

REDUCTION OF TRIHALOMETHANE PRECURSORS
BY OXIDATION, COAGULATION AND ADSORPTION

BY

DJOHAN HIDAJAT

A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfillment of the Requirements
for the Degree of

MASTER OF SCIENCE

Department of Civil Engineering
University of Manitoba
Winnipeg, Manitoba

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ABSTRACT

Trihalomethanes, toxic and carcinogenic halogenated organics, are formed during chlorination of drinking water. Reducing of the precursors is a method to reduce trihalomethane levels in finished drinking water. Oxidation followed by coagulation and then adsorption were employed to reduce the precursors in Rosenort's water, a high precursors containing water.

Treatment trains, each composed of a sand, followed by a granular activated carbon column were used to filter oxidized and coagulated waters in a direct filtration mode. Unoxidized water was also treated similarly as a control. A surface overflow rate of $90 \text{ l/m}^2\text{.min}$ and an empty bed contact time of 10 minutes were chosen as rates of sand and carbon filtration, respectively. Oxidation was conducted for a 1 hour detention time with either 1.5 mg/l potassium permanganate or 2.0 mg/l ozone. Samples were taken from each column effluent. Total organic carbon and chloroform potential were used to measure the treatment trains' effectiveness. Chloroform levels on 1, 3, and 7 days incubation were measured to determine formation rate.

Sandfiltration reduced organics by 9% and precursors by 12%. Subsequent carbon filtration removed 79% of the organ-

ics and 84% of the precursors. Permanganate oxidation reduced organics by 2% and increased precursors by 11%, while ozone increased organics by 2% and precursors 3%. Productivity of organics was 1.2%, and was not altered by oxidation. Formation rate was reduced by oxidation.

Activated carbon adsorption was the only effective process to reduce precursors in Rosenort's water. While coagulation very marginally reduced precursors. Oxidation before coagulation was not an effective process to reduce precursors.

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NOMENCLATURE

- ACU : Apparent Color Unit is a measure of color in a natural water without any turbidity removal.
- AOP : Advanced Oxidation Process is an oxidation process using ozone with either ultra violet or hydrogen peroxide.
- BDCM : Bromodichloromethane (CHBrCl_2).
- CU : Color Unit.
- DBCM : Dibromochloromethane (CHBr_2Cl).
- DNA : Deoxyribonucleic acid is a polymer that constitutes the genetic material of all cellular organisms.
- DOC : Dissolved Organic Carbon is a measure of organics dissolved in a water determined by measuring the carbon content.
- EBCT : Empty Bed Contact Time is a measure of contact time between an adsorbent (GAC) and a solution determined by deviding the adsorbent bed volume with the solution flow rate.
- ED50 : Effect dose to 50% population.
- GAC : Granular Activated Carbon.
- LD50 : Lethal dose to 50% population.
- MAC : Maximum Acceptable Concentration.
- MCL : Maximum Contaminant Level.
- NTU : Nephelometric Turbidity Unit.
- PAC : Powdered Activated Carbon.
- SDSTCM : Simulated Distribution System Trichloromethane is a predictive TCM level in the distribution system determined by measuring the TCM level in water after 1 day contact time with a dose of chlorine at the conditions of $\text{pH} = 8.2$ and temperature = 30°C .

SGOT : Serum Glutamic Oxalacetic Transaminase.

SGPT : Serum Glutamic Pyruvic Transaminase.

TBM : Tribromomethane (CHBr_3).

TCM : Trichloromethane (CHCl_3).

TCMFP : Trichloromethane formation potential is a measure of THM precursors in a water determined by measuring the TCM level after 7 days contact time with chlorine at a dose of 3 times of the TOC level, in the conditions of pH = 8.2 and temperature = 30 °C.

TCU : True color unit is a measure of color in a natural water after turbidity removal.

TOC : Total Organic Carbon is a measure of organics in a water determined by measuring the carbon content.

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Chapter I

INTRODUCTION

1.1 NEED FOR TRIHALOMETHANE PRECURSOR REDUCTION

The practice of chlorination for drinking water disinfection has been done since the beginning of this century. This practice is now so well established that it appears that chlorine is irreplaceable. However, the discovery of trihalomethanes (THMs) in chlorinated water in the 1970's has forced people to reevaluate this practice.

THMs are known to be toxic, carcinogenic, and mutagenic, therefore, their removal from drinking water is an important consideration. There are various methods of removing THMs but the most preferred method is the reduction of THM precursors. Reducing precursors will not change the established chlorination practice.

The focus of this thesis is to present and evaluate various treatment processes to reduce THM precursors in water. The treatment train utilizes oxidation followed by coagulation, direct in line filtration, and granular activated carbon (GAC) adsorption. As shown in the following case study, GAC adsorption plays a major role in reducing THM precursors.

1.2 CASE STUDY : VILLAGE OF ROSENORT

Rosenort's water treatment plant has been in operation for 7 years and provides drinking water for the village of Rosenort and the community of Riverside. Currently, it has a capacity of 300 m³/d and provide potable water for 400 people (Poetker, 1988).

The plant is located adjacent to the Morris river, approximately 1 km south of Rosenort. Raw water for this plant is taken from an earthen reservoir adjacent to the plant. The source water is spring snowmelt which drains from an area of about 2,300 km² into the Morris River. The reservoir has a capacity of 62,000 m³, and is aerated to reduce organics. The reservoir is periodically filled by pumping water from the Morris river.

The plant (Figure 1.1) has two identical sand filters and a GAC filter with diameters and heights of 1.20 m and 0.90 m, respectively. The plant has three reservoir compartments for clear water. The compartment for sand filter effluent, has a capacity of 11 m³ and the other two, for the GAC filter effluent, have a total capacity of 226 m³.

Water from the reservoir is pumped to the two sand filters at a rate of 170 l/m²/min. Prior to filtration, approximately 10 mg/l of Aluminex3 (a coagulant) and 0.1 mg/l of potassium permanganate (an oxidant) are added. The effluent from the sand filter discharges into the first com-

partment, providing a residence time of 1 hour. The water, is then fed to the GAC filter with an EBCT (Empty Bed Contact Time) of 6 minutes. The GAC filter effluent is stored in the second compartment which provides a chlorine detention time of 18 hours. This water is then ready for distribution.

Although the quality of the finished water is generally quite good, the THM level in the consumer tap water increases significantly during summer time. Measurements between June 1985 and May 1987 by Tokarz and Belke (1987) indicated that the THM level exceeded 100 $\mu\text{g}/\text{l}$ in the months of July, August and September (Figure 1.2). The level reached a peak value of 379 $\mu\text{g}/\text{l}$ at the end of July and the beginning of August. It is likely that the higher temperatures during the summer increased the rate of THM formation. This study was focused on controlling the formation of THMs in Rosenort's drinking water.

1.3 OBJECTIVES

The primary objective of the laboratory study was to simulate unit processes and to evaluate the performance of various treatment processes to reduce THM precursors. The secondary objectives were as follows:

1. To optimize the various treatment processes in order to reduce organics and color in the finished water.

2. To determine the effects of permanganate and ozone oxidation on reducing THM precursor using the treatment processes identified in (1).
3. To develop a model to predict the THM formation as a function of time and treatment process.

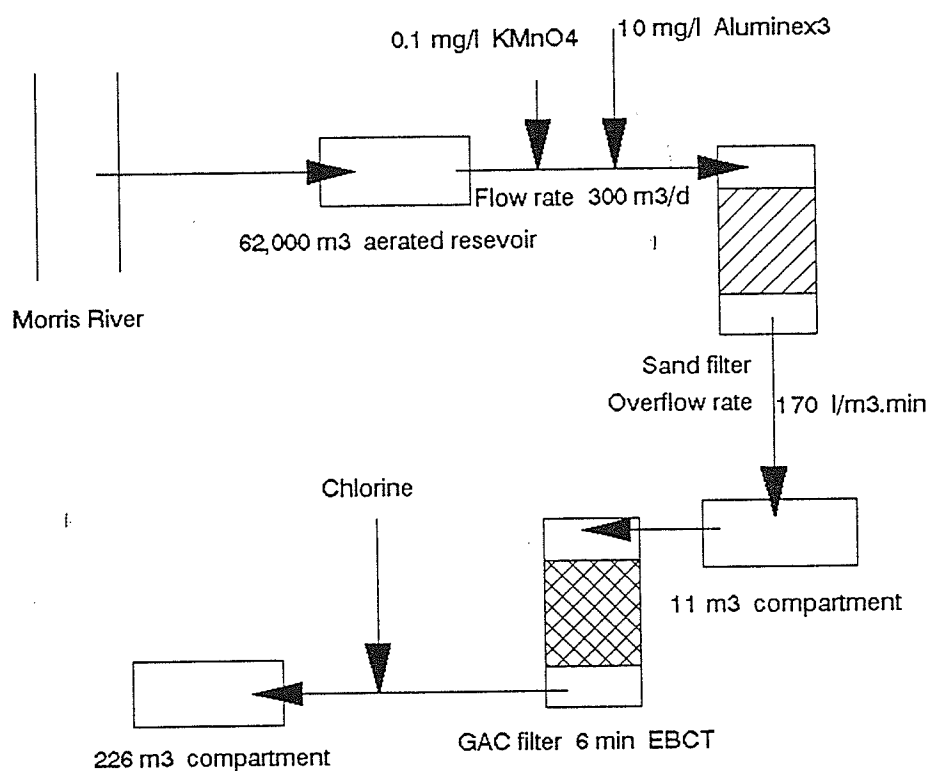


Figure 1.1: Schematic of water treatment plant at Røsenort (source: Poetker 1988).

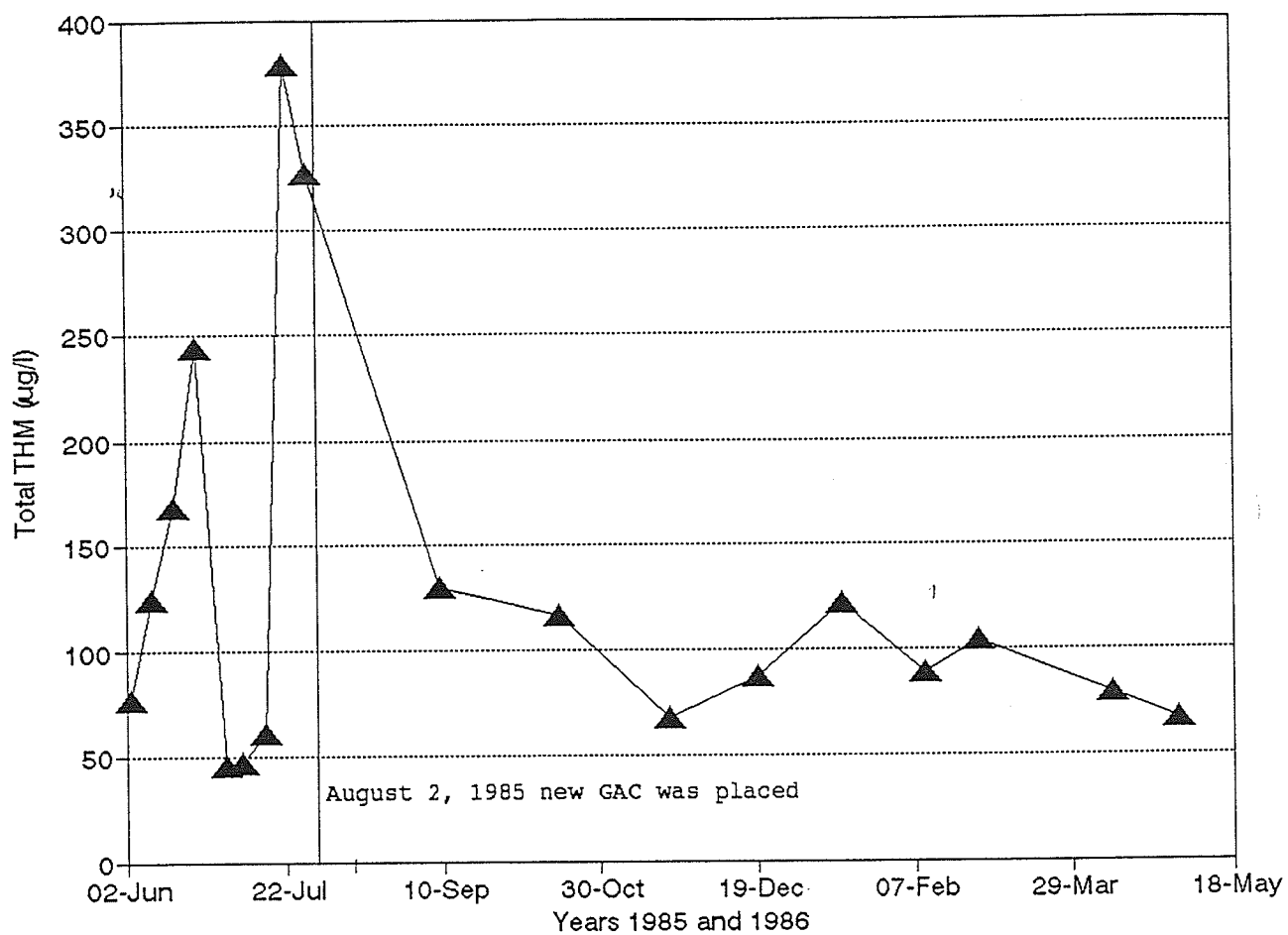


Figure 1.2: Annual (1985-1986) THM levels at the village of Rosenort (source: Tokarz and Belke 1987).

Chapter II

BACKGROUND

2.1 TRIHALOMETHANES: GENERAL

THMs are halogenated organics derived from methane in which 3 hydrogen atoms are replaced by 3 halogen atoms. These compounds are recognized as being toxic, mutagenic, and carcinogenic, therefore, human exposure to these compounds must be controlled. In 1974, J.J. Rook found large concentrations of THMs in drinking water produced by treatment plants which used chlorination as a means of disinfection (Arguello, 1979). Because drinking water is the way in which THM exposure to people mostly occurs, many investigations have been conducted concerning THM reduction in drinking water and their probable effects to human health.

2.1.1 Characteristics and Occurrence of THMs

There are many possible combinations of THM compounds. The four most common THM compounds found in drinking water include: trichloromethane (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), and tribromomethane (TBM). Table 2.1 shows the composition of THMs and the maximum levels found in a typical sample of chlorinated tap

water. The properties and characteristics of trihalomethanes are shown in Table 2.2 .

TABLE 2.1
TYPICAL COMPOSITION AND MAXIMUM LEVELS OF THMs IN
CHLORINATED TAP WATER

Compound	Percentage %	Max level µg/l
TCM (CHCl_3)	75	311
BDCM (CHBrCl_2)	12	116
DBCM (CHBr_2Cl)	10	100
TBM (CHBr_3)	3	92

source : Bull, 1982.

