS OF PREOXIDATION WITH PERMANGANATE ( $\text{pH}=10.5$ ), FOLLOWED BY ALUM COAGULATION AT  $\text{pH} 6$  ON THMFP OF THE PO RIVER, NI RIVER AND NI RIVER RESERVOIR WATERS

was more effective in reducing TOC at pH = 10.5 (Figure 7) especially in the Ni River and the Ni River Reservoir samples.

Trihalomethane formation potentials were reduced with increasing permanganate dose (Figure 9). Contrary to the TOC case, permanganate preoxidation was more effective at pH 7.0, the largest reduction (50.8 percent) in THMFP occurred in the Ni River Reservoir, while the smallest reduction (23.1 percent) occurred from treatment of the Po River water. Permanganate preoxidation at pH = 10.5 was only marginally effective in removing THM-precursors from all samples, ranging from 10 to 14.5 percent removal.

These data indicate that permanganate preoxidation will only slightly improve THM-precursors removal, but the removal rate depends on the chemical characteristics of the water and treatment conditions.

### Chlorine Dioxide

The combined effects of chlorine dioxide pretreatment followed by alum coagulation on TOC and THMFP of the Po River, the Ni River, and the Ni River Reservoir are presented in Figures 10 and 11 (Tables B9, and B10, Appendix B). Chlorine dioxide pretreatment combined with alum coagulation removed 46 and 28 percent of THM precursors from

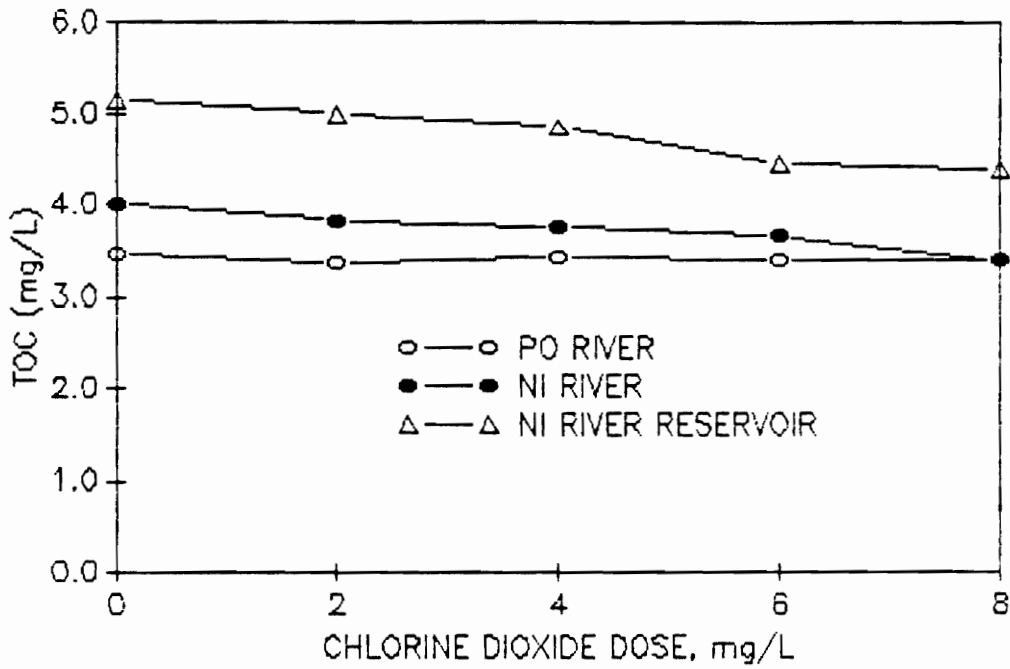


FIGURE 10. EFFECTS OF CHLORINE DIOXIDE PRETREATMENT FOLLOWED BY ALUM COAGULATION AT pH 6 ON TOC OF THE PO RIVER, NI RIVER AND NI RIVER RESERVOIR WATERS

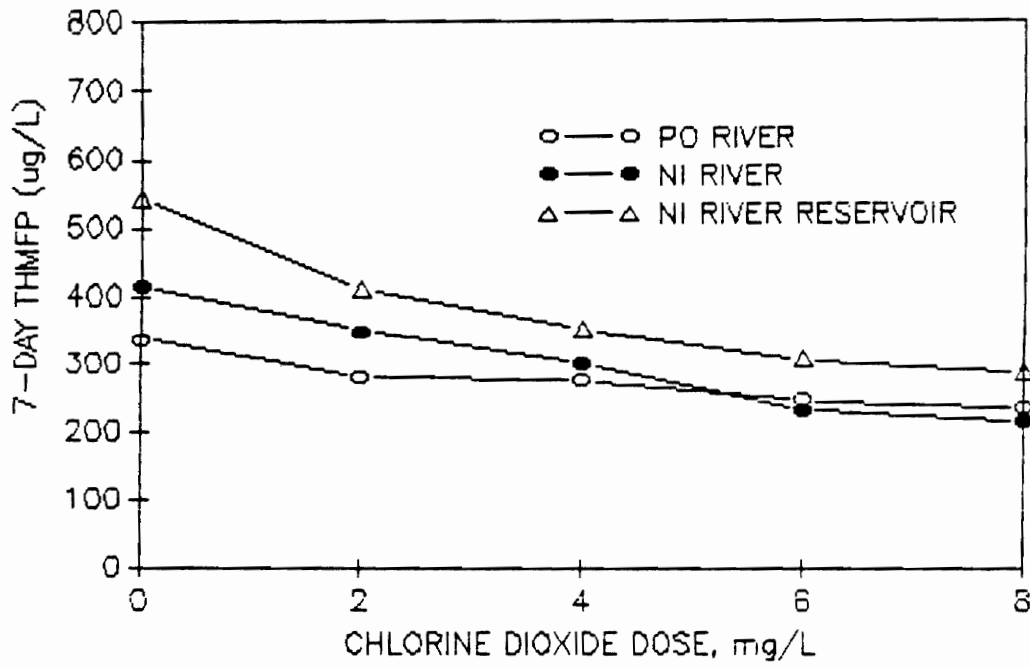


FIGURE 11. EFFECTS OF CHLORINE DIOXIDE PRETREATMENT FOLLOWED BY ALUM COAGULATION AT pH 6 ON THMFP OF THE PO RIVER, NI RIVER AND NI RIVER RESERVOIR WATERS



the Ni River and the Ni River Reservoir waters, respectively. Trihalomethane-precursor removal by chlorine dioxide pretreatment in the Po River was considerably less, and with application of 8 mg/L chlorine dioxide, only 14 percent more THM-precursors were removed from this water (Figure 11). Part of the difference in THM removal in these waters may be because of the differences in the types and forms of organic molecules present in these samples. The Po River water may contain soluble organic compounds which are less oxidizable than those present in the Ni River and the Ni River Reservoir waters. Note that chlorine dioxide applied at dosages less than 4 mg/L reduced THMFP by 8 to 27 percent in these waters. Chlorine dioxide reacts primarily as a one-electron acceptor in contrast to chlorine which acts via a variety of electrophilic oxidative and radical pathways. Consequently, the reactions of chlorine dioxide with THM-precursors are much more selective and specific than those of chlorine (Acha, 1984). More data in regard to the type and size of organics should be collected in order to evaluate the effectiveness of chlorine dioxide for THM-precursor removal in these samples.

The use of chlorine dioxide dosages of higher than 1-2 mg/L for pretreatment is not feasible in most cases. Chlorine dioxide appears to alter the human metabolism and

bioavailability of iodine, which causes the formation of iodinated organic compounds in vivo and specially causes problems in individuals who are sensitive to hemolytic agents, or who are taking medication that can produce hemolytic anemia (Condie, 1986). Of course there are other side effects of chlorine dioxide exposure which are out of scope of this discussion. For more information in this regard the reader is referred to a recent review of the uses, chemistry and health effects of chlorine dioxide and the chlorite ion prepared by Chemical Manufactures Association (1989).

Another problem with using chlorine dioxide as an oxidant for THM removal is the production of chlorite and chlorate, and the health effects which are associated with both of these by-products. Although it is possible to remove chlorite by additional treatment with activated carbon or sulfur dioxide, the practical technology for the removal of these by-products is not yet available. Most likely, EPA in the future will regulate the chlorine dioxide by-products, and this fact should be considered in any future planning for the use of chlorine dioxide as an oxidant. Regardless of all these problems, the data in this study indicate that pretreatment of water with even low dosages (1-2 mg/L) of chlorine dioxide will cause a

reduction of between 5-10 percent in THM formation, and this level of reduction in THMs may be critical in meeting future MCL's.

#### Reduction in TOC and THMFP by Pretreatment with PAC

The effectiveness of powdered activated carbon (PAC) for reducing TOC and THM in the Po River, the Ni River and the Ni River Reservoir is shown in Figures 12 and 13 (Tables B11 and B12 in Appendix B). The water samples were pretreated with PAC 30 minutes prior to coagulation with 60 mg/L alum at pH 6.0. Note that the pretreatment with PAC was not as effective in reducing TOC from the Po River as it was from the Ni River and the Ni River reservoir (Figure 12). Pretreatment with 60 mg/L PAC followed by coagulation with 60 mg/L alum, reduced TOC in the Po River by only 9.3 percent, while the same treatment reduced TOC in the Ni River and the Ni River Reservoir waters by 18 and 26.7 percent, respectively. Part of the difference in TOC reductions may be attributed to the nature of organics in these samples. Better PAC effectiveness might have been obtained in the Po River if different types of PAC were used, but the carbon that was used (CECA B) had been proven to be a good THM-precursor adsorber in waters of similar type (Hoehn, 1990).