TABLE 2.2
PROPERTIES AND CHARACTERISTICS OF THM COMPOUNDS

Property	TCM	BDCM	DBCM	TBM
molecular weight	119.39	163.80	208.30	252.77
density at 25 °C	1.50	1.97	2.44	2.89
melting point (°C)	-63.5	n/a	n/a	6.0 - 7.0
boiling point (°C)	61.3	89.2 - 90.6	118 - 122	149.5
Henry's constant	0.152	0.095	0.035	0.024

source: AWWA, 1982 and Sax, 1979.

2.1.2 Health Effect of THMs

TCM (chloroform) was first used in the medical field as an anaesthetic, but because of its toxic effects, it was eventually abandoned. Similar toxic effects have been observed for BDCM, DBCM, and TBM. Table 2.3 shows the lethal dose to 50 % population (LD_{50}) for each compound.

The health effects associated with THMs at levels commonly found in drinking water are not clear. Most epidemiological studies have used high dosage treatments to demonstrate the toxic effects of THMs. Balster and Borzelleca (1982) investigated the behavioral acute toxicity of THMs on mice and found that the effect dose to 50% population (ED_{50}) was approximately 500 mg/kg for each THM compound. A more sensitive test resulted in an ED_{50} of 100 mg/kg. However, the latter test effect was only observed at the first administration and apparent acclimation was observed at the subsequent administration of THMs. The authors have concluded that there would be no acute toxicity effect of THMs below 100 mg/kg

For drinking water that exposes people to THMs continuously, a test other than the acute test could be more significant. Munson et al. (1982), who investigated the subchronic toxicity of THMs, found that one tenth the LD_{50} created CD-1 mice liver disturbances were associated with an increase in liver weight, serum glucose level and serum glutamic pyruvic transaminase (SGPT) and serum glutamic oxalacetic transaminase (SGOT). This investigation was conducted for 14 days of exposure. Longer exposure times (>14 days) resulted in similar effects. Based on this result, it can be concluded that the acute and subchronic toxicity effects of THMs in drinking water would be minimal.

Chronic toxicity testing employing longterm administration of low level THMs has never been reported although there is evidence of chronic toxicity and carcinogenicity for high dosage levels.

Tests of mutagenicity of THMs utilizing Salmonella typhimurium cited by Cotruvo (1981) , showed that mutagenicity is associated with THMs. These test were conducted because mutagenicity in some cases can lead to carcinogenicity. It is known that TCM is not mutagenic although previous tests showed it is carcinogenic.

A chemical carcinogen is a compound which increases the incidence of cancer through initiation and promotion mechanisms. Initiation is a process in which a carcinogen forms a covalent bond with DNA which leads to a somatic mutation and the formation of a clone of transformed cells. Promotion is a process in which a carcinogen alters the control of cellular differentiation and replication.

The roles of initiation and promotion are quite different (Bull, 1982). An initiator will produce irreversible change and will react by a nonthreshold mechanism in which a finite dose of carcinogen will result in a finite amount of cancer initiation. In this mechanism, a very low level of TCMS will still result in cancer initiation. A promoter requires a continuous exposure to produce effects that are believed to be reversible. In this latter process, a revers-

ible mechanism governs so that a definite level of carcinogen is required below which there will be no cancer promotion.

As summarized by Savage et al. (1981), TCM is unlikely a cancer initiator for two reasons. Firstly, the initiation is believed to involve somatic mutation. Secondly, the covalent bonds made by TCM with DNA in rats and mice was shown to be low, that is, about 0.1% of the covalent bonds resulting from a standard initiator (Pereira et al., 1981).

There have been no reports of carcinogenicity resulting from continuous exposure of THMs in drinking water. However, there are some epidemiological studies that shown the relationship of an increase of cancer incidence with chlorinated drinking water. This increase in the incidence of cancer could be associated with the presence of THMs.

Carcinogenicity is reported to be the most important health effect resulting from THMs in chlorinated drinking water (Reitz et al., 1982). The US Environmental Protection Agency (USEPA) has promulgated 100 $\mu\text{g}/\text{l}$ of total THM level as a maximum contaminant level (MCL). The determination of this level has been on the basis of a model in which the risk of cancer incidence is 100 cases per million exposed population (Reitz et al., 1982). Canadian Water Quality Guidelines has recommended a maximum allowable concentration (MAC) of 350 $\mu\text{g}/\text{l}$. This maximum level is based on the con-

clusion that it would have no significant hazard, particularly with respect to the incidence of cancer (Health and Welfare Canada, 1987).

TABLE 2.3
LETHAL DOSE (LD₅₀) OF THM COMPOUNDS

Compound	LD ₅₀ (mg/kg)
TCM	800 (mouse)
BDCM	n/a
DBCM	n/a
TBM	1820 (rat)

source: Sax, 1979.

2.1.3 Methods to Remove THMs

There are several methods for reducing THM level in drinking water. AWWA (1982) divided the methods into four groups which include: changing the point of chlorination, removing the THMs after formation, utilizing alternative disinfectants and removing the THM precursors. Several of these methods have been used to reduce THMs and others are under study.

THM formation is a slow reaction, therefore, reducing the contact time of chlorine to precursors may reduce THM level in drinking water. In practice, this method can be accomplished by changing the point of chlorination. For example,

chlorine could be applied after filtration rather than before coagulation. Thus, prechlorination is not recommended to be used as a coagulant aid.

Studies have been conducted to remove THMs after formation. The methods investigated include: oxidation, aeration, and adsorption. Oxidation was found not to be an effective method, although advanced oxidation processes (AOPs), such as ozone oxidation amplified by ultraviolet radiation, were effective. However, AOPs took a long time in removing THMs (the half life of surface water originating THMs is about 60 minutes). Adsorption was not an effective method to reduce THMs, because TCM, the primary THM compound, was poorly adsorbed. The only promising method could be aeration because the solubility of TCM in water is relative low (Table 2.2), thus, making it easy to remove.

Removing THMs after formation is not a preferred method due to two reasons. First, this method does not remove potential health effects associated with chlorinated drinking water since other halogenated organics, which exhibit similar effects as THMs, may not be removed. Second, this method does not remove the precursors which could eventually form THMs.

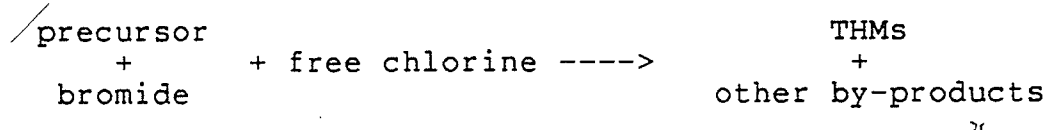
Alternative disinfectants such as chloramines, chlorine dioxide, and ozone have been used to control the formation of THMs. Chloramines are able to maintain a residual in the

distribution system and are easy to apply. They are considered weak disinfectants and produce more chlorinated organics than chlorine. Chlorine dioxide is a strong disinfectant which maintains a residual but produces toxic by-product such as chlorite and chlorate. Ozone is a strong disinfectant with no significant hazardous byproduct. One disadvantage of ozone is that disinfectant residual can not be maintained in the distribution system.

The most preferable method is the removal of THM precursors. There are three advantages of removing THM precursors. First, existing chlorination practices do not have to be altered. Second, a lower chlorine dosage is achieved due to less organics and microorganisms. Thirdly, the concentration of halogenated organics are reduced.

2.2 THM PRECURSORS

THMs in water are formed by reactions between precursors and chlorine. The precursors of unknown organic origin can react with chlorine as follows:



The reaction is a substitution rather than an oxidation reduction reaction. The rate of reaction is considered slow because it involves some intermediate reactions.

2.2.1 Organics Serving as Precursors

Humic and fulvic acids are well known as organic precursors. These acids are part of aquatic humus substances, which result from vegetation decay, soil and microbial activities. Humus substances which are alkali insoluble are referred to as humin. Some alkali soluble substances include fulvic acids, hymatomelanic acids, and humic acids. Fulvic acids are acid soluble; hymatomelanic acids are acid insoluble but soluble in ethanol; and humic acids are insoluble in acidic condition as well as in ethanol. There is no information about the roles of humin and hymatomelanic acids as precursors.

The exact organic structures of humic and fulvic acids are not well established. Humic and fulvic acids are believed to be polymeric organics with the molecular weights higher than 100,000 and in the range of 100 to 1000 g/mole, respectively. They make up about 50% of the organics in natural water. Humic acids compose about 10% of these organics and exhibit the highest yield of THMs (Rook, 1977). On the other hand fulvic acids, about 85%, show a lower yield of THMs (Table 2.4). Fulvic acids are also responsible for color in water.

Degradation of fulvic and humic acids produces monomers such as resorcinol, phloroglucinol, pyrogallol, catechol, orcinol, 2,6 dihydroxytoluena, o and m phthalic acids,

and 3,5 dihydroxybenzoic acids (Rook, 1977). Recorcinol and other m dihydroxy aromatic compounds are known of having high yield of THMs.

Methyl ketones are also monomers that can form THMs upon chlorination under basic conditions. However, their contribution to THM levels in drinking water is believed to be very limited. Very low concentration of these monomers occur in natural water and low yields of THMs have been reported (Oliver and Lawrence, 1979).

Algae can also serve as THM precursors. Algal biomass and algal extracellular products yield 0.2-4% and 0.04-5% TCM, respectively, on a carbon basis (Hoehn et al, 1980). Algal biomass may be less important because it is suspended and easy to remove by conventional treatment. However, algal metabolites that are more soluble may require additional treatment.

Other monomers with a potential for forming THM in drinking water are phenols, anilines and quinones. Phenols (Arguello et al., 1979) maybe present in raw water as contaminants from household activity.

TABLE 2.4
SOURCE AND YIELD OF PRECURSORS

Source	Precursors	Yield in % (TCM-C/TOC)
Plant decay	Humic acids	0.7-1.4
	Fulvic acids	0.3-0.9
	Resorcinol	16.7
	3,5 dihydroxybenzoic acids	14.7
Algae	Algal biomass	0.2-4.0
	Algal metabolites	0.04-5
Man made	Phenols	20-30 (in mole basis)

2.2.2 Formation

The formation of THMs is complex and involves many pathways. One well known pathway is the reaction of methyl ketones (Figure 2.2). This reaction consists of alternate hydrolysis and halogenation steps which the hydrolysis are the limiting step. In this reaction, reduction and oxidation take place among the carbon atoms.

A second pathway (Figure 2.3) was suggested by Rook (1977) in which m hydroxy aromatics are the precursor models. This reaction involves two substitutions that break aromatic into aliphatic compounds. These reactions are followed by hydrolysis steps which form THMs. Similar to methyl ketones, there is no chlorine reduction with m hydroxy aromatics.

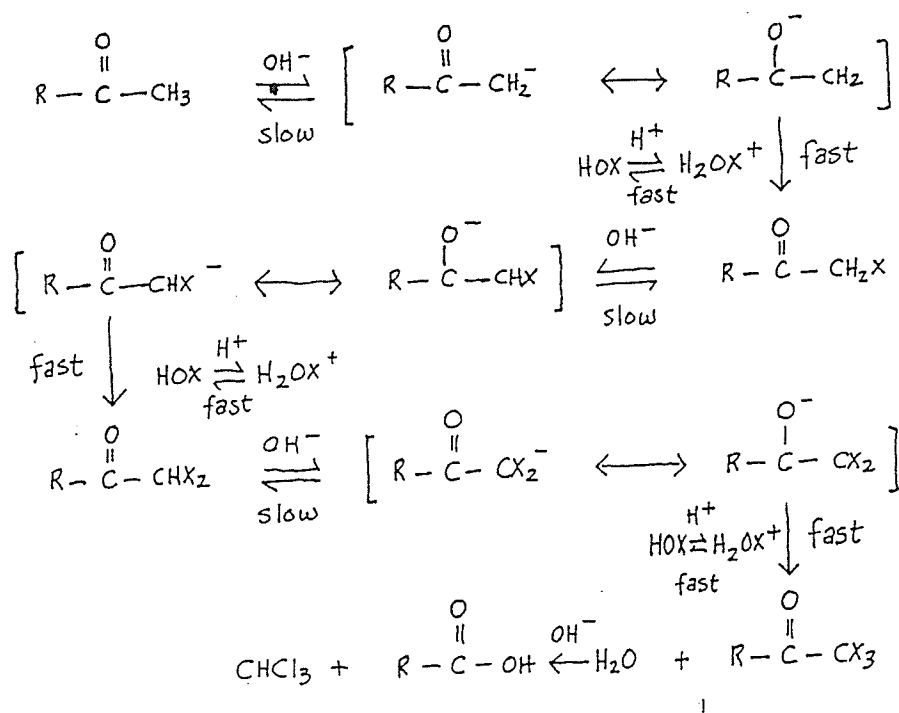


Figure 2.2: Methyl Ketones THM formation (source: Trussell and Umphres, 1978)

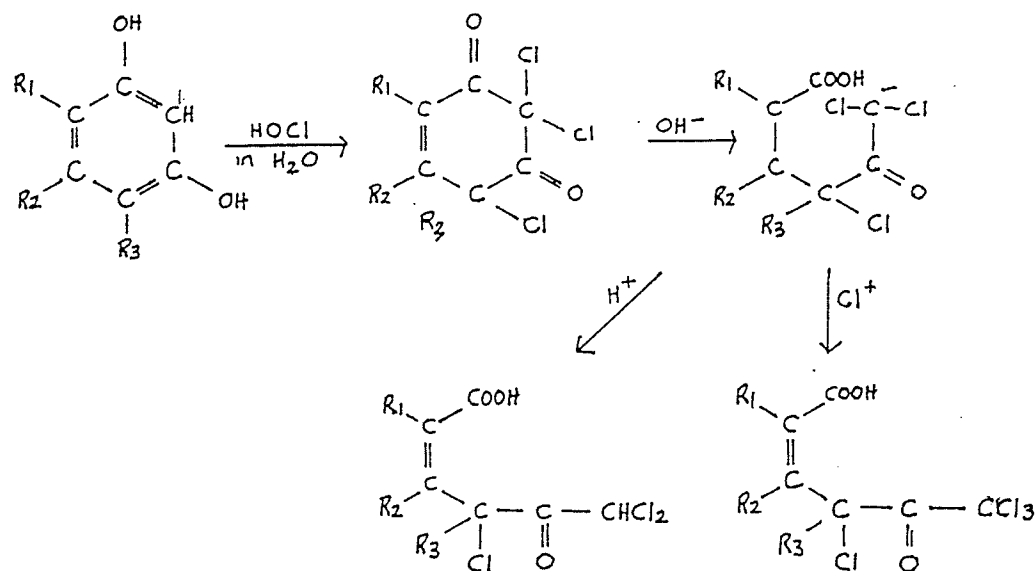


Figure 2.3: m Hydroxy Aromatics THM formation (source: Rook, 1977)

The formation of THMs is influenced by the bromide level and chlorine dose. Chlorination will oxidize bromide to Br_2 , HOBr , OBr^- and to a limited extent, BrCl and BrCl_5 (Trussell and Umphres 1978). These compounds are effective in increasing the formation of THMs in terms of mol THMs/mol TOC. Bromide is also speculated to increase the reaction rate during the first hours of formation (Figure 2.4).