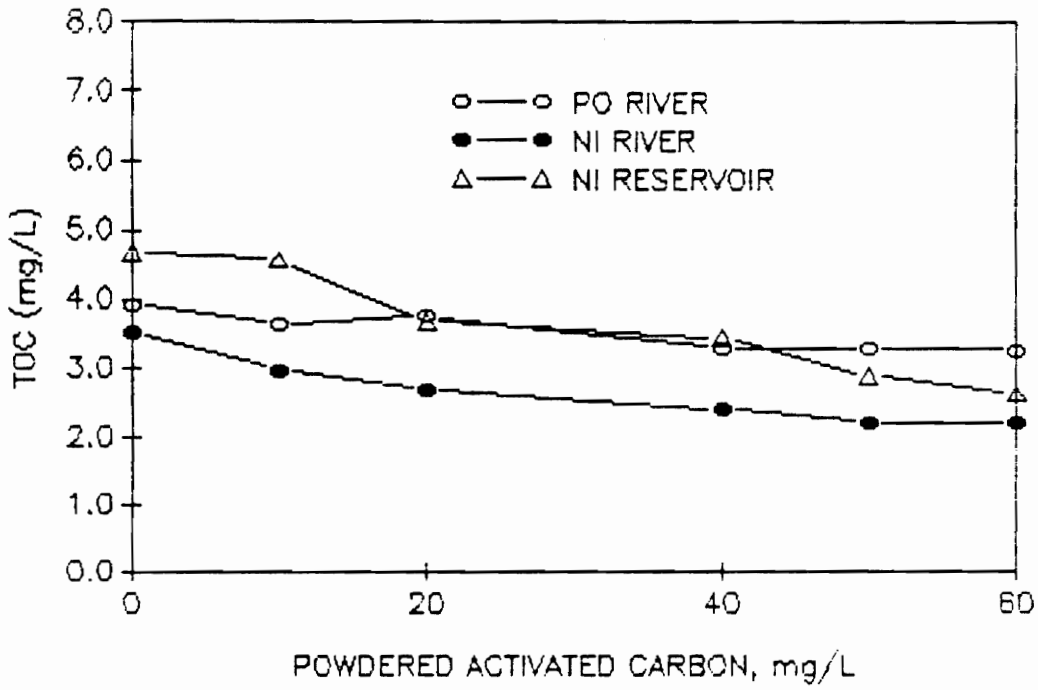


FIGURE 12. EFFECTS OF POWDERED ACTIVATED CARBON (PAC) FOLLOWED BY ALUM COAGULATION AT pH 6 ON TOC OF THE PO RIVER, NI RIVER AND NI RIVER RESERVOIR WATERS

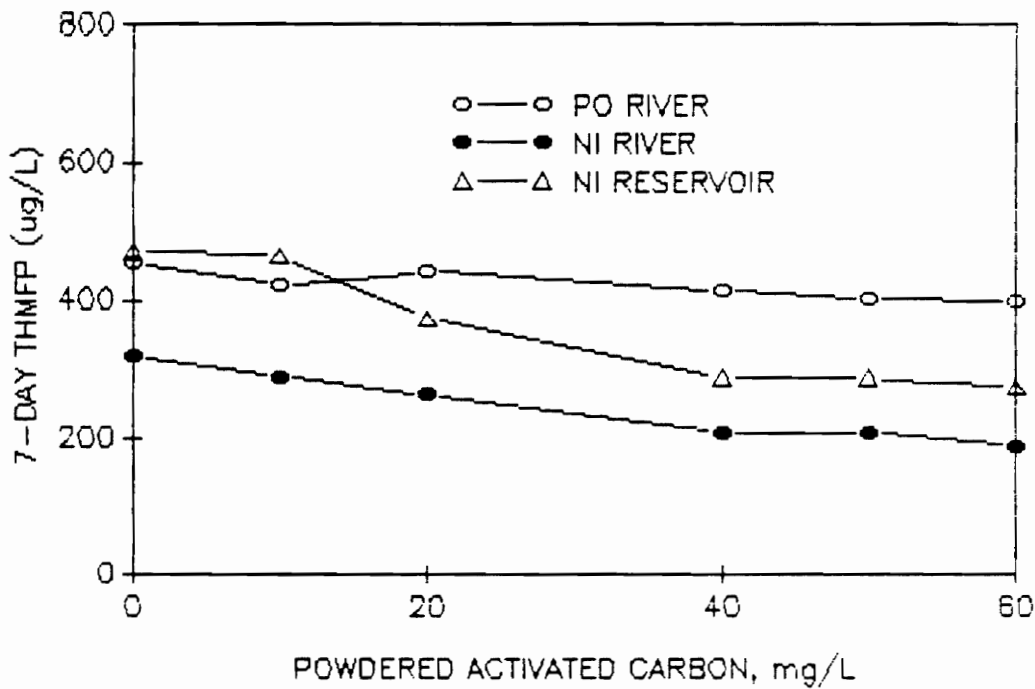


FIGURE 13. EFFECTS OF POWDERED ACTIVATED CARBON (PAC) FOLLOWED BY ALUM COAGULATION AT pH 6 ON 7-DAY THMFP ( $\mu\text{g/L}$ ) OF THE PO RIVER, NI RIVER AND NI RIVER RESERVOIR WATERS

Trihalomethane precursor removal by PAC followed the same trend as that observed for TOC removals (Figure 13). The largest THM removal (21.4 percent) occurred when 60 mg/L PAC was used to pretreat the Ni River Reservoir water. The carbon was least effective in removing THM precursors from the Po River water. A dose of 60 mg/L, combined with alum coagulation reduced the 7-day THMFP by only 6.7 percent.

These data indicate that the pretreatment of impounded water with PAC was effective for THM removal but only at higher PAC dosages. Impoundment and biological activity in the Ni River Reservoir may result in the production of entirely different organics than those are present in the river.

The use of 60 mg/L PAC as a pretreatment for TOC and THM removal is unrealistic, and even the use of 10-20 mg/l PAC for an extended period of time is not economically feasible. More data in regards to the nature of organics in these samples are needed in order to fully evaluate the potential use of PAC for TOC and THM removal.

### Effects of Long-Term Storage of Water on TOC and THMFP

#### Experiment I

Studies were conducted to evaluate the effects of long-

term storage of Po and Ni River waters on TOC and THMFP. The Po River sample was collected on June 10, 1989, while the Ni River sample was collected on August 14, 1989. Figures 14, 15, 16, and 17 (Tables B-13 and B-14 in Appendix b) show the data obtained from this experiment. These studies were designed to simulate, at least to some degree, the potential impact of the impoundment of the river waters. As can be seen, the TOC and THMFP decreased with increasing storage and the maximum reductions were about 40 and 60 percent, respectively, in the Po River water and 35 and 40 percent, respectively in the Ni River water. Notice the sharp decrease in TOC and THMFP in both samples during the first 30 days (Figures 14 and 16). This reduction likely was caused by the settling of the larger size organic molecules. Also, microbial activity could have played a role. It should be noted that although the impoundment of water may improve the water-quality by physical and biochemical processes that cause the precipitation of organic matter from these samples, the improvements may be offset by biological activities that occur in the impoundment. Seasonal growth of algae and continuous bacterial decomposition and decay contribute organic matter to the water, and since algal products can produce THMs when they are chlorinated (Hoehn et al., 1980), algal growth