The effects of pH were observed by Trussell and Umphres (1978) who concluded that high pH condition increase the rate and yield of THM formation in terms of TCM-C/TOC. The authors also concluded that THMs were formed even if chlorine was completely removed following chlorination in high pH condition. Lower pH, however, increases formation yield in terms of TCM/ Cl_2 .

The influence of chlorine dose on THM formation is shown on Figure 2.5. In the first stage, chlorine is consumed to oxidize inorganic impurities such as Fe^{2+} , Mn^{2+} and S^{2-} . The second stage reaction is very fast and chlorine substitutes organics to form halogenated organics such as THMs. This stage is slow and the THMs produced is proportional to the chlorine consumed. In the last stage the chlorine starts to build up as chlorine residual and there is no significant increase in THMs. The last stage is of particular interest to water treatment engineers since a chlorine residual is required in the distribution system.

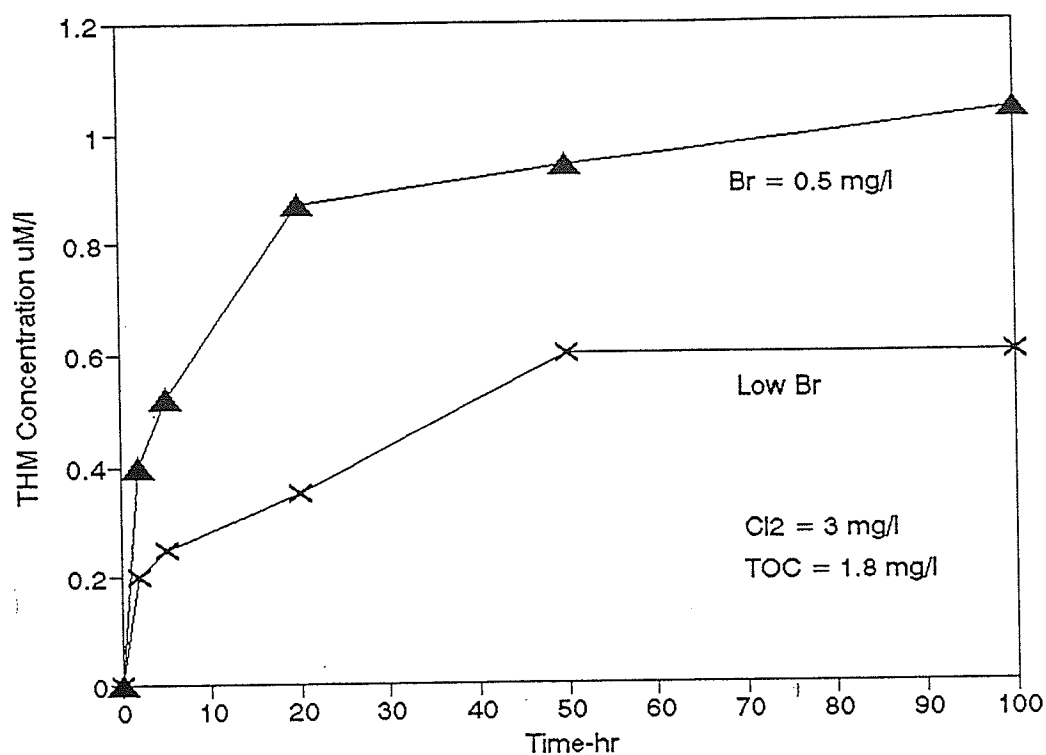


Figure 2.4: Bromide effect on THMs (source: Trussell and Umphres, 1978)

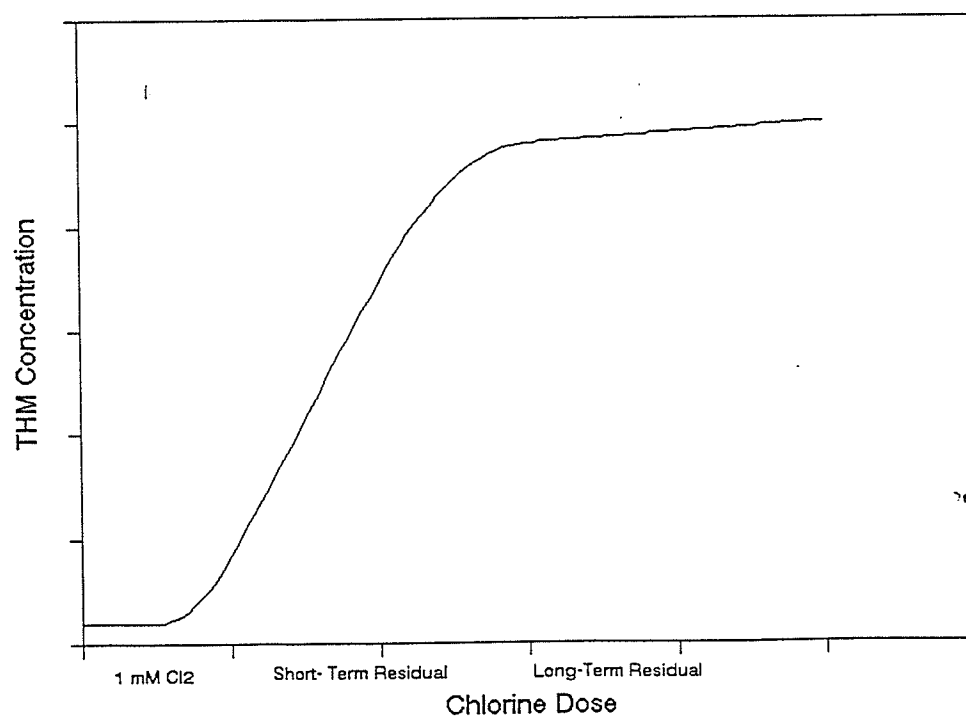


Figure 2.5: THM concentration vs. chlorine dose curve (source: Trussell and Umphres, 1978)

2.2.3 Kinetics: Model Development

There is a need to develop a kinetic model that relates chlorination contact time to THM formation. A kinetic model would be useful for small systems the time duration from chlorine application to consumption is short. The model, however, would be less useful for very large distribution systems which multiple chlorination is practiced and a very long chlorine contact time occurs.

There is very little work that has been done on the kinetics of the THM reaction. Trussell and Umphres (1988) reported that THM formation followed a third order reaction with respect to precursors as described by this following equation.

$$dTHM/dt = -dC/dt = k_1 [Cl_2] [C]^3 \quad (1)$$

Where $dTHM/dt$ is the rate of THM formation

$-dC/dt$ is the rate of precursor disappearance

k_1 is the reaction rate constant

$[Cl_2]$ is the chlorine residual

C is the precursor residual

Urano et al. (1983) also reported that the concentration of THM during formation is a function of many parameters as follows:

$$[THM] = k_2 (pH-a) [TOC]^m [Cl_2]_0^n t \quad (2)$$

Where THM is the THM formed

pH is the pH condition

k_2 is the reaction rate constant

$[Cl_2]_0$ is the chlorine dose
t is the chlorine contact time
a, m, and n are the parameters

2.3 PRECURSORS REMOVAL

Three treatment processes that have been used for precursors removal include: coagulation followed by filtration, adsorption, and oxidation. These are used individually or in combination. Ultrafiltration is another process that has limited use.

2.3.1 Coagulation

Coagulation is a process in which small thermodynamically unstable particles in water are forced to agglomerate. Most of humic substances are considered as thermodynamically unstable.

Thermodynamically unstable particles are divided into kinetically stable and unstable particles. Kinetically stable particles agglomerate slowly while the unstable ones do so rapidly. The coagulation process converts kinetically stable particles to unstable ones. Particles of concern have diameter higher than 10^{-8} m, and are known as colloids and suspended particles (Amirtharajah and O'Melia, 1990).

The stability of a particle in water is related to its electrical charge. This electric charge is obtained three ways, accepting or donating protons (H^+) or ions, imperfection in the particle structure, and adsorbing electrically charged polymers. A particle that is charged by one or a combination of the first two ways is recognized as an electrostatic stable particle. Particles that adsorb electrically charged polymers are referred to as steric stable particles.

A particle will accept or donate protons if the particle surface is active. The activity of a particle surface is related to certain groups of chemical structures in the particle. In water, protons or ions are attracted to either the water or the groups. This attraction depends on affinity of protons to water or protons to the groups.

The imperfection of a chemical structure (in a particle) occurs when atoms in the structure are replaced with the others of different valence. This causes a surplus of electrical charge that leads to an electric charging of the particle.

It is known that electrically charged polymers such as humic substances may adsorb on a particle which is then stabilized. (Amirtharajah and O'Melia, 1990). Because of this, humic substances are considered as stabilizing agents in natural water.

A charged particle in a solution can be described as a ball surrounding which primarily, opposite charged ions (counterions) are distributed in a certain way so that inside a radius, say the outer radius, the total charge is balance. This is actually a layer covering the charged particle. Then, whenever the particle moves, ions inside a radius shorter than the previously mentioned radius, say inner radius, will also move. The layer that is formed inside the inner radius is called Stern layer while the layer that is formed outside the inner, but inside the outer radii is called the diffuse layer. As a unity those layers are referred to as a double layer.

The coagulation process involves three sequential steps: coagulant formation, particle destabilization, and interparticle collision. Coagulant formation will be occur if a certain chemical is introduced to water. For example, the introduction of aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 14.3\text{H}_2\text{O}$) in water, results in hydrolysis and formation of coagulants such as Al^{+3} , $\text{Al}(\text{OH})_3$, and $\text{Al}_8(\text{OH})_{20}^{+4}$. The coagulant will initiate destabilizing the particles.

A coagulant destabilizes particles in four ways: compression of the double layer, adsorption to produce charge neutralization, enmeshment in a precipitate and adsorption to permit interparticle bridging. Firstly, compression of the double layer is actually achieved by increasing counterion concentration in the diffuse layer of a particle. This

will make the double layer thinner and allow other particles to move closer to cause agglomeration. Secondly, adsorption and charge neutralization will occur if the opposite electrically charged coagulant adsorbs on the particle surface. This will reduce particle charge and will make the other particles come closer together. Thirdly, during precipitation of coagulant, some particles will be enmeshed and settled down. Finally, adsorption in interparticle bridging is achieved when a long chain coagulant adsorbs on two or more particles.

Following destabilization of particles, the collision of the particles will result in agglomeration. Agglomeration increases the settling rate of destabilized particles.

Coagulation of humic substances is influenced by pH. Aluminum and iron(III) salts exhibit the best performance at pH around 5. This is indicated by achieving the optimum dose for coagulation. In this condition, the coagulation is believed to be dominated by charge neutralization with alum or iron(III) humate as the precipitate product. In a pH around that of natural water (pH=8), the adsorption of humic substances by aluminum or iron(III) precipitate takes place. In the adsorption by precipitates, more coagulant is required than that in the charge neutralization.

Other coagulants usually used are organic and inorganic polyelectrolytes. Cationic polymers are widely used espe-

cially in a treatment processes utilizing direct filtration (Markowsky et al., 1990). A cationic polymer stabilizes negatively charged particles through charge neutralization and bridge formation.

The presence of hardness causing metal ions assists in the coagulation of humic substances. Ca^{2+} and Mg^{2+} are believed to compress the double layer and to reduce the repulsive force between polymers and a colloid. Ca^{2+} influences a fulvic acid stabilized colloid by increasing the possibility to agglomerate in the colloids collision.

In natural water, humic substances compose about 50% of the precursors. The efficiency of humic substance coagulation increases with the increase of molecular weight. Precursors of low molecular weight humic substances and non humic substances are considered hard to coagulate. For these types of precursors, GAC adsorption is usually used.

2.3.2 Direct Filtration

Direct filtration is a water treatment process utilizing coagulant addition, rapid mixing, flocculation and filtration. Direct filtration is used for relatively low turbidity water. This process is favored because of low capital and operation cost due to the omission of the sedimentation tank. However, it is not effective in treating high turbidity and colored water. Cleasby (1990) listed the character-

istics of water which is appropriate for a direct filtration process (Table 2.5).

Aluminum sulfate may be used in a direct filtration process, but the dose is limited to less than 15 mg/l due to the potential aluminum breakthrough in the finished water. For a time when a higher dose is required, aluminum sulfate is suggested to be used in a combination with a polymeric coagulant to reduce the aluminum sulfate dose.

TABLE 2.5
CHARACTERISTICS FOR DIRECT FILTRATION

Parameter	Quantity
color	< 40 CU
turbidity	< 16 NTU
algae	< 200 asu/ml
iron	< 0.3 mg/l
manganese	< 0.05 mg/l

A polymeric coagulant may also be used solely. For treatment of a very low turbid water using a polymeric coagulant when only color or humic substance removal is intended, the flocculation tank may not be needed because flocculation time is not required. Glaser and Edzwald (1979) reported that in humic substance removal by direct filtration using polyethylenimine, the filter efficiency was not affected by flocculation time.

A direct filtration process that does not utilize a flocculation tank is referred to as a direct in line filtration process. Rosenort's plant is an example.

2.3.3 Granular Activated Carbon (GAC) Adsorption

Adsorption is a process of accumulating or adsorbing a molecule in a liquid or gas phase onto the interface of a solid. The molecule, then, is called the adsorbate while the solid is referred to as the adsorbent. In water treatment practice, adsorbates can be organics or inorganics while the adsorbent may be activated carbon, activated alumina, ion exchange resin, or adsorbent resin and bentonite (Snoeyink, 1990). Activated carbon is the most widely used adsorbent to remove precursors. The efficiency of a particular adsorbent is governed by two aspects: equilibrium and kinetics.

Equilibrium. Adsorption is considered a reversible process in which the adsorbates may also be desorbed (released from the adsorbent) into the solution. An equilibrium will be achieved if the adsorption rate is equal to the desorption rate. During an equilibrium and constant temperature condition, a relationship (adsorption isotherm) between adsorbate concentration on the adsorbent and adsorbate concentration in the solution can be established. Two well known adsorption isotherms are expressed as follows:

$$\text{Freundlich isotherm: } q_e = k C_e \quad (3)$$

$$\text{Langmuir isotherm: } q_e = (q_m b C_e) / (a + b C_e) \quad (4)$$

Where q_e is the adsorbate concentration on the adsorbent.