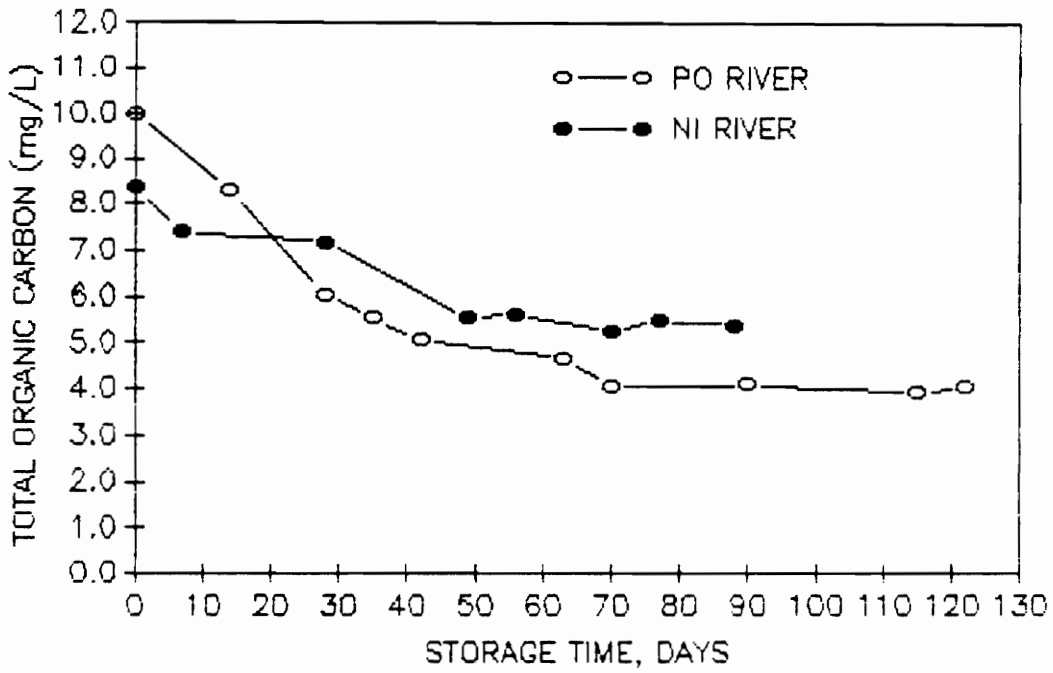


FIGURE 14. EFFECTS OF STORAGE AT ROOM TEMPERATURE (22–24°C) ON TOC (mg/L) OF THE PO AND NI RIVER WATERS



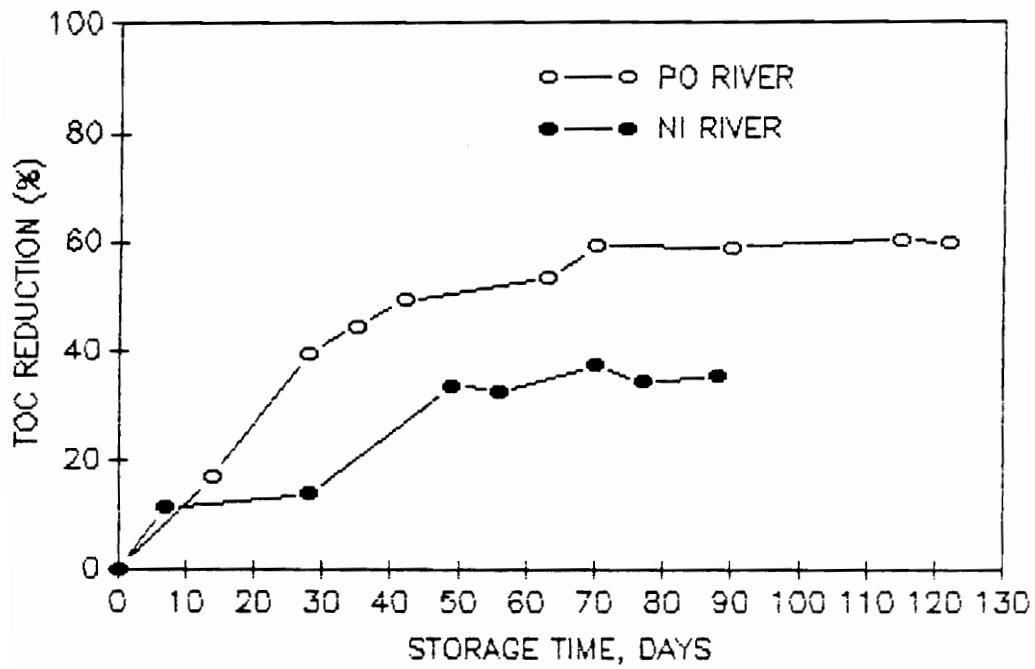


FIGURE 15. PERCENT REDUCTION IN TOC OF THE PO RIVER AND NI RIVER WATERS STORED AT ROOM TEMPERATURE (22-24 °C)

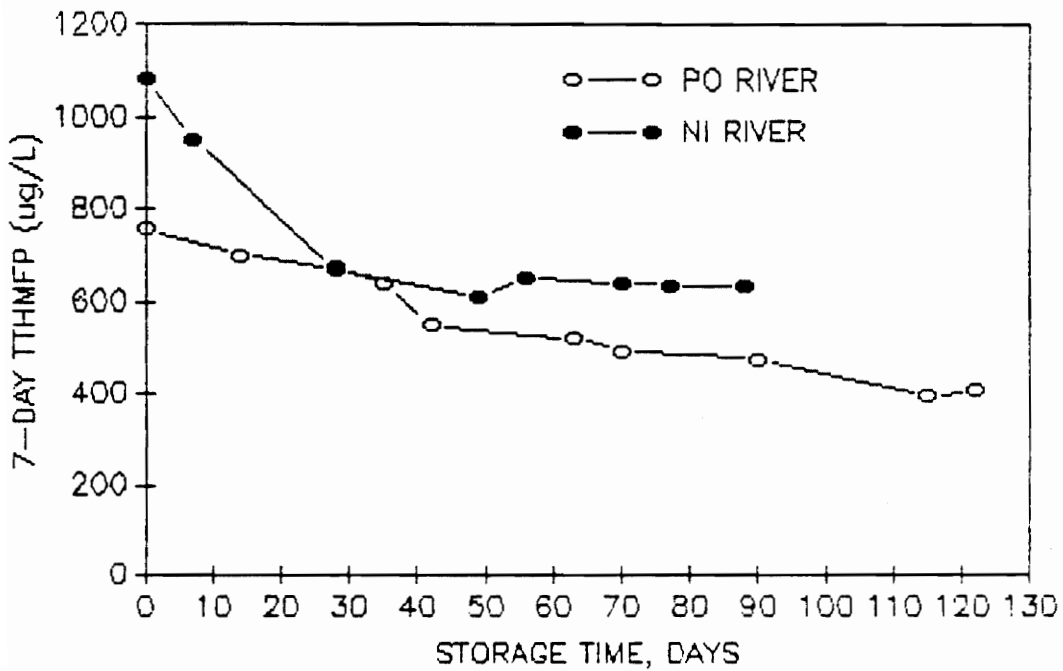


FIGURE 16. EFFECTS OF STORAGE AT ROOM TEMPERATURE (22-24 °C) ON 7-DAY THMFP ( $\mu\text{g}/\text{L}$ ) OF THE PO AND NI RIVER WATERS

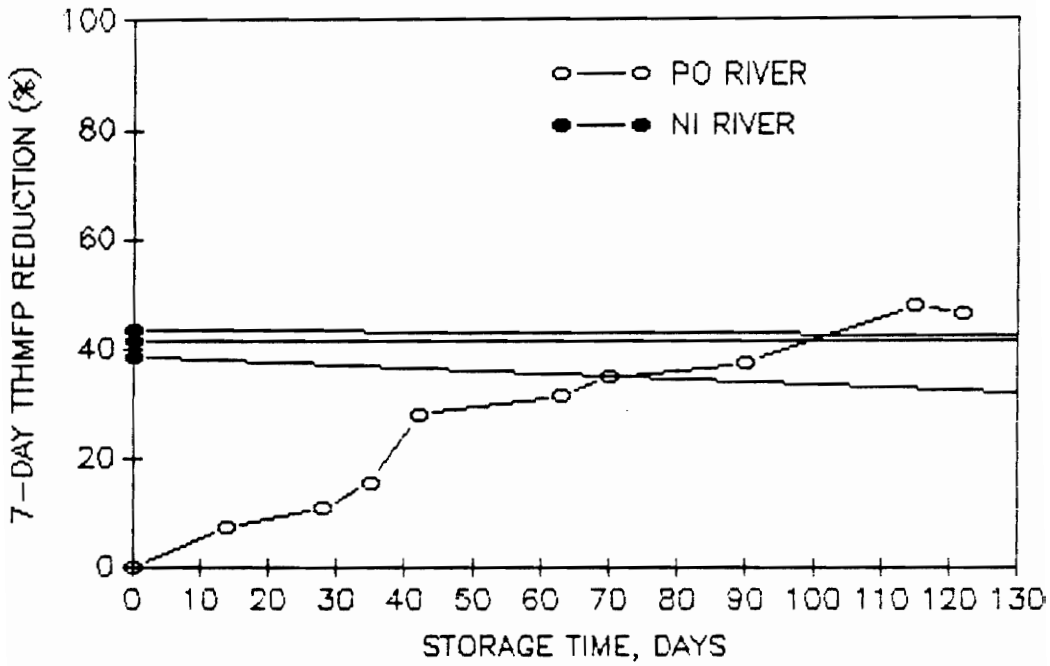


FIGURE 17. PERCENT REDUCTION (%) IN 7-DAY TOTAL THMFP OF THE PO AND NI RIVER WATERS STORED AT ROOM TEMPERATURE (22-24°C)

should be controlled.

### Experiment II

Another water sample was collected from the Po River on January 10, 1990, for a more detailed study to evaluate the effects of storage and temperature on TOC and THMFP. The results of these studies are presented in Figures 18, 19, 20, 21, 22, 23, and 24 (Tables B-15 to B-20 in Appendix B). As can be seen, generally in all treatments, increasing storage time reduced TOC and THMFP. Shaking the samples daily, caused a slight increase in both TOC and THMFP. This is expected, because shaking resuspends the larger organic compounds that had settled, increasing both TOC and THMFP. Filtration of water through Whatman #42 filter paper reduced the TOC concentration and, hence, the THMFP after 35 days of storage. The reductions were not significant however, when compared to those observed from analysis of the unfiltered water stored under the same conditions. Note the sharp decreases in both TOC and THM formation (except for the alum treated samples) in all other treatments (Figures 18 and 19). Generally, TOC and THM reductions were no longer significant after 2-3 weeks of storage, likely because most of the large organic molecules settle to the bottom of the container during this period. Colored sediment at the

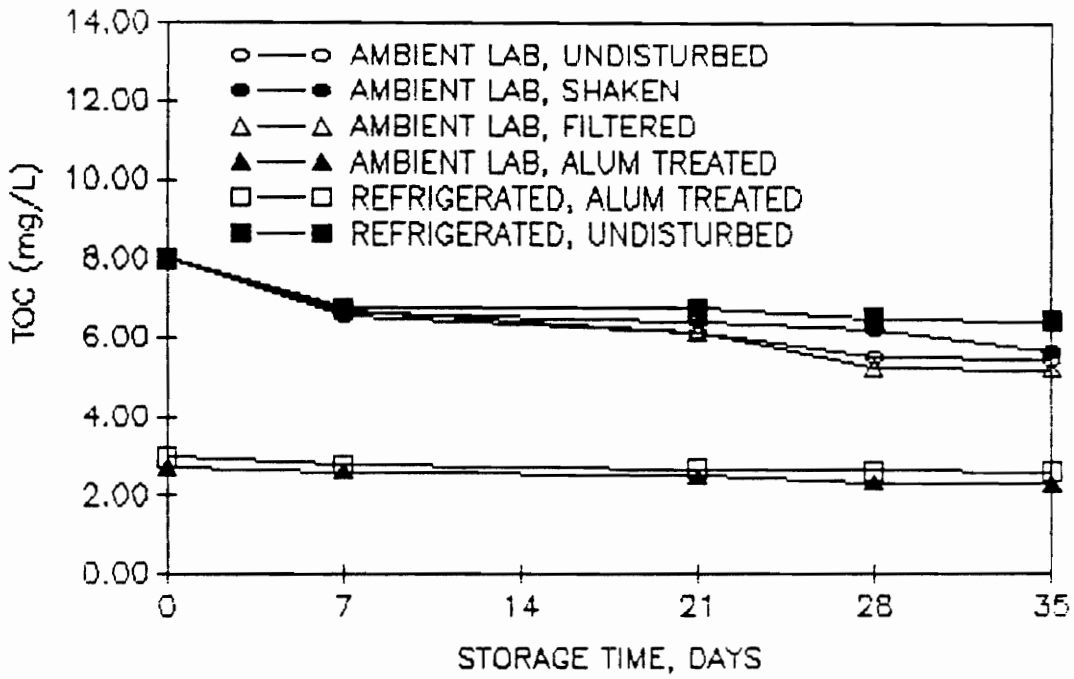


FIGURE 13. EFFECTS OF STORAGE AND TEMPERATURE ON TOC OF THE PO RIVER WATER

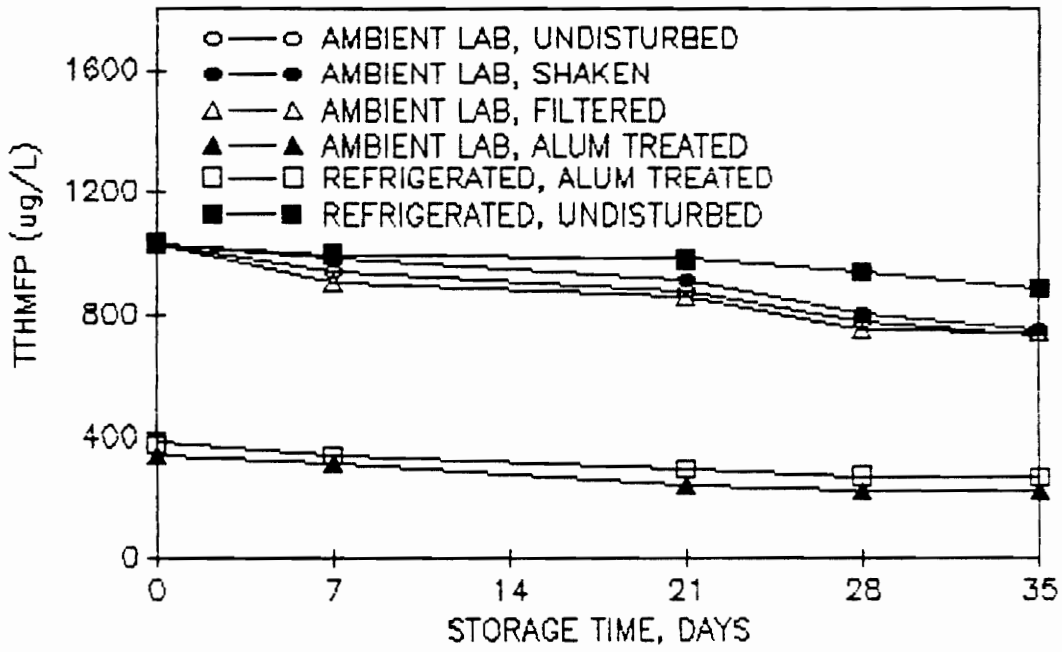


FIGURE 19. EFFECTS OF STORAGE AND TEMPERATURE ON TTHMFP (ug/L) OF THE PO RIVER WATER

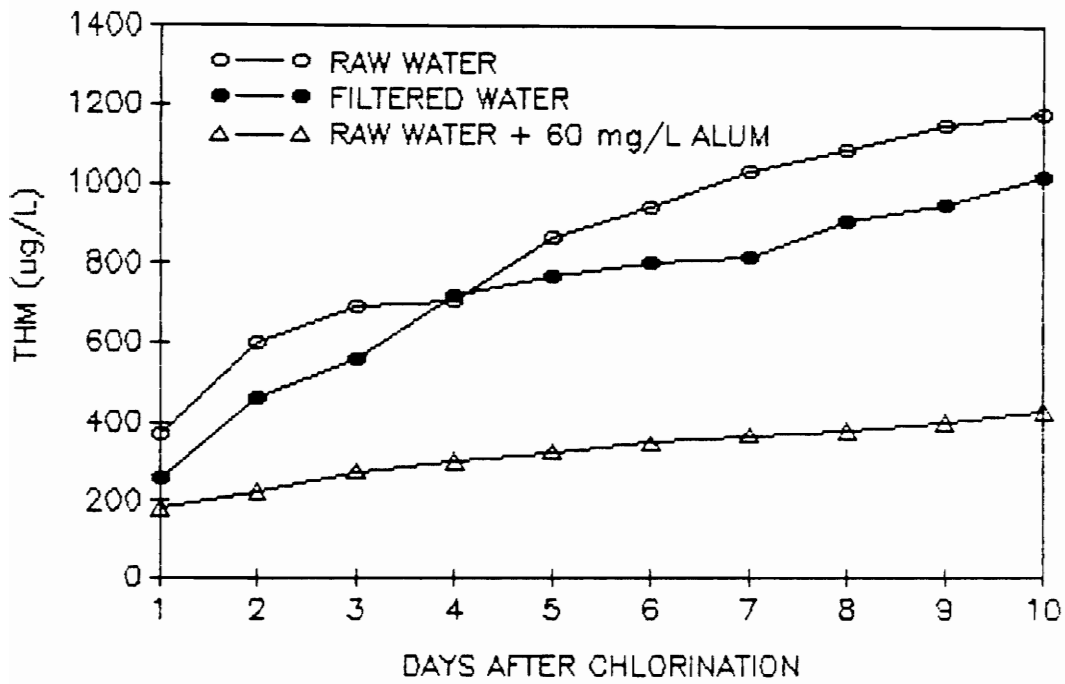


FIGURE 20. EFFECT OF CHLORINE CONTACT TIME ON THM (ug/L) OF THE PO RIVER WATER.