C_e is the adsorbate concentration in the solution.

q_m is the maximum concentration of single layer adsorbate on the adsorbent.

k , n , a , and b are constants.

Freundlich isotherm is the most widely used in water treatment practice. It is practical to estimate the amount of GAC required to reduce organics in water to a certain level.

The equilibrium is affected by adsorbent surface area, pore size distribution and surface chemistry (Snoeyink, 1990). The quantity of adsorbed adsorbate is proportional to the surface area of the adsorbent. The pore size affects the transport of adsorbate molecules to the adsorbent surface. The affinity of surface to adsorbate affects the adsorption equilibrium.

Kinetics. Adsorption on activated carbon involves 3 steps: film diffusion transport, pore transport and adsorption (Faust and Aly, 1987). Film diffusion transport is a step of transporting a molecule from a bulk solution to the outer surface of the adsorbent granule. Pore transport is a step of transporting a molecule from the outer surface through a pore. Adsorption is the final step of attaching a molecule

on an active site on the interior surface of a pore. For a dilute solution, film diffusion transport is the rate limiting step. For a very concentrated solution which rarely occurs, the pore transport is the rate limiting step.

The adsorption rate, the rate of adsorbate transport onto the adsorbent, is influenced by the size of the adsorbate molecule and the size of the adsorbent particle. A large molecule will be transported slowly and a large carbon particle will have long pores. The rate of adsorption influences the design of a GAC filter column.

GAC filter column. The GAC filter column is a reactor to contact the adsorbate in a solution with the GAC adsorbent bed. A running GAC column has 3 zones: saturated, mass transfer, and fresh GAC zones. The concentration of each zone can be described as in Figure 2.6. C_0 is the influent adsorbate concentration, C_b is the desired effluent adsorbate concentration, AB is the length of saturated zone, $BC=L_{mtz}$ is the length of mass transfer zone, CD is the length of fresh GAC, and L_c is the critical length to reach a maximum concentration C_b in the effluent. For a constant flow rate of an adsorbate, L_{mtz} is constant. The length of saturated zone grows with time.

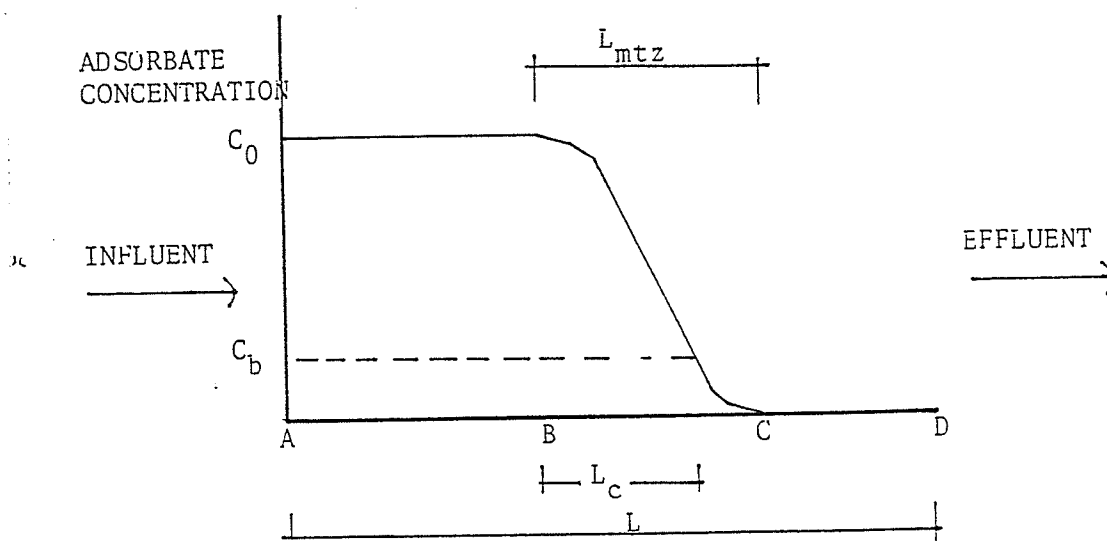


Figure 2.6: Effluent Concentration of GAC Column

The contact time of adsorbate and adsorbent is measured by Empty Bed Contact Time (EBCT). This is not actually the real contact time or residence time of adsorbate. EBCT is defined as volume of GAC bed divided by flow rate. The minimum EBCT for achieving maximum concentration C_b is calculated as follows.

$$EBCT_{min} = (L_c/L) EBCT \quad (5)$$

L_c is determined by an experiment.

GAC media. The selection of media is one of the most important consideration in the preparation of a GAC column. In order to get an idea of the properties and characteristics of the media, the following parameters should be understood.

Surface area is a measure of the available surface on the activated carbon, measured by maximum adsorption of nitrogen gas in a monolayer. The iodine number is a measure of the adsorption capacity for small molecule adsorbates, measured by the adsorption of iodine. Bed density is a measured of density after backwashed, drained and selected for a range of particle size. Particle density is a measure of the extent of fluidation and expansion, measured by wetting the GAC. Total pore is a measure of total pore volume. Apparent density is a measure of the density on purchase. The molasses number is a measure of adsorption capacity for large molecule adsorbates. Tannin value is a measure of the adsorption capacity for tannin.

2.3.4 Oxidation

The oxidation processes involve the exchange of electrons between chemical species, one species loses electrons while another gains electrons or is reduced. The first species is called a reductant and the latter is oxidant. Oxidation is always coupled with reduction. In water treatment the reductant may be an organic or a soluble metal. Table 2.6 lists a number of oxidants.

In the future, greater use of chemical oxidants and disinfectants such as ozone and chlorine dioxide is expected to remove precursors to control the formation of THMs (Glaze, 1990). Other chemicals including potassium permanganate may be used as alternative oxidants.

TABLE 2.6
OXIDANT OXIDIZING POTENTIAL

Oxidant	Reduction half-reaction	E°, V
Chlorine	$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-$	1.36
Hypochlorous acid	$\text{HOCl} + \text{H}^+ + 2\text{e}^- \rightarrow \text{Cl}^- + \text{H}_2\text{O}$	1.49
Hypochlorite	$\text{ClO}^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Cl}^- + 2\text{OH}^-$	0.90
Chloramines, basic		
Monochloramine	$\text{NH}_2\text{Cl} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Cl}^- + \text{NH}_3 + \text{OH}^-$	0.75
Dichloramine	$\text{NHCl}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 2\text{Cl}^- + \text{NH}_3 + 2\text{OH}^-$	0.79
Chloramines, acidic		
Monochloramine	$\text{NH}_3\text{Cl}^+ + \text{H}^+ + 2\text{e}^- \rightarrow \text{Cl}^- + \text{NH}_4^+$	1.40
Dichloramine	$\text{NHCl}_2 + 3\text{H}^+ + 4\text{e}^- \rightarrow 2\text{Cl}^- + \text{NH}_3 + 2\text{OH}^-$	1.34
Ozone, acidic	$\text{O}_3 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{O}_2 + \text{H}_2\text{O}$	2.07
Ozone, basic	$\text{O}_3 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{O}_2 + 2\text{OH}^-$	1.24
Hydrogen Peroxide		
Acidic	$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$	1.78
Basic	$\text{HO}_2^- + 2\text{e}^- + \text{H}_2\text{O} \rightarrow 3\text{OH}^-$	0.85
Chlorine dioxide	$\text{ClO}_2 + 2\text{H}_2\text{O} + 5\text{e}^- \rightarrow \text{Cl}^- + 4\text{OH}^-$	1.71
Permanganate†		
Acidic	$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{MnO}_2 + \text{H}_2\text{O}$	1.68
	$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.49
Basic	$\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{MnO}_2 + 4\text{OH}^-$	0.58
Oxygen		
Acidic	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	1.23
Basic	$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$	0.40

source: Glaze, 1990.

Oxidation of an organic in water does not stabilize it to water and carbon dioxide. Oxidation only alters an organic to a higher oxidation state organic such as an alcohol to a carboxylic acid. By this way, oxidation is believed to reduce precursors by altering precursor organics to less

reactive organics. A less reactive organic will produce less THM or form THM slower upon chlorination than the original organic. The TOC after oxidation is expected to remain constant.

An advanced oxidation process (AOP) is an oxidation process which utilizes a strong oxidant such as ozone or hydrogen peroxide coupled with ultra violet (UV) radiation. With this process an organic expectedly is stabilized to water and carbon dioxide. This process has not been used in a full scale treatment plant.

Potassium permanganate and ozone are strong oxidants, however, under basic condition they are weaker than chlorine (Table 2.6). Consequently, they oxidize narrower spectrum of organics in a natural water than chlorine does. Chlorination after permanganation or ozonation will proceed oxidation of the remaining organics. This process is maybe responsible for forming THMs. The following sections focus on the use of potassium permanganate and ozone in reducing THM precursors.

Potassium Permanganate. Potassium permanganate reduces precursors in 2 ways: by facilitating coagulation and by reducing THM productivity of organics. Colthurst and Singer (1982) reported that potassium permanganate reduces precursors by adsorption of the precursors onto manganese dioxide precipitates. This adsorption is facilitated by the presence of Ca^{2+} ions.

Potassium permanganate in excess of 10 mg/l in a contact time of 21 hours reduced precursors by 35% (AWWA, 1982). However, the dosage and contact time used were not applicable to values used in real water treatment practice. To avoid excessive concentration of permanganate and manganese oxide in the effluent, treatment plants usually limit the maximum potassium permanganate dosage to 2 mg/l. Gifford et al. (1989) reported that a dose of 2 mg/l reduced the precursors 13.5%. By the addition of 30 mg/l powdered activated carbon (PAC) a synergistic effect of potassium permanganate and PAC was achieved, reducing the precursors by 35%. Addition of PAC also controls the permanganate residual.

Ozone. Ozone reduces precursors in 3 ways: by facilitating coagulation, by converting organics to more biodegradable organics and by reducing the THM productivity of organics. Ozone at a low dose has been reported (Farvardin and Collins, 1989) as creating microfloculation so that coagulation was easier improved resulting in a lower optimum coagulant dose. However, when the ozone dose was increased, the efficiency of coagulation was reduced causing an increase of organic precursors in the effluent.

Ozonation prior to GAC adsorption converts organics to more biodegradable organics allowing enhanced microbial activity on the GAC bed. This increases the life of the GAC media reduces the chlorine demand of the effluent.

Ozonation of the final effluent prior to chlorination reduces THM productivity of organic and reduces the chlorine dose.

2.4 MEASURE OF TRIHALOMETHANE

One of the final objectives of THM removal is to reduce THM concentrations in the distribution system. This concentration is referred to as the Instantaneous (Inst) THMs concentration and is obtained by the addition of a reductant in the sample bottle prior to sampling. The reductant is intended to stop the formation of THMs.

However, the Inst THM concentration of a particular location in the distribution system may be different than those located at other points in the same distribution system. This is because conditions in which the THMs are formed at various locations may be different. Parameters that are reproducible and meaningful are required to estimate the formation of THM in a distribution system. Standard Methods (Clesceri et al., 1990) proposed 5 parameters to measure THM formation: Trihalomethane Formation Potential (TFP), Basic Trihalomethane Formation Potential (BTFP), Ultimate Trihalomethane Formation Potential (UTFP), Maximum Trihalomethane Potential (MTP), and Simulated Distribution System Trihalomethane Concentration (SDSTHMC). A brief description of each test procedure is as follows:

(a) TFP is a measure of precursors determined by measuring the THM concentration formed in water buffered at pH 7.0, containing an excess of free chlorine with a chlorine residual of 1 to 5 mg/l after being incubated 7 d at 25 °C.

(b) BTFP is a measure of precursors determined with a procedure similar to that of TFP except the pH is 9.2. This measure is to simulate lime-softened or naturally high pH water and accelerate THM formation.

(c) UTFP is a measure of the estimated highest THM concentration that may be produced at the extreme condition of a public water supply system determined by measuring the THM concentration formed in water buffered at a specific pH and spiked with a dose of chlorine after being held at a specific time and temperature.

(d) MTP is a measure of the precursors determined by measuring the THM concentration in triplicate samples taken from a point in the distribution system that reflects maximum resident time, after being incubated for 7 d at a temperature of 25 °C or above and a free chlorine residual is detectable from at least one of the samples.

(e) SDSTHMC is a measure of the estimated THM concentration in a distribution system determined by measuring the THM concentration in a previously chlorinated water sample after being stored in a condition representing the utility's distribution system.

These parameters which measure or estimate precursor and THM concentrations, are based on different control variables. These variables include: sampling point, type of water, pH, temperature, and time of incubation. The control variables can be changed to represent condition can be created to measure or estimate the precursor and in a distribution system.

Chapter III

EXPERIMENTAL APPROACH

This study is focused on controlling the formation of THMs in Rosenort's drinking water. An experimental investigation was conducted to simulate unit processes and to evaluate the performance of various treatment processes to reduce THM precursors. Bench scale experiments were conducted to evaluate the effectiveness of oxidation, coagulation followed by direct in line filtration, and GAC adsorption in removing THM precursors.

3.1 SCOPE OF STUDY

The study was designed on the basis of three experiments. These experiments include: a preliminary, a treatment evaluation, and trichloromethane (TCM) formation. The preliminary experiment was designed to determine the optimum chemical dosage and detention time for the treatment evaluation experiment. The treatment evaluation was designed to evaluate the efficiency of each treatment process in term of organic and color removal. The TCM formation experiment was directed to evaluate the efficiency of each treatment process in term of precursors and to develop a model to predict THM precursors and THM level in Rosenort drinking water under the warmest condition.

The preliminary and treatment evaluation experiments were performed using bench scale treatment trains utilizing potassium permanganate and ozone preoxidation followed by coagulation, direct in line sand filtration and GAC adsorption.

The experiments were conducted at room temperature. The primary test parameters for the first two experiments were Total Organic Carbon (TOC) and True Color Unit (TCU), while TCM was measured for the last experiment. Secondary test parameters such as pH, alkalinity, hardness and turbidity were also measured.

3.2 MATERIALS AND METHODS

General

Raw and finished water. Raw and finished waters were taken weekly from the Rosenort water treatment plant. One liter of the raw and finished waters were stored at 4 °C for further testing at a later date to determine the water characteristics. The remaining raw water was allowed to reach room temperature conditions prior to the test run.

Flow Rate Calibration. Sand and GAC filtration flow rates were determined for an overflow rate of 90 liter/m²/minute and an EBCT of 10 minutes, respectively. The surface area of the sand filter was 63.6 cm² and the volume of GAC media filter was 1145 cm³. Based on this information, the flow

rates for sandfiltration and GAC filtration were determined to be 0.57 liter/min and 0.115 liter/min, respectively.

The peristaltic pumps were calibrated prior to setting the flow rate. This was achieved by pumping a quantity of water into a 1 liter graduated cylinder at a number positions of the dials. The times required were recorded to find the flow rates.