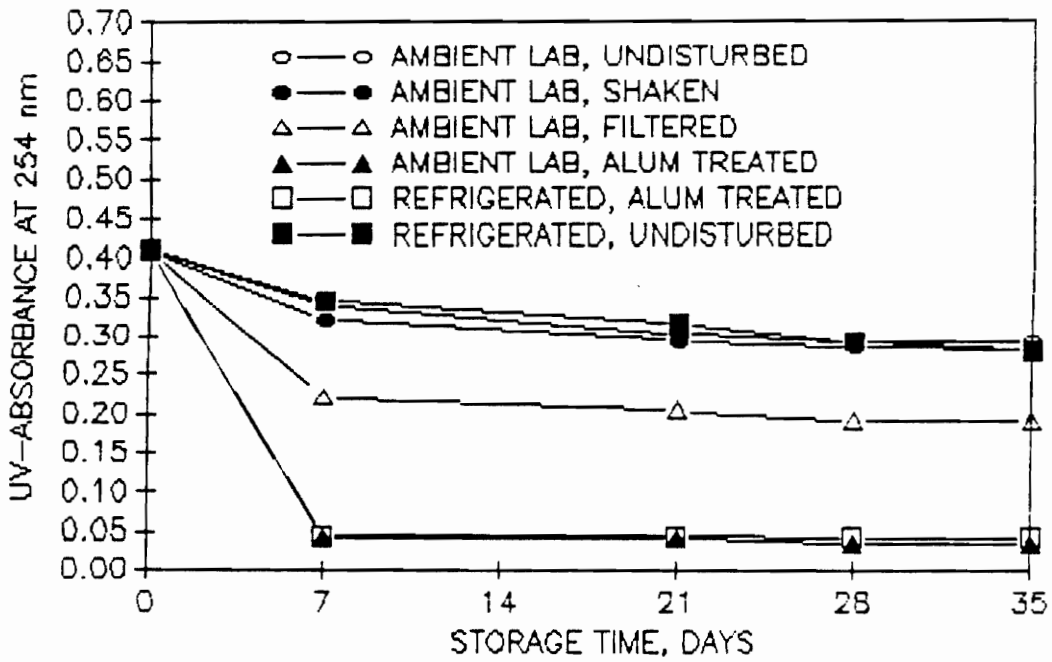


FIGURE 21. EFFECTS OF STORAGE AND TEMPERATURE ON UV-ABSORBANCE AT 254 nm OF THE PO RIVER WATER



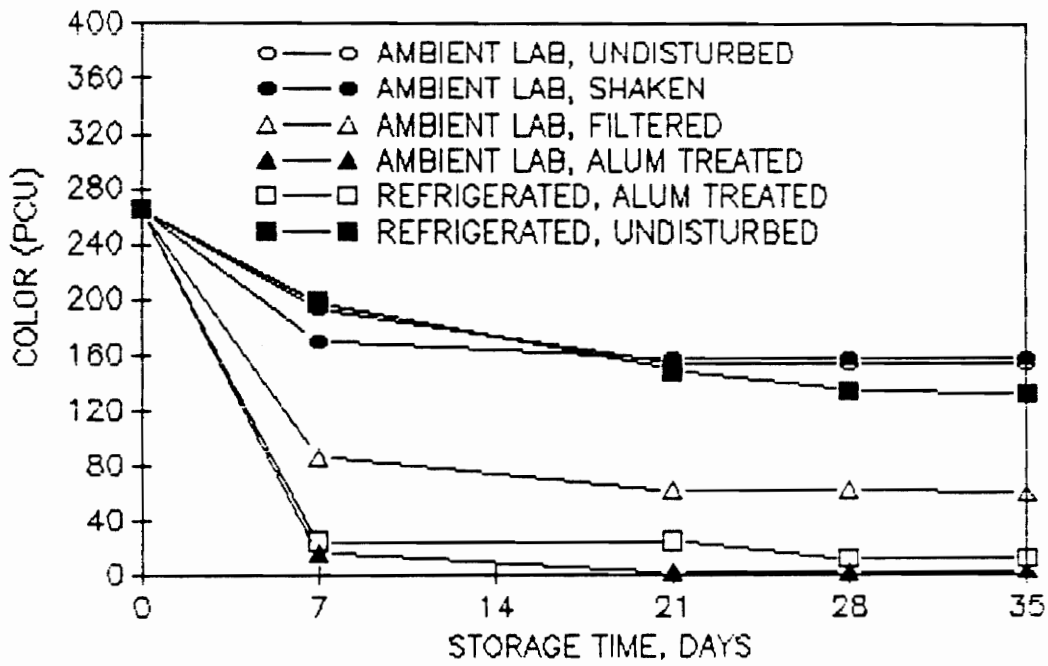


FIGURE 22. EFFECTS OF STORAGE AND TEMPERATURE ON COLOR (PCU UNITS) OF THE PO RIVER WATER

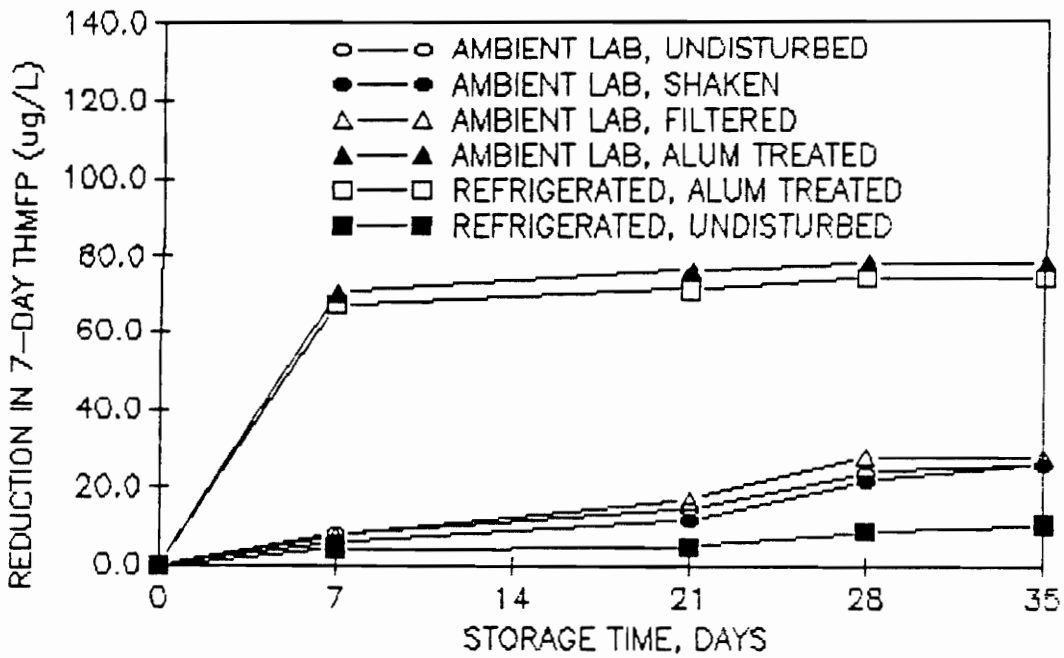


FIGURE 23. EFFECTS OF STORAGE AND TEMPERATURE ON THM REDUCTION (%) OF THE PO RIVER WATER

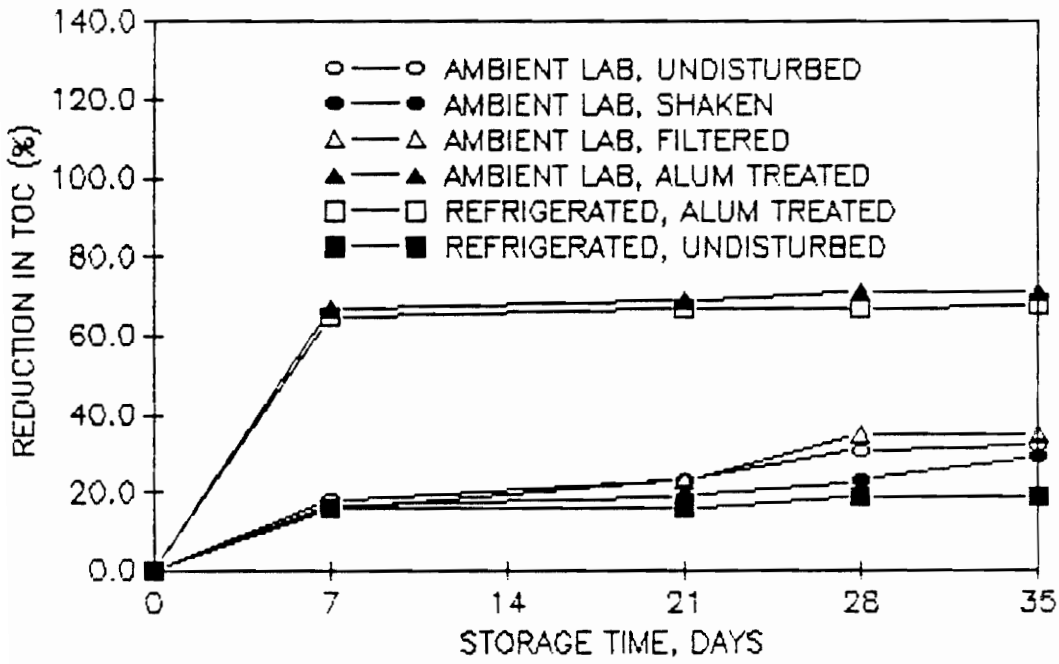


FIGURE 24. EFFECTS OF STORAGE AND TEMPERATURE ON TOC REDUCTION (%) OF THE PO RIVER WATER

bottom of the vessel containing undisturbed samples was observed.

Alum coagulation, as expected, was very effective in reducing levels of both TOC and THM-precursors in the Po River water. Note that the TOC and THMFP concentrations in alum-treated, refrigerated samples were higher than in samples stored at ambient laboratory temperature. Total organic carbon and THMFP were reduced by 18 and 26 percent, respectively, in the water stored at room temperature, while the TOC and THMFP in the refrigerated samples were reduced only by 15 and 11 percent, respectively. Note from Figures 18 and 19 that the levels of TOC and THMFP after coagulation with alum were virtually the same over the entire storage time. Therefore, storage may improve raw water quality, but it does not improve finished-water quality. These data indicate the pronounced effects of temperature on the water quality characteristics. Part of these differences in TOC and THMFP in samples stored at two different temperature were the result of reduced chemical reactions and microbial activity at the colder temperature.