Permanganation. Permanganation (permanganate oxidation) was achieved by potassium permanganate introduction into the raw water, with flash mixing using a jar test apparatus and 2 liter beakers. Potassium permanganate (Fisher Scientific and Co.) was prepared from a standard solution of 1 mg/ml. The concentration was measured 24 hours after the solution was made and checked every month to ensure stability. The concentration of potassium permanganate was measured using a method outlined in Standard Methods (Clesceri et al., 1990). A jar test apparatus (Phipps & Bird, Inc.) was used to ensure controlled mixing condition.

Ozone generation and measurement. Dry air (Linde, Union Carbide) was passed sequently through an ozone generator (Ozonair, Canatraco Ltd.), a flow meter (Mark III Flowmeter Kit, Fisher Scientific Co.) and bottles containing potassium iodide (20%) solution (Figure 3.1). The ozone generator was set at 120 volt while air flow was controlled at 50 ml/min by adjusting the valves at the dry air tank head and the

flow meter. The ozone flow rate was measured by measuring the iodine liberated in the potassium iodide solution (Standard Methods, 1985).

Ozonation. Ozonation (ozone oxidation) was achieved by introducing ozone into the raw water using an arrangement composed of a 2.5 liter contactor and 2.5 liter bottles. The contactor (Figure 3.2) was connected to the bottles so that the ozonated water could be recycled from the bottles and back to the contactor (Figure 3.3) by using a peristaltic pump. The contactor was made of plexiglass and contained two compartments. Bubbles at the top of the contactor were drawn by a peristaltic pump into bottles containing potassium iodide solution to measure the ozone liberated from the water.

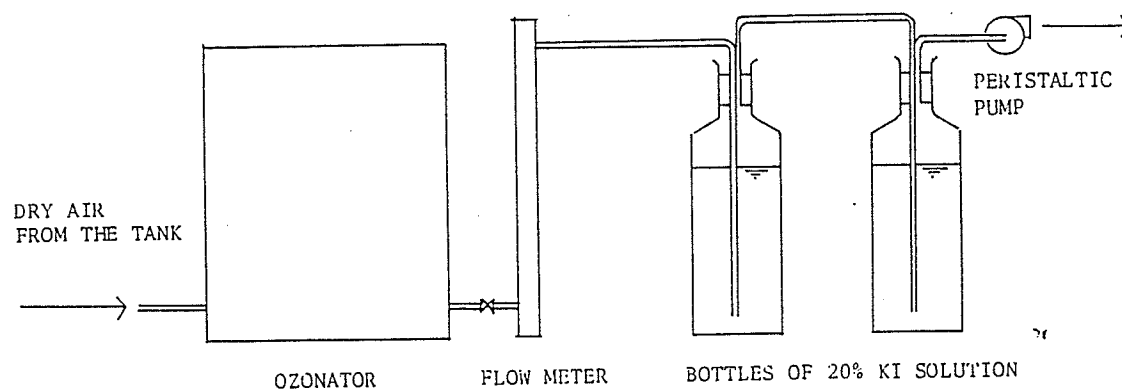


Figure 3.1: Ozone generating apparatus

Coagulation. Oxidized water was placed in 2 liter beakers and flash mixed. While mixing, a coagulant was introduced into one of the beakers for a specific time. This water would undergo sand filtration. When the first beaker was almost empty, coagulant was added to the second beaker. Subsequently the additional beakers were utilized in the same way to obtain the same flocculation time. The coagulant dosage was based on a standard solution of 1mg/ml.

Direct sand filtration. Coagulated water was pumped into the sand filter column. The overflow rate was controlled by drawing the effluent from the outlet at the bottom of the column so that the water level in the column was constant (Figure 3.4). The column was a plexiglass cylinder with a diameter and height of 9 cm and 18 cm, respectively. The silica sand media had a 0.4 mm effective diameter and a uniformity coefficient of 1.4.

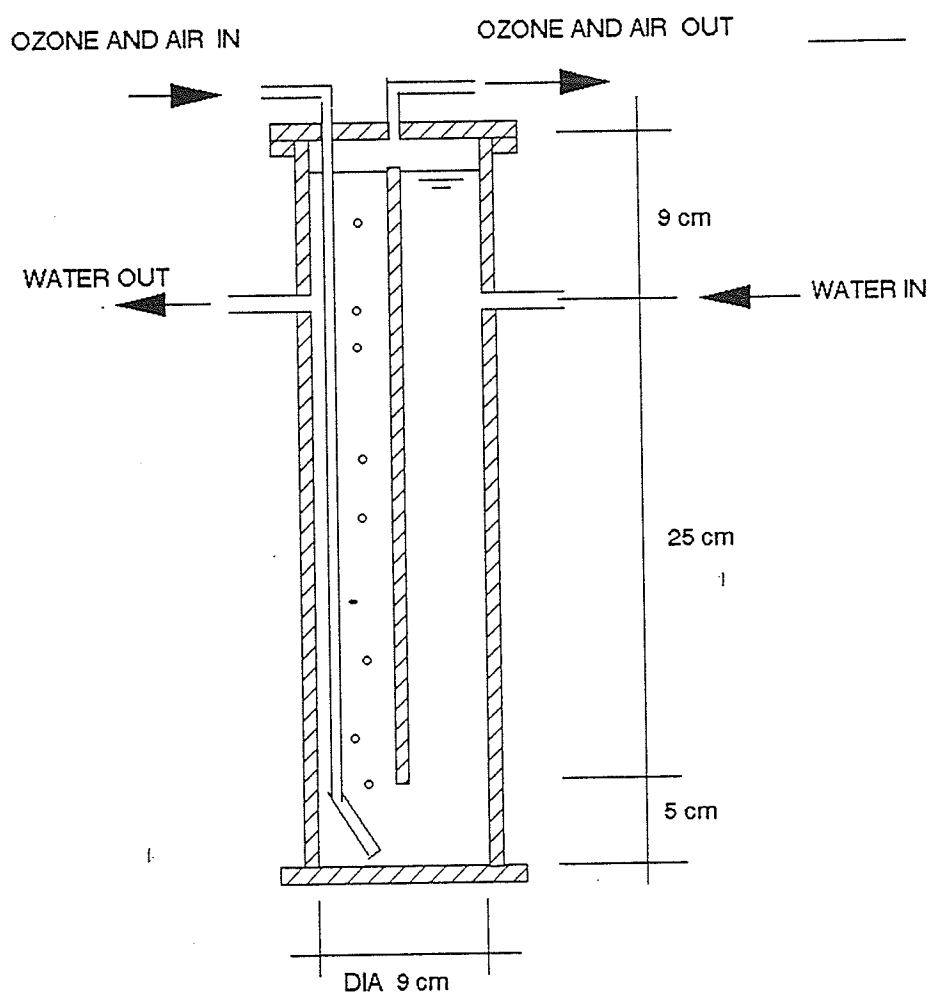


Figure 3.2: Ozone contactor unit

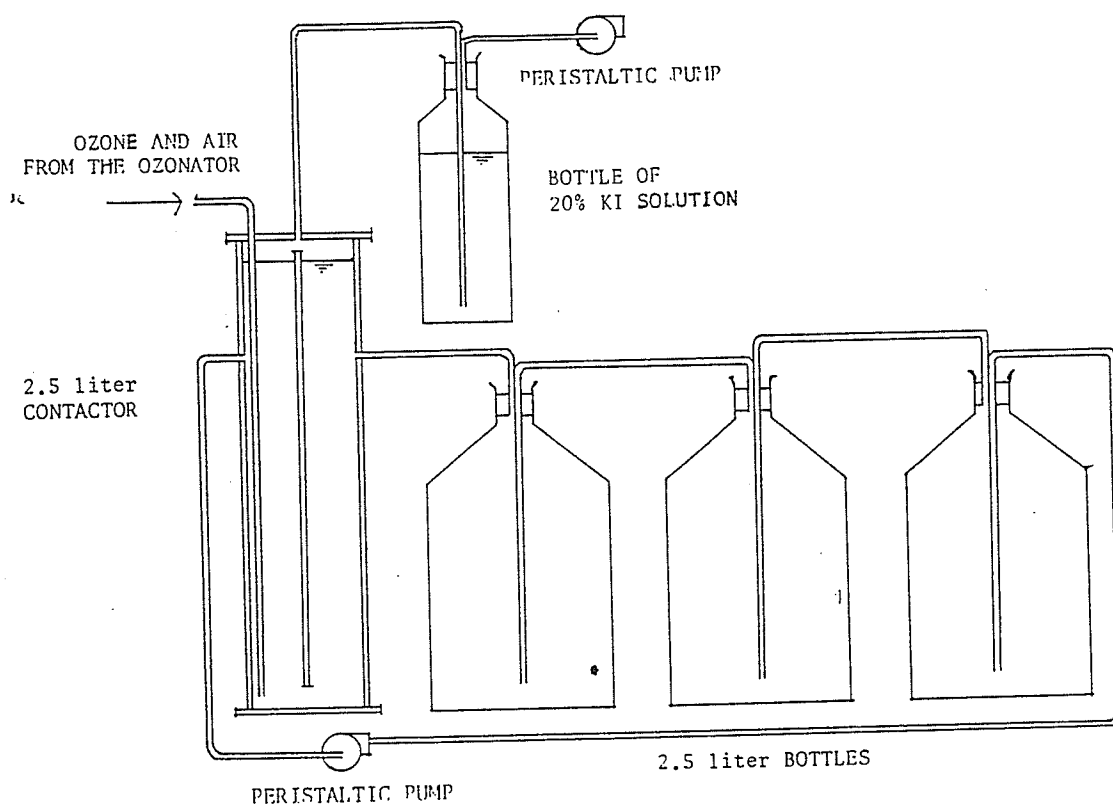


Figure 3.3: Ozonation apparatus: contactor and 2.5 l bottles

GAC filtration. Sand filtered effluent was pumped into the GAC filter column at a specific rate. The overflow rate was controlled by drawing the effluent from the outlet so that the water level in the column was constant. The column was identically to the sand filter column. The GAC media (American Norit Company, Inc.) used had properties and specification as shown at Table 3.1 and Table 3.2.

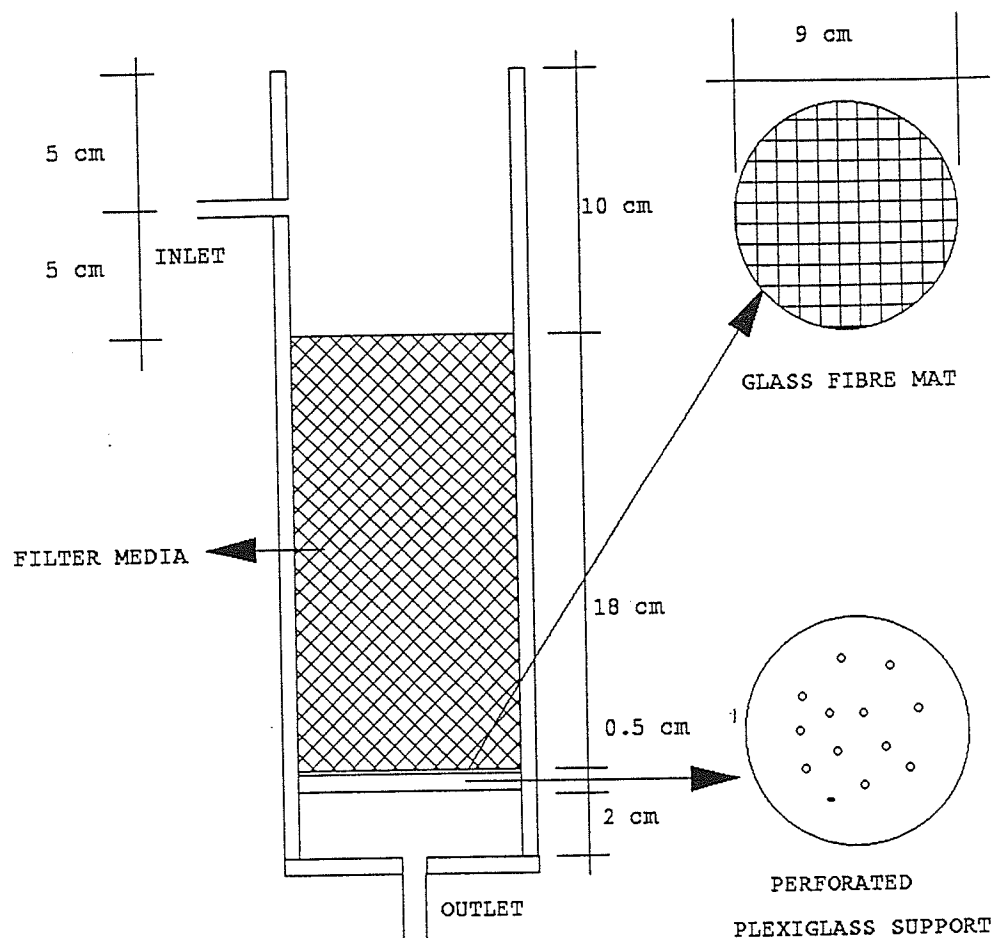


Figure 3.4: Filter (sand and GAC) columns

TABLE 3.1

GAC MEDIA PROPERTIES

Property	Quantity
Total surface area (N ₂ BET method) m ² /g	625
Iodine number	600
Bed density, backwashed and drained (g/ml)	0.39
Particle density - wetted in water (g/ml)	1.4
Total pore volume (ml/g)	1.0
Apparent density, vibrating feed (g/ml)	0.39
Mollases number	350
Mean pore radius (nm)	2.9
Tannin Value (ppm max.)	280
Voids in packed bed %	50

TABLE 3.2

GAC MEDIA SPECIFICATION

Sieve analysis (U.S. Sieve Series)	
Larger than #8 - Max. %	8
Smaller than #30 - Max. %	5
Iodine number - Min	500
Moisture content, %	8
Abrasion % Retention - Min. (Stirring Abrasion Test)	70
Effective Size (mm)	0.8-1.0
Uniformity Coefficient (Max.)	1.9

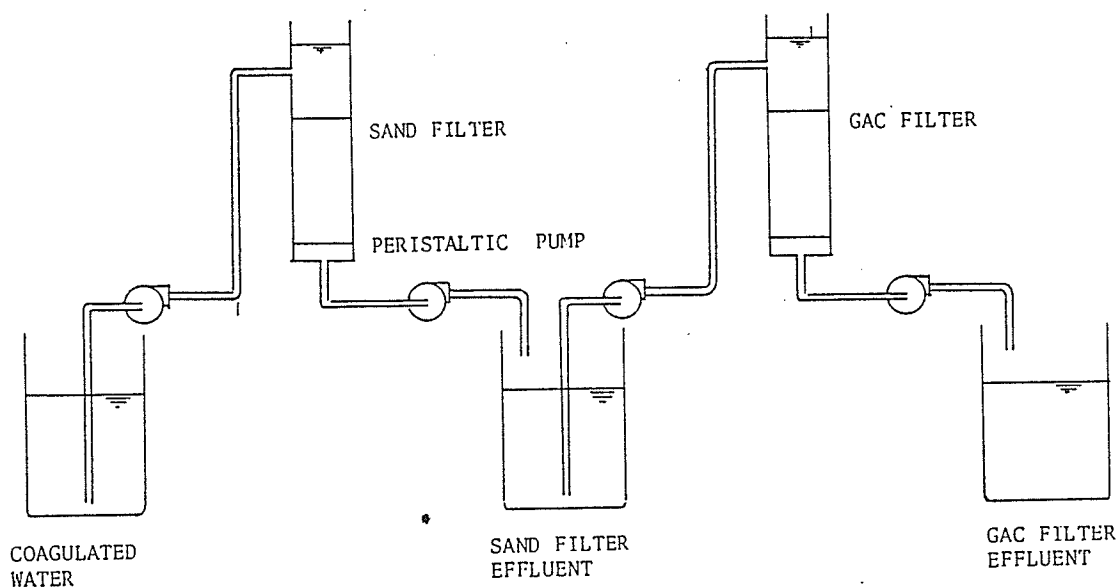


Figure 3.5: Filtration

Preliminary Experiment.