Figure 20 shows the rate of THM formation in the Po River water. As can be seen, almost 50 percent of the THMs was formed during the first three days of chlorine contact time, indicating the presence of the fast-reacting THM-

precursors that produce high concentration of fast-reacting THM-precursors. Generally, THMFP increased with increasing chlorine contact time; however, the rate of THM production became constant after seven or eight days. Note that the final THM level in this sample was higher than in the sample collected during the previous summer. In January 1990, when these samples were collected Po River was at its highest stage because of heavy precipitation, water was very turbid and the water temperature was 2 °C. These conditions were exactly the opposite of the conditions at the time of sample collection during the summer. These data indicate the effects of seasonal variation on TOC and THM of the Po River water. Flooding and runoff from the soil in the watershed likely increased the level of THM-precursors in the water.

The total THM formation in a Po River water sample that was coagulated with 60 mg/L alum before chlorination is shown in Figure 20. Note that only 368 ug/L TTHMs were formed after 7-days. These data indicate that alum was very effective in removing THM precursors. Note also that 50 percent of the THMs were formed after one day of chlorine contact time, suggesting that alum was not effective in removing fast THM-forming precursors from the Po River water. A preoxidant such as chlorine dioxide or potassium

permanganate might help alleviate this problem.

The THM rate study with the filtered water indicated that filtration through Whatman #42 filter paper alone was not effective in reducing THM precursors (Figure 20). Note that THM formation increased with increasing chlorine-contact time, and the rate of increase did not become constant after seven days.

Figures 21 and 22 show the effects of storage and temperature, respectively, on UV-absorbance (ultraviolet absorbance) and color of Po River water. Note that UV-absorbance at 254 nm and color measured at 420 nm were both reduced with increasing storage time, most occurring during the first three weeks of storage. The UV-absorbance and color were highest in the water sample stored at ambient temperature and shaken daily. Reduction in both color and UV-absorbance are caused by loss of soluble organic matter, and resuspension of settled material increased both only because of interference by particulate matter.

Filtration of the water through Whatman #42 filter paper effectively reduced both color and UV-absorbance. As can be seen (Figures 21 and 22), alum coagulation was very effective in reducing UV-absorbance and color (91.2 and 98 percent, respectively). Alum precipitates organic molecules in the water and improves water quality characteristics.

Note that alum was more effective in reducing color and UV-absorbance in the water sample stored at room temperature than the sample which was refrigerated (Both were at room temperature when flocculated). Usually at higher temperatures chemical reaction rates are faster, and, thus temperature affects the fate of organic molecules present in the water. Note that as in the case of TOC and THM-precursor reduction most of the changes in color and UV-absorbance happened during the first three-weeks of storage. This was the time that most of the larger organic molecules settled at the bottom of the container.

A convenient way to examine THM formation data is by expressing it in terms of yields which is defined as ug THM produced per mg TOC for extended chlorine reaction times. Edzwald (1987) in a literature survey reported yields ranging from 70 to 140 for different surface waters with different precursor types. Yields (THM/TOC) were very high for all treatments (Table 2). This may be because of the type and amount of organics and also the molecular size of the organics present. Storage and temperature did not have a significant effect on yields, as they remained almost constant during the storage time. Note that alum treatments reduced the yields by 16.5 percent. This was expected because alum coagulation treatment removes the larger

Table 3. Effects of storage and temperature on yield and UV absorbance per unit TOC of Po River water.

Temperature and Treatment	Storage time, days							
	7		21		28		35	
	A*	B**	A	B	A	B	A	B
Ambient lab	145	5.2	143	4.9	141	5.3	140	5.4
Ambient lab, Shaken	147	4.9	141	4.6	130	4.6	136	5.0
Ambient lab, Filtered	142	3.3	140	3.3	143	3.7	143	3.7
Ambient lab, Alum treated	121	1.6	99	1.7	97	1.5	98	1.5
Refrigerated, Alum treated	122	1.6	110	1.6	103	1.6	104	1.7
Refrigerated	147	5.1	146	4.7	145	4.5	143	4.4

\* Yield = THM/TOC, ug/mg

\*\* (UVx100)/TOC

Lab temperature 22-24 °C

Refrigerator temperature 5-7 °C



molecular weight organic compounds, which produce more THMs per unit TOC when chlorinated. Total organic carbon and THMs both were reduced by storage; however, the rate of the reduction in TOC was higher than that of THMs (Figure 23 and 24). Note that the greater reduction in raw-water TOC concentrations occurring after 35 days of storage was 26 percent as compared to 78 percent for alum-treated water. The lowest TOC and THM reductions occurred in the refrigerated sample. Apparently, refrigeration decreases the rate of chemical and biological processes that would reduce the TOC and THM-precursor levels. Note that the rates of TOC and THM reductions in samples stored for 35 days at room temperature were almost twice as great as those in samples refrigerated at 5-7 °C.

## CHAPTER V

### SUMMARY AND CONCLUSIONS

The objectives of this study were to:

1) evaluate the relative effectiveness of several treatment procedures for reducing trihalomethane (THM) precursor concentrations in the Po River and Ni River waters in eastern Virginia. The processes included: a) alum coagulation, b) preoxidation with chlorine dioxide and permanganate, and c) adsorption by powdered activated carbon (PAC).

2) compare the characteristics and treatability of the Ni River and Ni River Reservoir so that inferences regarding the effects of impounding the Po River could be made.

3) evaluate the effects of storage and temperature on the level of organic carbon and THM-formation potential (THMFP) in the river waters.

The water samples were collected from the Po River, the Ni River and the Ni River Reservoir in eastern Virginia and

were analyzed for TOC, pH, color and UV-absorbance at 254 nm. Samples were then treated in a manner similar to that in a typical water treatment plant with a bench-scale, jar-test apparatus. Treatment included preoxidation with either potassium permanganate or chlorine dioxide or pretreatment with powdered activated carbon. After pretreatment, samples were coagulated with alum, flocculated, settled, and filtered.

Treated samples were analyzed for TOC, THMFP, color and UV-absorbance at 254 nm. Trihalomethane analyses were performed by gas chromatography using a purge-and-trap technique. River samples were stored for long periods at either ambient room temperature (22-24 °C) or under refrigeration (5-7 °C), and the effects of storage and temperature on TOC, THMFP, color and UV-absorbance were evaluated.

The following conclusions were derived from the results obtained during this investigation:

- 1) The 7-day THM-formation potential (THMFP) of raw Po River is quite high (>680 ug/L), and reduction of THMFP by conventional water treatment techniques to levels that will meet existing or future maximum contaminant levels for drinking water will be most difficult, if not impossible.

2) Alum coagulation at pH 6.0 reduced TOC and THM-precursors. Increasing the alum dose increased the THM-precursor removal; however, little improvement was seen at dosages greater than 60 mg/L. Application of 60 mg/L alum reduced THMFP by 68, 42 and 42 percent in the Po River, the Ni River and the Ni River Reservoir, respectively. Both color and UV-absorbance were also reduced significantly.

2) Permanganate preoxidation was marginally effective for reducing concentrations of either manganese or THM precursors. Removals of THM precursors were less than 14 percent at dosages as high as 2 mg/L permanganate.

4) Chlorine dioxide as a preoxidant at dosages of 6 to 8 mg/L in the Po River water reduced THMFP by as much as 14 percent over what could be achieved by alum coagulation alone. Application of 2 mg/L chlorine dioxide, which is a more reasonable dose, reduced THMFP in the Po River water by 8 percent. Application of higher dosages would be feasible only if some chlorite-removal mechanism were available.

5) Powdered activated carbon (PAC) pretreatment at dosages of 10 to 20 mg/L reduced THM-precursors by less than four percent.

6) Long-term laboratory storage (120 days) at ambient room temperatures (22-24 °C) reduced TOC from the Po River by 60 percent, while the THMFP reduction was 47 percent for the same time period. Storage at cold temperatures (5-7 °C) had little effect on TOC and THMFP. When the samples were coagulated by alum treatment, the beneficial effects of storage were no longer demonstrable.

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**APPENDIX A**

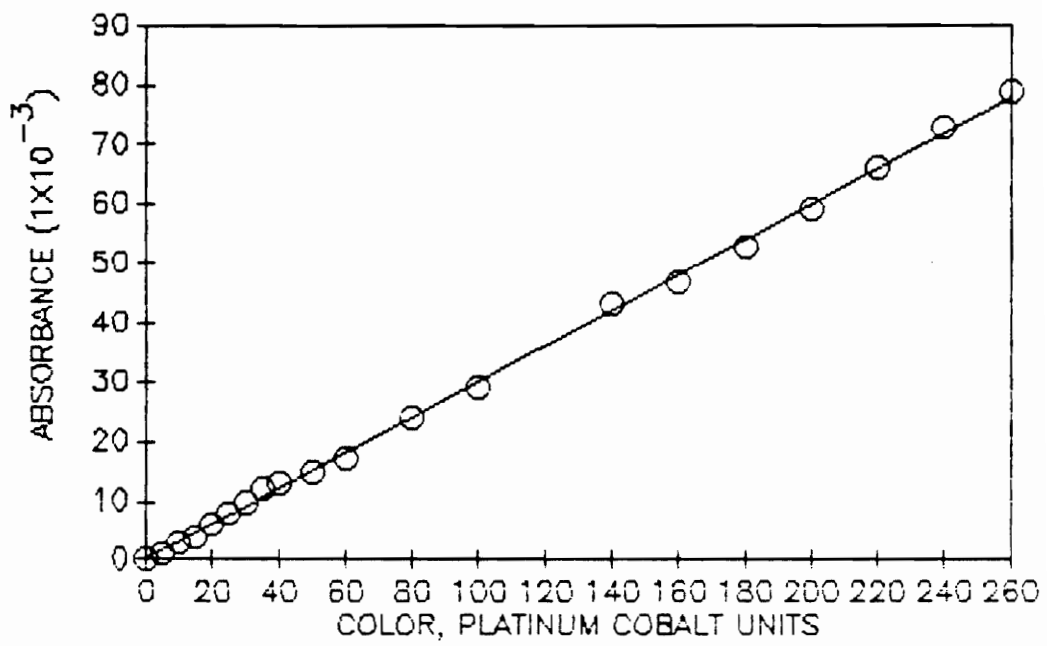


FIGURE 1-A. STANDARD CURVE FOR COLOR ANALYSIS

**APPENDIX B**



Table B-1. Reductions in total organic carbon by alum coagulation of the water from the Po River, the Ni River, and the Ni River Reservoir

Alum Dose mg/L	Po River		Ni River		Ni Reservoir	
	TOC mg/L	Reduction %	TOC mg/L	Reduction %	TOC mg/L	Reduction %
0	7.28	-	8.35	-	8.45	-
20	6.38	12.4	5.78	30.8	5.88	30.4
40	4.37	39.9	5.22	37.5	4.98	41.1
60	3.92	46.1	4.28	48.7	4.72	44.1
80	3.15	56.7	4.10	50.9	4.51	46.4
100	2.93	59.8	3.98	52.3	4.40	47.9

Note : Alum coagulation carried out at pH=6.0

Table B-2. Reductions in trihalomethane precursors by alum coagulation of the water from the Po River, the Ni River, and the Ni River Reservoir

Alum Dose mg/L	Po River		Ni River		Ni Reservoir	
	THMFP ug/L	Reduction %	THMFP ug/L	Reduction %	THMFP ug/L	Reduction %
0	707	-	1068	-	1061	-
20	543	23.2	822	23.0	817	23.0
40	323	54.5	740	30.7	693	34.7
60	256	63.8	671	37.2	658	38.0
80	231	67.3	621	41.9	630	40.6
100	229	67.6	616	42.3	621	41.5

Note : Alum coagulation carried out at pH=6.0

THMFP = 7-day total trihalomethane formation potential

Table B-3. Effects of alum coagulation on color reduction of water from the Po River, the Ni River, and the Ni River Reservoir

Alum Dose mg/L	Po River		Ni River		Ni Reservoir	
	Color pcu	Reduct. %	Color pcu	Reduct. %	Color pcu	Reduct. %
0	225	-	174	-	110	-
20	40	82.0	32	81.6	16	85.5
40	25	88.0	22	87.4	12	89.1
60	5	97.8	20	88.5	11	90.0
80	3	98.7	17	90.2	15	86.4
100	2	99.0	17	90.2	15	86.4

Note : Alum coagulation carried out at pH=6.0

pcu = platinum cobalt units

Table B-4. Rate of trihalomethane formation in Po River, Ni River, and Ni River Reservoir (Cl<sub>2</sub> to TOC: 3 to 1)

Chlorine Contact Time (days)	Sample Name	Trihalomethane Concentration (ug/L)				
		CHCl <sub>3</sub>	CHCl <sub>2</sub> Br	CHClBr <sub>2</sub>	CHBr <sub>3</sub>	Total
1	Po River	390	11	0	0	401
	Ni River	391	11	0	0	402
	Ni Reservoir	377	10	0	0	387
2	Po River	457	11	0	0	468
	Ni River	532	11	0	0	543
	Ni Reservoir	515	13	0	0	528
3	Po River	520	10	0	0	530
	Ni River	624	14	0	0	638
	Ni reservoir	599	13	0	0	612
4	Po River	558	12	0	0	570
	Ni River	664	15	0	0	679
	Ni reservoir	637	14	0	0	651
5	Po River	582	11	0	0	593
	Ni River	689	15	0	0	704
	Ni Reservoir	670	10	0	0	680
6	Po River	638	11	0	0	649
	Ni River	700	16	0	0	716
	Ni Reservoir	709	11	0	0	720
7	Po River	670	12	0	0	682
	Ni River	740	15	0	0	755
	Ni Reservoir	715	11	0	0	726

Table B-5. Effects of permanganate preoxidation at pH=7, followed by alum coagulation (60 mg/L) at pH 6.0 on TOC (mg/L) and Manganese concentration (mg/L) in the Po River, Ni River, and Ni River Reservoir waters (Raw water TOC mg/L: Po=7.20, Ni=8.06, and Ni River Reservoir=8.50)

Permanganate Dose mg/L	Po River		Ni River		Ni Reservoir	
	TOC	Mn	TOC	Mn	TOC	Mn
	mg/L					
0.00	3.24	0.02	4.20	0.15	5.78	0.02
0.25	3.20	0.04	4.15	0.08	5.25	0.03
0.50	3.13	0.04	4.03	0.04	5.06	0.03
1.00	3.14	0.04	3.65	0.05	5.00	0.04
1.50	3.20	0.05	3.63	0.09	4.08	0.09
2.00	3.20	0.06	3.44	0.14	4.55	0.14

Table B-6. Effects of permanganate preoxidation at pH=10.50, followed by alum coagulation (60 mg/L) at pH 6.0 on TOC (mg/L) and Manganese concentration (mg/L) in the Po River, Ni River, and Ni River Reservoir waters (Raw water TOC mg/L: Po=7.20, Ni=8.06, and Ni River Reservoir=8.50)

Permanganate Dose  mg/L	Po River		Ni River		Ni Reservoir	
	TOC	Mn	TOC	Mn	TOC	Mn
	mg/L					
0.00	3.38	0.05	3.80	0.10	5.25	0.03
0.25	3.37	0.02	3.80	0.10	4.82	0.03
0.50	3.24	0.03	3.76	0.09	4.80	0.09
1.00	2.97	0.05	3.70	0.08	4.75	0.04
1.50	3.34	0.09	3.57	0.05	4.61	0.05
2.00	3.25	0.12	3.05	0.05	4.55	0.09

Table B-7. Effects of permanganate preoxidation at pH=7.0, followed by alum coagulation (60 mg/L) at pH 6.0 on THMFP (ug/L) and Manganese concentration (mg/L) in the Po River, Ni River, and Ni River Reservoir waters (Raw water THMFP, ug/L: Po=824, Ni=761, and Ni River Reservoir=1180)

Permanganate Dose mg/L	Po River		Ni River		Ni Reservoir	
	THMFP ug/L	Mn mg/L	THMFP ug/L	Mn mg/L	THMFP ug/L	Mn mg/L
0.00	338	0.02	304	0.15	749	0.02
0.25	308	0.04	300	0.08	678	0.03
0.50	327	0.04	283	0.04	482	0.03
1.00	305	0.04	281	0.05	431	0.04
1.50	298	0.05	266	0.09	403	0.09
2.00	258	0.06	257	0.14	368	0.14

THMFP = 7-day total trihalomethane formation potential

Table B-8. Effects of permanganate preoxidation at pH=10.50, followed by alum coagulation (60 mg/L) at pH 6.0 on THMFP (ug/L) and Manganese concentration (mg/L) in the Po River, Ni River, and Ni River Reservoir waters (Raw water THMFP, ug/L: Po=824, Ni=761, and Ni River Reservoir=1180)

Permanganate Dose mg/L	Po River		Ni River		Ni Reservoir	
	THMFP ug/L	Mn mg/L	THMFP ug/L	Mn mg/L	THMFP ug/L	Mn mg/L
0.00	382	0.02	340	0.15	412	0.02
0.25	300	0.04	326	0.08	404	0.03
0.50	270	0.04	307	0.04	393	0.04
1.00	291	0.04	300	0.05	380	0.04
1.50	309	0.05	293	0.09	379	0.09
2.00	329	0.06	291	0.14	370	0.14

THMFP = 7-day trihalomethane formation potential



Table B-9. Effects of chlorine dioxide preoxidation followed by coagulation with 60 mg/L alum at pH 6.0 on TOC of the water from Po River, Ni River and Ni River Reservoir waters (Original TOC, mg/L : Po River = 7.17, Ni River = 7.67, and Ni River Reservoir = 7.50)

Chlorine Dioxide Dose mg/L	Po River		Ni River		Ni Reservoir	
	TOC mg/L	Reduct. %	TOC mg/L	Reduct. %	TOC mg/L	Reduct. %
0	3.46	51.7	4.01	47.7	5.15	31.3
2	3.38	52.9	3.84	49.9	5.00	33.4
4	3.44	52.0	3.77	50.8	4.86	35.3
6	3.42	52.3	3.68	52.0	4.45	40.7
8	3.41	52.4	3.40	55.7	4.40	41.4

Table B-10. Effects of chlorine dioxide preoxidation followed by coagulation with 60 mg/L alum at pH 6.0 on THM precursor removal from Po River, Ni River and Ni River Reservoir waters (Original THMFP, ug/L : Po River = 735.17, Ni River = 710, and Ni River Reservoir = 715)