This experiment was conducted to determine the optimum oxidant and coagulant dosages and the optimum GAC EBCT. Other controlled parameters were chosen arbitrarily. These all parameters were then used in subsequent experiments.

The oxidation time was set at 1 hour, with a consideration that in practice this detention time could be easily provided by rearranging the existing plant compartments. A detention time of 20 seconds was selected for flash mixing. This time was similar to that required for raw water flowing from time required by water flowing from the coagulant introduction the point of coagulant application to the inlet of sand filters in the existing treatment plant. An overflow rate of 90 liter/m²/minute, was approximately half the overflow rate of the existing treatment plant. A lower overflow rate was selected to improve water quality.

Coagulant. Three different coagulants were examined: aluminum sulfate, Aluminex3 and Nalcolyte (Alchem, Inc.). Aluminex3 is a coagulant mixture which contains aluminum chloride and cationic polymer. Nalcolyte is a cationic polymeric coagulant.

A jar test procedure was employed to select the most effective coagulant. Various doses of coagulants were introduced into 1.5 liters of raw water, then, flash mixed for 20 seconds. The water was filtered through the sand filter with

an overflow rate of 90 liter/m²/minute. The first 1 liter of effluent was discarded prior to taking sample for TOC testing. The first test run used raw water taken on 15 May 1990 and utilized aluminum sulfate and Aluminex3. The second run used raw water dated 14 June 1990 and aluminum sulfate and Nalcolyte.

Adsorption time. Time for GAC adsorption was measured as Empty Bed Contact Time (EBCT). The longer the EBCT, the more organics are adsorbed onto the GAC bed. However, after a long EBCT, the addition of organics adsorbed onto GAC per unit time will be very small. The following procedure was used to select the appropriate EBCT of the GAC filter column.

Three and a half liters of the sand filtered water was passed through the GAC filter column with 2 minutes EBCT. The first 1 liter of effluent was discarded and the remainder (2.5 l) was used for sampling and refiltration. The GAC effluent was then filtered in succession at 2 minutes EBCT intervals so that water samples of 0, 2, 4, 6, 8, and 10 minutes EBCT could be obtained. The TOC level of these samples were then measured.

Oxidant. Two oxidants, potassium permanganate and ozone, were used in the preliminary experiment. These two oxidants were considered easily applied in water treatment plants. The following procedure was used to select the optimum doses.

Ten liters of raw water was flash mixed in (2 l) beakers. Five liters of the water was spiked with 1.5 mg/l potassium permanganate and five liters water was spiked with 2.0 mg/l of the same oxidant. Following 1 hour of mixing, the permanganated water was dosed with 1 mg/l of (Nalcolyte) cationic polymeric coagulant and passed through a sandfilter with an overflow rate of 90 liters/m²/minute. The first 1.5 liters of the sand filtered effluent was discarded. The following 2.5 liters of the sand filtered was passed through the GAC filter. The last one liter sand filter effluent was collected for testing. The first 1.5 liters of the GAC filtered effluent was discarded, and the last one liter GAC filtered effluent was collected for testing.

Twenty liters of water was prepared using the ozone contacting apparatus (Figure 3.3). The apparatus consisted of a 2.5 liter contactor that was connected to seven 2.5 liter bottles in series. Ozone was bubbled into the reactor. The recycled water flow rate was established at 3 liters/minute. When 14 mg of ozone had been introduced into 20 liters of water (equivalent to dose of 0.7 mg/l), two bottles with a total of 5 liters water were disconnected from the arrangement. When an additional 19.5 mg of ozone (equivalent to additional dose of 1.3 mg/l) had been introduced into the remaining 15 liters of water, two more bottles were disconnected. This procedure was repeated until ozonated waters concentration of 0.7, 2.0, 5.0, and 10.0 mg/l were

obtained. These ozonated water were then filtered through the sand and GAC columns under the similar condition to the permanganated waters.

Conclusion It was concluded from the result of the preliminary experiment (see Chapter IV and V) that the optimum dosages and permanaganate and ozone were 1.5 and 2.0 mg/l, respectively. The optimum coagulant was a cationic polymer (Nalcolyte) at the dosage of 1.0 mg/l. These parameters were used in the design of the treatment evaluation experiment. As summary of the optimum design control parameters are shown in Table 3.3.

TABLE 3.3
OPTIMUM DESIGN CONTROL PARAMETERS

Process	Parameter	Quantity
Oxidation	Detention time	1 hour
	Ozone dose	2 mg/l
	Potassium permanganate	1.5 mg/l
Coagulation	Flash mixing	20 seconds
	Overflow rate	90 l/m ² /min
	Cat. polymer	1 mg/l
Adsorption	EBCT	10 min

Treatment Evaluation (TE) Experiment

The TE experiment was designed to evaluate the efficiency of each process in terms of TOC and color removal. Nine test runs were conducted over a two month period. Table 3.4 outlines the design and test parameters used during the experiment. The experiment was conducted at room temperature (20 - 25 °C) condition.

Two treatment trains were used in the experiment. Permanganated water was coagulated and passed through a treatment train consisting a sand and a GAC filter columns. Ozonated and unoxidized raw water were also coagulated and passed through the second treatment trains.

Twenty liters of raw water was oxidized using potassium permanganate (10 liters) and ozone (10 liters) and passed through each treatment train. An additional ten liters of unoxidated raw water underwent coagulation, sandfiltration and, GAC filtration.

Of the ten liters of water, the first 4 liters of sand filter effluent was discarded, the following 5 liters of effluent underwent GAC filtration and the final 1 liter of effluent was taken for examination. Of the 5 liter GAC filter effluent, the first 4 liters of effluent was discarded and the final 1 liter of effluent was taken as samples.

TABLE 3.4
DESIGN AND TEST PARAMETERS

Process	Control parameters	Measured parameters
Oxidation	det. time = 1 hour	
Permanganate	dose = 1.5 mg/l	
Ozone	dose = 2.0 mg/l	ozone dissipated
Coagulation	det. time = 20 seconds	
C.Polymer (Nalcolyte)	dose = 1 mg/l	
Sandfiltration	flow rate = 90 l/m ² /min	turbidity; color;
GAC filtration	EBCT = 10 min	TOC; alkalinity;
		pH; hardness;
		manganese.

At the end of this procedure, 8 samples of water would be collected. These were raw, finished water of Rosenort water treatment plant, control sand, control GAC, permanganated sand, permanganated GAC, ozonated sand and ozonated GAC filtered effluent. Sample examination was on the following day.

TCM Formation Experiment

Samples of the last two test runs of the TE experiment were collected and analyzed to determine the potential for TCM formation after each unit process. The results were used to determine the effect of each treatment process on the removal of precursors and to develop a model to predict THM level in Rosenort under warm (summer) temperature condition.

Two liter samples were collected after each treatment process. One liter of sample was collected for the TE experiment and one liter of sample was collected for the TCM formation experiment.

The TCM samples were buffered, spiked with chlorine and stored in an incubator at 30 °C. The TCM sample was buffered with borate buffer and adjusted to a pH of 8.2 by the addition of either sodium hydroxide or hydrochloric acid. The adjusted samples were transferred into three 300 ml BOD bottles and then spiked with sodium hypochlorite solution (equivalent of 3 mg Cl_2 per 1 mg TOC). Stoppers were placed with no air bubble inside the bottles. Finally the bottles were incubated for 1, 3, and 7 days.

The incubated water samples were transferred into two 40 ml amber glass vials which contained sodium thiosulfate granules. These vials were closed with screw caps and teflon septa and then were sent to W. M. Ward Technical Service Laboratory for TCM testing. The remaining water samples were analyzed for pH and chlorine residual.

In this work, the 1 day TCM level is referred to as the Simulation Distribution System TCM (SDSTCM). The 3 day TCM is referred to as the 3d-TCM. The 7 day TCM is referred to as the TCM Formation Potential (TCMFP).

To predict the THM level in Rosenort water, the TCM level was assumed to be 80% of the THM level.

3.3 ANALYTICAL TECHNIQUES

Most analytical techniques used were analytical techniques described in Standard Methods (Clesceri et al., 1990). Some techniques were modified to fit with the reagents available in the laboratory.

pH. The sample pH was determined by Glass Electrode Method described in Standard Methods (Clesceri et al., 1990). A pH meter model PHM 29b were used in this experiment. Prior to pH determination, the pH meter was calibrated with 3 buffer solutions of pH 4, 7, and 10. The solutions were prepared by Canlab.

The sample of 50 ml was measured in a porcelain casserole. During measurement a magnetic stirrer was used to agitated the sample.

Alkalinity. The sample alkalinity was determined by Titration Method described in Standard Methods (Clesceri et al., 1990). After pH determination, the sample was titrated with sulfuric acid solution 0.02 N. The titration end point was determined at pH 4.5. The solution was prepared by diluting a certified sulfuric acid solution of 10 N from Fisher Scientific Company.

Total and Calcium Hardness. The sample hardness was determined by EDTA Titrimetric Method described in Standard Methods (Clesceri et al., 1990). A certified sodium (di) ethylenediamine tetraacetate solution of 1 mg CaCO_3/ml was

prepared by Fisher Scientific Company. The solution and the related indicators and buffers were checked previously to Ca and Mg standards. The sample of 25 ml in a porcelain casserole was agitated with a magnetic stirrer during titration.

Hardness indicator and buffer from Betz Inc. were used to measure total hardness. With those reagents the sample color was wine red and it would turn blue as drops of EDTA solution was introduced. The end point was reached when an additional drop did not increase the color intensity.

For the calcium hardness test, sodium hydroxide was added to the sample to raise the pH to 11. Calcium indicator from Betz Inc. was used in this measurement. With those reagents the sample color was pink and would turn to violet if the end point was almost reached. The end point was when the additional drop did not increase the color intensity.

Turbidity. The sample turbidity was measured by the Nephelometric Method as described in Standard Methods (Clesceri et al., 1990). Turbidimeter model DRT 15B manufactured by H.F. Instrument Ltd. was used in this experiment.

Color. The sample color was measured by Visual Comparison Methods as described in Standard Methods (Clesceri et al., 1990). A Hellige Aqua Tester manufactured by Hellige Inc. was used in this experiment.

Total Organic Carbon (TOC). The sample TOC (non purgable portion or NPOC) was measured by the Persulfate Ultraviolet Oxidation Method as described in Standard Method. An oxidation reactor Dohrmann Carbon Analyzer from Xertex Corporation and a gas analyzer model PIR 2000 from Horiba Instrument Inc. were used in this experiment. A potassium hydrogen phthalate standard solution of 10 mg TOC/l was prepared weekly by diluting standard solution of 2000 mg/l.

Dissolved Organic Carbon (DOC). The sample DOC was measured similarly to the sample TOC after the sample underwent a membrane filtration. A METRICEL™ DM-450 filter with a pore size of 0.45 μm from Gelman Instrument Company was used for this experiment after being washed. The pore size of 0.45 μm provides an operational definition of dissolved organic matter.

Manganese. The sample manganese was measured by a modified method of Persulfate Method as described in Standard Methods (Clesceri et al., 1990). The sample was previously concentrated ten times to enable permanganate color develop. The color intensity was measured using a Hach Kit comparator.

Chapter IV

EXPERIMENTAL RESULTS

4.1 PRELIMINARY EXPERIMENT

Characteristics of Rosenort's water raw water were determined and are presented in Table 4.1. During the period from May 24 to August 29, 1990 the color increased with time. The turbidity ranged from 8 to 40 NTU and the TOC ranged from 6.1 to 14.7 mg/l.

(a) Coagulant

Raw water samples collected from May 24 to June 14, 1990 were treated by coagulation followed by direct sand filtration. Table 4.2 shows that optimum doses of aluminum sulfate (alum) and aluminex3 were 60 and 50 mg/l, respectively. The influent TOC after direct filtration was reduced from 14.7 to 5.54 and 6.6 mg/l, respectively. In comparison, Table 4.3 shows optimum removal of TOC using a cationic polymer is 1 mg/l. This removal would be similar to an alum dosage of 40 mg/l.

(b) EBCT

To determine the optimum EBCT, raw water with a TOC of 10.32 mg/l was coagulated using a cationic polymer (1 mg/l)

and passed through the sand column. The initial TOC of the sand filtered effluent was 9.9 mg/l. Table 4.4 shows the effluent TOC for various EBCT.

(c) Oxidant

Tests to determine optimum oxidant doses were conducted on raw water samples collected from July 24 to August 29, 1990. The concentration of ozone released from the contactor was measured (Table 4.5). The average lost of ozone range from 14 to 21%.

The concentrations of TOC in the raw water and sand filtered effluent are shown in Table 4.6. A comparison of TOC in finished water of Rosenort and the effluent of the GAC filter is shown in Table 4.7. It is evidence that the TOC removal efficiency is greater in the laboratory GAC filter than in the plant. The results also indicate that oxidation increases the TOC level in both the sand and GAC filtered effluents.

The effect of oxidation on color after GAC and sand filtration is shown in Tables 4.8 and 4.9. The results show that permanganation increased color level while ozonation reduced color.

The increase of ozone concentration (greater than 5 mg/l) had no effect on the removal of color for the sand and GAC filtered effluents. However, it is evidence that excessive

dosage of potassium permanganate is harmful and could also produce unaesthetic water due to accumulation of manganese dioxide. Table 4.10 shows the manganese level in the waters.

Other test parameters are presented in Appendix A.