Chlorine Dioxide Dose mg/L	Po River		Ni River		Ni Reservoir	
	THMFP ug/L	Reduct. %	THMFP ug/L	Reduct. %	THMFP ug/L	Reduct. %
0	337	54.1	416	41.4	543	24.1
2	280	61.9	349	50.8	411	42.5
4	275	62.5	298	58.0	350	51.0
6	246	66.5	231	67.5	306	57.2
8	235	68.0	215	69.7	286	60.0

THMFP = 7-day total trihalomethane formation potential

Table B-11. Reduction in total organic carbon by pretreatment with Powdered Activated Carbon (PAC) followed by alum coagulation (60 mg/L, at pH=6.0) of Po River, Ni River, and Ni River Reservoir waters (Initial TOC mg/L : Po = 7.21, Ni River = 7.30, and Ni River Reservoir = 8.00)

Powdered Activated Carbon mg/L	Po River		Ni River		Ni Reservoir	
	TOC mg/L	reduct. %	TOC mg/L	Reduct. %	TOC mg/L	Reduct. %
0	3.29	45.6	3.50	52.0	4.66	41.8
10	3.63	49.7	2.97	59.3	4.56	43.0
20	3.75	48.0	2.67	63.4	3.68	51.8
40	3.29	54.4	2.40	67.1	3.42	57.3
50	3.37	53.3	2.21	69.7	2.88	64.0
60	3.25	54.9	2.19	70.0	2.62	68.5

Table B-12. Removal of THM precursors from Po River, Ni River and Ni River Reservoir waters by pretreatment with Powdered Activated Carbon (PAC), followed by coagulation with 60 mg/L alum at pH 6.0 (Original THMFP ug/L : Po = 824; Ni River = 714; and Ni River Reservoir = 927)

Powdered Activated Carbon mg/L	Po River		Ni River		Ni Reservoir	
	THMFP ug/L	Reduct. %	THMFP ug/L	Reduct. %	THMFP ug/L	Reduct. %
0	454	44.9	320	55.2	471	49.2
10	424	48.8	288	59.3	465	49.8
20	442	46.4	262	63.3	373	59.8
40	415	49.6	208	70.9	286	69.1
50	403	51.1	208	70.9	286	69.1
60	398	51.6	188	73.3	273	70.6

THMFP = 7-day total trihalomethane formation potential

**Table B-13. Effect of storage on TOC and THMFP of the Po River water stored at ambient room temperature (22-24 °C)**

<b>Incubation Time Days</b>	<b>TOC mg/L</b>	<b>Reduction in TOC %</b>	<b>THMFP ug/L</b>	<b>Reduction in THMFP %</b>
0	10.00	-	758	-
14	8.32	16.8	702	7.4
28	6.05	39.5	675	10.9
35	5.54	44.6	640	15.6
42	5.08	49.2	550	27.9
63	4.67	53.3	520	31.4
70	4.09	59.1	493	34.9
90	4.10	59.0	475	37.3
115	3.95	60.5	395	47.9
122	4.04	59.6	405	46.6

Table B-14. Effect of storage on TOC and THMFP of the Ni River water stored at ambient room temperature (22-24 °C)

Incubation Days	TOC mg/L	Reduction in TOC %	THMFP ug/L	Reduction in THMFP %
0	8.35	-	1085	-
7	7.40	11.4	952	14.7
28	7.20	13.8	669	38.3
49	5.55	33.5	613	43.5
56	5.64	32.4	654	39.0
70	5.25	37.2	640	41.0
77	5.49	34.3	634	41.4
88	5.40	35.3	630	41.6

Table B-15. Effects of storage and temperature on TOC (mg/L) and THMFP (ug/L) in Po River water. TOC=8.0, THMFP=1036

Temperature and Treatment	Storage time, days							
	7		21		28		35	
	TOC mg/L	THMFP ug/L	TOC mg/L	THMFP ug/L	TOC mg/L	THMFP ug/L	TOC mg/L	THMFP ug/L
Ambient lab, Undisturbed	6.56	950	6.16	880	5.55	784	5.45	765
Ambient lab, Shaken	6.61	972	6.45	912	6.20	806	5.67	770
Ambient lab, Filtered*	6.71	955	6.13	858	5.23	750	5.20	742
Ambient lab, Alum treated	2.62	316	2.48	245	2.33	227	2.30	225
Refrigerated Alum treated	2.80	341	2.68	296	2.63	272	2.60	270
Refrigerated	6.75	990	6.74	984	6.52	943	6.45	920

\*Filtered = Sample was filtered through Whatman #42  
filter paper  
Lab temperature 22-24 °C  
Refrigerator temperature 5-7 °C

Table B-16. Effects of storage and temperature on UV absorbance at 254 nm and color(platinum cobalt units) in Po River water. Original UV-absorbance =0.409 and color (pcu) = 265

Temperature and Treatment	Storage time, days							
	7		21		28		35	
	UV	COLOR	UV	COLOR	UV	COLOR	UV	COLOR
Ambient lab, Undisturbed	0.34	194	0.30	154	0.29	154	0.29	154
Ambient lab, Shaken	0.32	170	0.29	158	0.28	157	0.28	158
Ambient lab, Filtered	0.22	86	0.20	62	0.19	62	0.19	59
Ambient lab, Alum treated	0.04	16	0.04	2	0.03	2	0.03	3
Refrigerated, Alum treated	0.04	25	0.04	25	0.04	12	0.04	12
Refrigerated, Undisturbed	0.34	198	0.31	149	0.29	134	0.28	132

\*UV at 254 nm

\*\*Color at 420 nm, platinum-cobalt units.



Table B-17. THM rate study with raw water from the Po River. TOC = 7.88 mg/L.

Chlorine Contact time Days	CHCl <sub>3</sub>	CHCl <sub>2</sub> Br	CHClBr <sub>2</sub>	CHBr <sub>3</sub>	Total
	ug/L				
1	361.5	7.5	0	0	369
2	594.7	8.3	0	0	603
3	683.0	9.0	0	0	692
4	694.2	9.8	0	0	704
5	855.4	9.6	0	0	865
6	933.8	10.2	0	0	944
7	1026.3	9.8	0	0	1036
8	1080.0	10.0	0	0	1090
9	1139.8	10.2	0	0	1150
10	1169.3	10.7	0	0	1180

Table B-18. THM rate study with Po River water treated with 60 mg/L alum. TOC = 2.93 mg/L.

Chlorine Contact Time Days	CHCl <sub>3</sub>	CHCl <sub>2</sub> Br	CHClBr <sub>2</sub>	CHBr <sub>3</sub>	Total
	ug/L				
1	173.0	7.0	0	0	180
2	213.0	7.0	0	0	220
3	268.8	6.2	0	0	275
4	291.7	6.7	0	0	298
5	316.6	7.4	0	0	324
6	340.0	7.0	0	0	347
7	358.9	7.1	0	0	366
8	368.1	6.9	0	0	375
9	392.6	7.4	0	0	400
10	420.7	7.3	0	0	428

Table B-19. THM rate study with Po River which was filtered through Whatman filter # 42, before chlorination. TOC = 8.0.

Chlorine Contact Time Days	CHCl <sub>3</sub>	CHCl <sub>2</sub> Br	CHClBr <sub>2</sub>	CHBr <sub>3</sub>	Total
	ug/L				
1	249.2	6.8	0	0	256
2	455.0	7.0	0	0	462
3	548.2	7.8	0	0	556
4	713.5	8.5	0	0	721
5	757.9	8.1	0	0	766
6	792.2	8.8	0	0	801
7	811.4	8.6	0	0	820
8	898.9	9.1	0	0	908
9	938.4	9.6	0	0	948
10	1010.7	9.3	0	0	1020

Table B-20. TOC and THM reduction (%) in Po River water due to different treatments. TOC=8.0, and THMFP=1036.

Temperature and Treatment	Storage time, days							
	7		21		28		35	
	% Reduction		% Reduction		% Reduction		% Reduction	
	TOC	THM	TOC	THM	TOC	THM	TOC	THM
Ambient lab, Undisturbed	18	8.3	23	15	31	24	32	26
Ambient lab, Shaken	17	6.2	19	12	23	22	29	26
Ambient lab, Filtered	16	7.8	23	17	35	28	35	28
Ambient lab, Alum treated	67	70	69	76	71	78	71	78
Refrigerated, Alum treated	65	67	67	71	67	74	68	74
Refrigerated, Undisturbed	16	4.4	16	5	19	9	19	11

Lab temperature 22-24 °C

Refrigerator temperature 5-7 °C

## Vita

Siroos Mostaghimi was born on May 24, 1951, in Neiriz , Iran. He graduated from Pahlavi University in Shiraz, Iran in 1974 with a BS degree in Agriculture. The author came to the United States in 1976 and graduated from Texas A&I University in Kingsville, Texas in 1978 with a Master of Science degree in soil chemistry. He then went to the Ohio State University and graduated with a Ph.D. degree in Agronomy in 1982. He worked for University of Illinois, Texas A&I University and Texas Agricultural Experiment Station from 1984 to 1988. The author was married to Shahnaz Motamedi on March, 1988. They have a son, Raamin, 16 months old. In January, 1989, he entered the Master of Science program in Environmental Science and Engineering at Virginia Polytechnic Institute and State University.