TABLE 4.1
ROSENORT RAW WATER CHARACTERISTICS

Date	pH	Alkali nity (mg/l)*	Hardness		Turb (NTU)	Color (ACU)	TOC (mg/l)
			Total (mg/l)*	Calc (mg/l)*			
24/05	8.8	160	120	80	8	40	14.70
14/07	8.2	124	148	88	16	40	8.24
10/07	8.4	130	160	100	40	50	18.97
24/07	8.6	138	168	104	25	60	6.10
14/08	8.2	230	240	128	40	60	10.26
22/08	8.2	184	250	140	24	60	10.32
29/08	7.8	184	248	140	24	100	9.38

* as CaCO_3

TABLE 4.2

EFFLUENT TOC OF ALUM AND ALUMINEX3 (24/05)

Dose (mg/l)	TOC effluent (mg/l)	
	Alum	Aluminex3
60	5.54	8.27
50	6.25	6.60
40	6.93	7.00
30	7.72	7.29
20	7.73	7.54
10	8.69	7.22
0	7.88	7.83

TABLE 4.3

EFFLUENT TOC OF ALUM AND NALCOLYTE (14/06)

Dose (mg/l)	TOC effluent (mg/l)	
	Alum	Nalcolyte
40	5.61	
30	6.39	
20	7.91	
10	7.28	
2.0		10.76
1.0		5.86
0.5		6.10

TABLE 4.4

EBCT EFFECT ON EFFLUENT TOC

EBCT (min)	TOC (mg/l)
0	9.9
2	3.24
4	2.78
6	2.27
8	2.28
10	2.34

TABLE 4.5

OZONE RELEASED FROM THE CONTACTOR (mg/l)

Date	Ozone introduced (mg/l)			
	0.7	2.0	5.0	10.0
24/07	0.1	0.6	0.9	2.5
14/08	0.1	0.5	1.6	1.8
22/08	0.1	0.3	1.0	1.2
29/08	0.1	0.3	0.9	2.2
avg (%)	14	21	22	19

TABLE 4.6

RAW AND SAND FILTERED EFFLUENT TOC (mg/l)

Date	Raw	Unoxi dized	Sand filtered effluents KMnO ₄ (mg/l)		Ozone (mg/l)			
			1.0	1.5	0.7	2.0	5.0	10.0
24/07	7.0	6.9	8.3	7.7	6.9	8.0	8.1	7.4
14/08	10.3	9.3	9.4	9.9	9.8	9.9	9.7	9.8
22/08	10.3	9.9	10.5	10.3	10.1	10.6	10.1	10.4
29/08	9.4	8.9	9.1	9.2	9.2	9.9	9.1	9.3

TABLE 4.7

FINISHED AND GAC FILTERED EFFLUENT TOC (mg/l)

Date	Fin	Unoxi dized	GAC filtered effluents KMnO ₄ (mg/l)		Ozone (mg/l)			
			1.0	1.5	0.7	2.0	5.0	10.0
24/07	5.9	2.5	2.8	2.8	2.4	2.2	2.7	2.6
14/08	9.5	2.1	2.7	3.2	2.7	2.6	2.7	2.6
22/08	9.9	2.3	3.4	3.4	2.8	2.7	3.0	3.2
29/08	8.3	2.4	3.0	3.2	2.5	2.8	3.0	3.1

TABLE 4.8

RAW AND SAND FILTERED EFFLUENT TCU

Date	Raw	Sand filtered effluents						
		Unoxi dized	KMnO ₄ (mg/l)		Ozone (mg/l)			
			1.0	1.5	0.7	2.0	5.0	10.0
24/07	60	15	20	25	15	8	5	5
14/08	60	20	20	30	15	10	5	5
22/08	60	25	30	35	15	15	5	5
29/08	100	20	15	20	15	10	5	5

TABLE 4.9

FINISHED AND GAC FILTERED EFFLUENT TCU

Date	Fin	GAC filtered effluents						
		Unoxi dized	KMnO ₄ (mg/l)		Ozone (mg/l)			
			1.0	1.5	0.7	2.0	5.0	10.0
24/07	5	5	10	15	5	<5	<5	<5
14/08	5	10	10	10	5	<5	<5	<5
22/08	15	10	15	15	10	5	<5	<5
29/08	10	8	5	5	5	5	<5	<5

TABLE 4.10

MANGANESE LEVEL (µg/l)

Date	Raw	Fin	Sandfiltered				GAC filtered			
			Unox idized	KMnO ₄ 1.0	Ozone 1.5	0.7	Unox idized	KMnO ₄ 1.0	Ozone 1.5	0.7
24/07	ud	ud	ud	50	--	ud	ud	80	--	20
14/08	100	ud	ud	ud	ud	ud	50	50	70	50
22/08	70	30	30	90	140	20	50	80	110	50
29/08	90	ud	70	40	50	30	50	30	30	40

ud : undetectable

4.2 TREATMENT EVALUATION EXPERIMENT

The TE experiment was conducted over a two month period during fall 1990. Table 4.11 shows the TOC in the raw, finished, the laboratory filtered effluents.

Plant and laboratory test results for color, turbidity, pH, alkalinity, total and Calcium hardness, and manganese are presented in Tables 4.13, 4.14, 4.15, 4.16, 4.17, and 4.18.

Other test parameters and adsorption isotherms are presented in Appendix B.

TABLE 4.11
PLANT AND LABORATORY TOC (mg/l)

Date	Plant Treatment		Laboratory treatment					
	Raw	Finis	Unoxidized Sandf	GACfi	Permanganate Sandf	GACfi	Ozonated Sandf	GACfi
06/09	10.72	9.60	9.46	2.55	9.33	2.11	9.64	2.42
17/09	9.26	10.02	9.10	1.60	8.96	1.02	8.81	1.62
25/09	10.14	9.05	9.15	1.10	8.91	1.01	9.35	1.01
01/10	9.37	8.67	8.61	0.84	8.29	1.04	8.90	1.22
05/10	14.10	9.82	9.13	0.75	8.70	0.71	8.81	0.77
10/10	11.07	9.16	10.26	1.16	10.00	1.16	10.80	1.27
15/10	11.76	11.16	11.20	1.56	11.31	1.28	11.01	1.72
22/10	11.31	10.48	10.75	1.05	10.52	0.77	10.97	0.98
05/11	10.95	8.63	10.51	1.29	10.63	0.81	10.38	1.42
avg(%)	100	89	91	12	89	10	91	13

TABLE 4.12
PLANT AND LABORATORY COLOR (TCU)

Date	Plant Treatment		Laboratory treatment					
	Raw	Finis	Unoxidized		Permanganate		Ozonated	
			Sandf	GACfi	Sandf	GACfi	Sandf	GACfi
06/09	25	10	20	5	35	10	10	<5
17/09	20	8	15	<5	30	5	10	<5
25/09	35	8	15	5	25	5	10	<5
01/10	20	8	15	5	20	10	5	<5
05/10	20	<5	15	<5	20	5	5	<5
10/10	20	10	15	<5	20	15	10	<5
15/10	25	10	15	<5	30	20	10	<5
22/10	20	5	15	5	20	15	10	<5
05/11	15	5	15	<5	50	40	10	<5

TABLE 4.13
PLANT AND LABORATORY TURBIDITY (NTU)

Date	Plant Treatment		Laboratory treatment					
	Raw	Finis	Unoxidized		Permanganate		Ozonated	
			Sandf	GACfi	Sandf	GACfi	Sandf	GACfi
06/09	24.0	2.6	2.3	1.3	2.5	1.8	1.3	1.0
17/09	18.0	1.2	1.6	1.2	3.4	1.4	1.6	1.2
25/09	8.0	0.8	1.5	1.3	2.1	1.2	0.9	0.8
01/10	20.0	0.7	1.3	1.2	2.0	1.4	0.6	0.7
05/10	8.0	0.4	0.9	0.8	1.3	1.0	0.6	0.6
10/10	9.0	0.9	1.4	1.2	2.6	1.6	0.9	0.9
15/10								
22/10			turbidimeter out of order					
05/11								

TABLE 4.14
PLANT AND LABORATORY pH

Date	Plant Treatment		Laboratory treatment					
	Raw	Finis	Unoxidized		Permanganate		Ozonated	
			Sandf	GACfi	Sandf	GACfi	Sandf	GACfi
06/09	8.1	7.8	7.7	4.5	7.7	5.3	8.0	5.7
17/09	8.1	8.0	8.1	6.4	8.1	5.4	8.0	5.8
25/09	8.2	8.0	8.2	7.0	8.2	6.4	8.2	6.7
01/10	8.5	7.8	8.5	7.4	8.5	6.6	8.4	7.2
05/10	8.5	8.3	8.4	7.4	8.5	7.0	8.4	7.2
10/10	8.2	8.2	8.0	7.5	8.3	7.0	8.2	7.2
15/10	8.1	8.1	8.2	7.5	8.2	7.0	8.2	7.2
22/10	8.2	8.2	8.3	7.6	8.3	7.0	8.2	7.3
05/11	8.2	8.2	8.2	7.7	8.2	7.0	8.2	7.4

TABLE 4.15
PLANT AND LABORATORY ALKALINITY (mg CaCO₃/l)

Date	Plant Treatment		Laboratory treatment					
	Raw	Finis	Unoxidized		Permanganate		Ozonated	
			Sandf	GACfi	Sandf	GACfi	Sandf	GACfi
06/09	188	188	182	0	182	8	188	30
17/09	194	182	190	106	194	6	192	30
25/09	186	190	190	156	194	24	188	90
01/10	192	195	192	172	194	118	196	154
05/10	192	192	196	180	194	120	200	170
10/10	200	200	198	186	200	150	202	170
15/10	204	204	204	194	204	168	202	180
22/10	204	206	208	192	208	170	198	190
05/11	200	202	202	196	202	170	200	182

TABLE 4.16

PLANT AND LABORATORY TOTAL HARDNESS (mg CaCO₃/l)

Date	Plant		Laboratory treatment					
	Treatment Raw	Finis	Unoxidized		Permanganate		Ozonated	
			Sandf	GACfi	Sandf	GACfi	Sandf	GACfi
06/09	252	244	252	216	248	204	248	220
17/09	260	260	260	228	260	212	260	208
25/09	256	256	252	236	252	208	260	208
01/10	260	260	264	240	264	240	260	240
05/10	256	260	256	256	260	240	260	240
10/10	280	260	272	260	272	256	280	264
15/10	284	284	292	276	296	256	292	280
22/10	292	292	292	272	292	276	292	272
05/11	300	300	292	300	288	280	292	280

TABLE 4.17

PLANT AND LABORATORY CALCIUM HARDNESS (mg CaCO₃/l)

Date	Plant		Laboratory treatment					
	Treatment Raw	Finis	Unoxidized		Permanganate		Ozonated	
			Sandf	GACfi	Sandf	GACfi	Sandf	GACfi
06/09	144	144	152	116	146	120	144	120
17/09	160	148	160	140	160	140	160	120
25/09	160	152	160	148	160	120	160	136
01/10	156	156	160	144	160	140	160	140
05/10	152	152	152	148	152	140	156	144
10/10	160	156	164	152	164	144	160	152
15/10	172	164	172	160	168	144	164	160
22/10	172	172	176	160	188	160	180	160
05/11	168	168	168	172	152	152	168	160

TABLE 4.18
PLANT AND LABORATORY MANGANESE ($\mu\text{g/l}$)

Date	Plant		Laboratory treatment					
	Treatment Raw	Finis	Unoxidized Sandf	GACfi	Permanganate Sandf	GACfi	Ozonated Sandf	GACfi
06/09	90	20	30	ud	190	180	ud	10
17/09	90	ud	40	ud	190	ud	60	60
25/09	45	20	40	40	200	140	50	50
01/10	80	ud	50	40	180	150	50	40
05/10	80	ud	40	40	120	100	60	40
10/10	60	ud	40	40	160	150	40	30
15/10	50	30	40	40	220	160	40	40
22/10	40	ud	30	30	200	180	60	40
05/11	50	ud	40	40	230	200	40	40

4.3 TCM FORMATION EXPERIMENT

TCM incubation was conducted twice using samples from the last two experiments of the treatment evaluation experiment. SDSTCM levels of the sand filtered effluent ranged from 283 to 503 $\mu\text{g/l}$, while TCMFP levels ranged from 785 to 1300 $\mu\text{g/l}$ (Tables 4.19 and 4.20).

Other test parameters are presented in Appendix C.

TABLE 4.19

TCM LEVEL ($\mu\text{g/l}$) OF THE SAMPLES 22/10/1990

Sample waters	TOC (mg/l)	DOC (mg/l)	Cl (mg/l)	SDSTCM 3d-TCM	TCMFP	Cl res. 1d 3d 7d		
raw	11.31	10.50	30		845			9
finished	10.48	9.85	30		835			9
control sandf.	10.75	10.34	30	480	1100	20		6
permang sandf.	10.52	9.99	30	460	1300	23		4
ozonate sandf.	10.97	10.34	30	495	1150	18		9
control gacfi.	1.05	1.01	5	17	52	4		4
permang gacfi.	0.77	0.73	5	10	39	4		4
ozonzte gacfi.	0.98	1.02	5	9	33	4		4

TABLE 4.20

TCM LEVEL ($\mu\text{g/l}$) OF THE SAMPLES 15/11/1990

Sample waters	TOC (mg/l)	DOC (mg/l)	Cl (mg/l)	SDSTCM 3d-TCM	TCMFP	Cl res. 1d 3d 7d
raw	10.95	10.38	31	460	630 1135	16 10 3
finished	8.63	8.42	25	283	435 785	12 12 6
control sandf.	10.51	10.34	31	458	715 1080	16 12 5
permang sandf.	10.63	9.78	30	503	628 1158	16 9 2
ozonate sandf.	10.38	10.40	30	438	555 1100	18 14 7
control gacfi.	1.96	1.82	6	13	24 42	5 4 3
permang gacfi.	1.61	1.47	6	15	26 55	5 4 3
ozonzte gacfi.	1.57	1.81	6	12	22 48	5 4 3

Chapter V

DISCUSSION OF EXPERIMENTAL RESULTS

5.1 PRELIMINARY EXPERIMENT

The objective of this experiment was to determine the optimum oxidant and coagulant dosages and the GAC EBCT. Other design parameters such as oxidation time, flash mixing detention time, and sand filtration rate were based on other studies.

(a) Coagulant and Coagulant Dose

The optimum doses of aluminum sulfate and Aluminex3 to achieve maximum TOC and color removals were at 60 and 50 mg/l, respectively. Since direct filtration does not employ sedimentation, the dose of aluminum sulfate should be limited to avoid aluminum breakthrough in the effluent. Direct filtration usually uses a maximum of 20 mg/l aluminum sulfate (Cleasby, 1990). The cationic polymer was the coagulant selected in the TE experiment at a concentration of 1 mg/l. This dose was able to substitute an alum dose of 40 mg/l.

(b) Oxidant Doses

Tables 4.6 and 4.7 show that oxidation increased the TOC both in the sand and GAC filter effluents. This can be interpreted that oxidation converted organics into less coagulable and less adsorbable organics. The oxidation might be chopping moieties from their main molecules. These moieties were uncoagulable and flowed through the sand filter. The oxidation might also convert small molecules to more hydrophilic molecules that are less adsorbable.

Tables 4.8 and 4.9 show that permanganation increased color, but ozonation decreased color. Color present in the permanganated effluent should be interpreted as the presence of permanganate and manganese dioxide rather than organics. Color removed from the ozonated effluent may be interpreted as a result of the conversion of humic substances to other substances. Reduction of color from the effluents expectedly indicates the reduction of precursors.

The dose of permanganate was chosen 1.5 mg/l because this was the highest dose that was expected give an acceptable manganese level in the effluents. Many reports concluded that the greater precursor removal can be achieved with the increased permanganate (Singer et al., 1980; Colthurst and Singer, 1982; Gifford et al., 1989).

The dose of ozone was chosen 2 mg/l because this was the level that produced the lowest TOC in the effluents. In

addition this dose achieved the same color removal as did ozone at higher doses.

(c) EBCT

As shown in figure 5.1, the EBCT of 4 minutes was adequate to adsorb organics maximally, because a longer time did not remove additional organics. However, a longer EBCT might be required because the top part of the carbon filter would be soon exhausted. This experiment, then, used an EBCT of 10 minutes. In practice, this EBCT is usually used.

(d) Other test parameters

Oxidation. Two oxidants were used in this experiment, potassium permanganate and ozone. Permanganate reacts with natural water slowly. Data from the study conducted by Spicher and Skrinde (1963) shows that the amount of permanganate that reacts with natural water in 1 hour at pH 7.5-8.5 and temperature 25 °C is about 70 % of that reacts in 5 hours. By assuming the data are applicable for Rosenort water, 1 hour oxidation time is adequate because a longer time will not give a significant additional oxidation. That oxidation time may be provided by rearranging the existing plant compartments.

In the case of ozone, oxidation time is almost unimportant because ozone reacts with water impurities instantaneously. In the experiment, 5 l of water was ozonated for about 30 minutes to reach a dose of 2 mg/l.

Flash Mixing. For direct filtration, short flocculation is sometimes provided to enable agglomeration (Cleasby, 1990). This flocculation time varies from 0 to 60 minutes. In the experiment, 20 seconds was selected as flash mixing detention time based on the estimation that the time required for water to move from the point of coagulant introduction to the top layer of sand filter in the plant is 20 seconds.

Sand Filtration Rate. In full scale plants, the rate for direct filtration varies from 40 to 250 l/m²/minute (Cleasby, 1990). Rosenort's treatment plant uses 170 l/m²/minute but, organics removal is almost non existant. In the experiment, 90 l/m²/minute was expected to improve water quality.

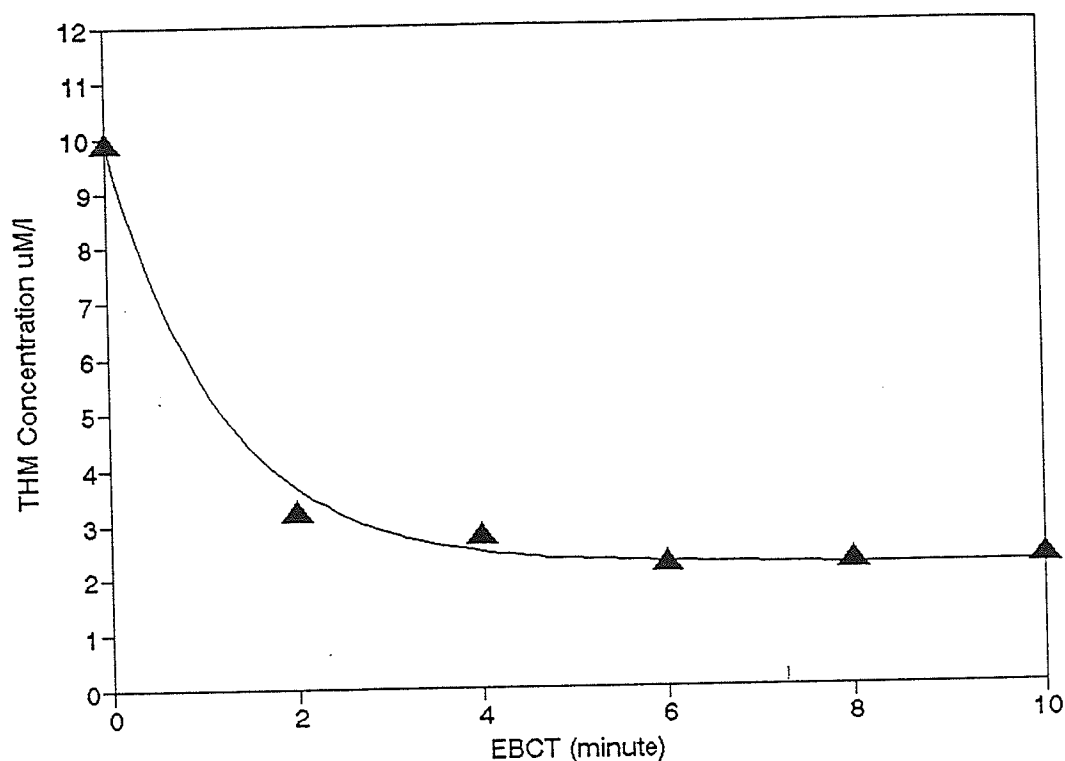


Figure 5.1: Effluent TOC as function of EBCT

5.2 TREATMENT EVALUATION EXPERIMENT

The objective of this experiment is to evaluate the treatment performance in terms of organics (TOC) and color (TCU). Reduction of TOC and TCU were used to indicate the precursors removal from water. Other parameters were discussed to evaluate the effluents quality.

TOC Removal

A plot of TOC versus time for the raw water, coagulated followed by sand filtered water, and GAC filtered water are presented in Figure 5.2. TOC removal was accomplished by

coagulation and adsorption. Coagulation of unoxidized water followed by direct in line sand filtration removed on average 9% of TOC while subsequent GAC filtration removed an additional 79% (Table 4.11). The same treatment processes for permanganated and ozonated waters removed on average 11% and an additional 79%, and on average 9% and an additional 78%, respectively. In conclusion, GAC adsorption is the main process to remove organics from Rosenort's water.

The TOC removal by coagulation appeared very low. However, this reduction is similar to removals in the existing treatment involving coagulation and GAC filtration. This means that the existing GAC filter had been exhausted.

The GAC media at the Rosenort plant was replaced at the end of October 1990. Measurement on 05 November 1990 indicated that the TOC removal was only 20%. If it was assumed that the coagulation efficiency was 9%, the GAC filter was removing only 11%. This is very low for a new GAC. This indicated that the selection of GAC is very important to the success of organics removal.

Color Removal

Color was removed by ozonation, coagulation and adsorption. Coagulation reduced color from average 25 TCU to 15 TCU; by ozonation this color was further reduced to 10 TCU; and GAC adsorption removed color to a level that could not be detected visually. Ozonation might remove precursors by removing color.

In contrast, permanganation increased color. Color in the coagulated water was increased from 15 TCU to average 30 TCU. This color would result from the presence of permanganate rather than humic substances. Because of that, color induced by permanganation can not be used to indicate precursor presence.

Manganese

Coagulation reduced manganese; adsorption did not; and oxidation increased it. Coagulation reduced it in the water to the acceptable level ($<50 \mu\text{g/l}$) although the level in the raw water was usually higher than $50 \mu\text{g/l}$ (Table 4.18). GAC adsorption did not reduce the manganese level. This might indicate that $50 \mu\text{g/l}$ is about the lowest limit a conventional treatment can reduce manganese.

The manganese level was higher in the ozonated sand filter effluent than that in the control sand filter effluent. Ozonation might oxidize manganese in raw water to permanganate that is unfilterable. However, the levels were still about the allowable level.

Permanganation increased the manganese level excessively. Subsequent GAC filtration could not reduced it to an allowable level. Permanganation should not be used as a method to reduced organics or precursors in a direct filtration process due to the potential breakthrough of permanganate in the effluent.

Turbidity

Table 4.13 shows that the processes can remove turbidity to levels around the acceptable level (1 NTU). In contrast, the existing plant removed turbidity to less than 1 NTU. This is maybe caused by the provision of compartments in the existing treatment plant that enables sedimentation.

pH, alkalinity and hardness

The pH and alkalinity of the raw water were always acceptable. This enables the use of aluminum sulfate for coagulation. The pH and alkalinity drops in the GAC effluent (Table 4.14 and Table 4.15) during the first use of GAC were caused by the presence of acidic impurities in the GAC.

Softening maybe required for this water because the hardness level is fairly high (Table 4.16 and Table 4.17). Softening processes to remove hardness may contribute to the THM precursor removal.

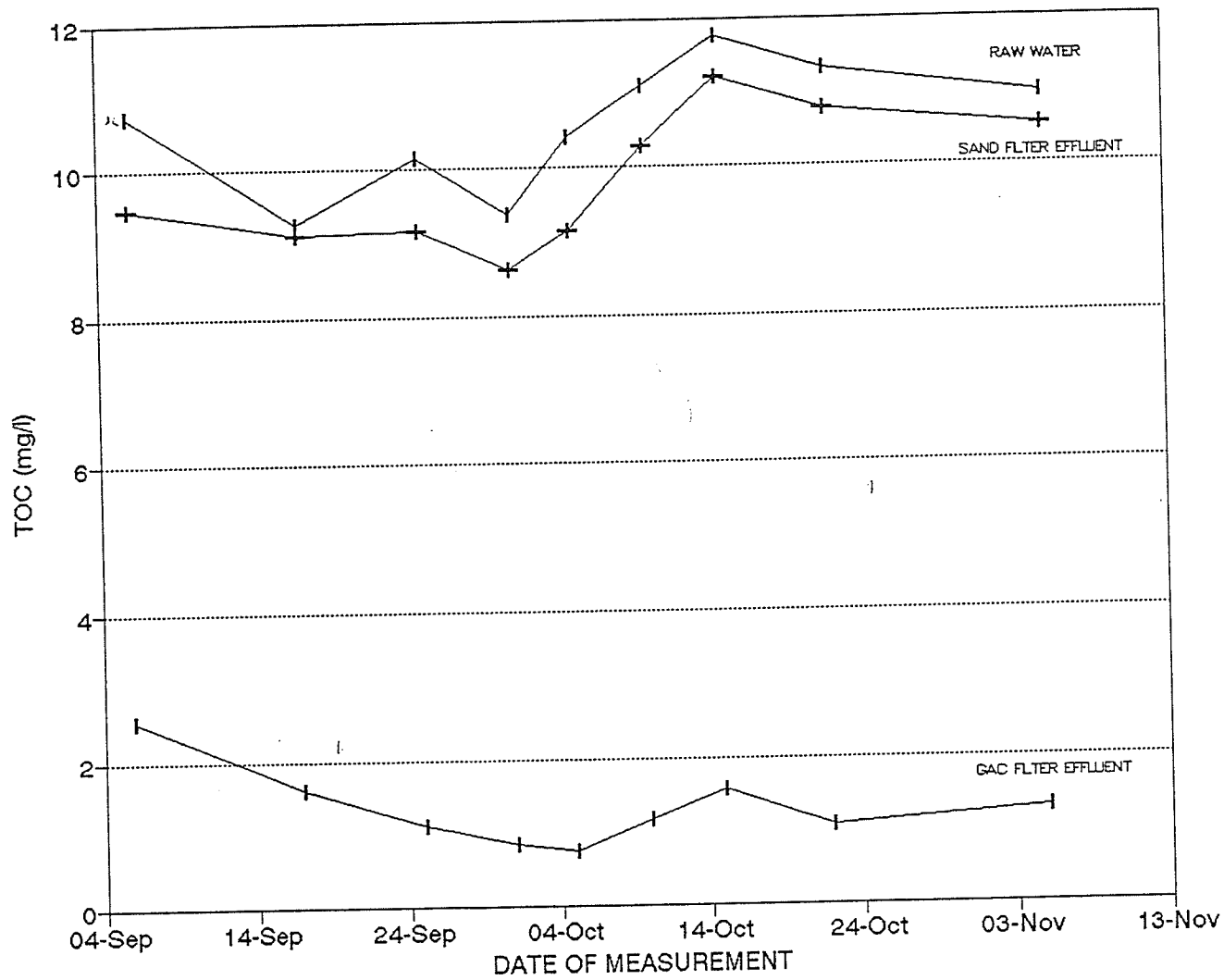


Figure 5.2: TOC Profile

5.3 TRICHLOROMETHANE FORMATION EXPERIMENT

The experiment was directed to determine the THM precursor level, to predict the TTHM level in Rosenort's water under the warmest condition, and to evaluate the effect of preoxidation on formation rate and yield.

Data generating

Some data were generated to complete the data shown in Table 4.19. The complete data are shown in Table 5.1. Data in the bracket were generated by comparing TOC and TCM associated with the data in Table 4.20. For example, TCMFP of raw water of 1347 $\mu\text{g/l}$ was obtained as follows:

$$1135 * (11.31/10.93 + 845/630)/2 = 1347$$

Where 1135 is TCMFP,

10.93 is TOC, and

630 is 3d-TCM of the raw water from Table 4.20.

11.31 is TOC and

845 is 3d-TCM of the raw water from table 4.19.

Table 5.1 and 4.20 were used to determine the treatment effectiveness and to develop kinetic models.

DOC and TOC

DOC was used primarily to estimate the chlorine dose for the incubation step to maintain a certain level of chlorine residual at the end of the incubation. All DOC measurements

show that the DOC levels were very close to the TOC level. Because of this the TOC can replace the DOC for future experiments. Moreover, this indicated that the organics that existed in the water were all soluble and may be difficult to coagulate.

TCM, Color, And TOC

The last two experiments in the TE experiment (22/10 and 15/11/90) showed that control, permanganated, and ozonated sand filter effluents were almost the same although the color level was different. The TCMFP levels were also almost the same. This indicated that TOC could be used to predict precursors, but color could not. Color removal by ozone was not a sign of precursors removal.

Yield and Treatment Effectiveness

The yield was determined by comparing precursor level (TCMFP) and TOC. The results was presented in the Table 5.2. Table 5.2 shows that TCM yields of sand filter effluents are about 1.1% means that of 1 mg TOC of organics will yield 11 μg of carbon in TCM. This yield is about the yield of algal metabolites and or humic acids.

Table 5.2 also shows that precursors level of 1241 $\mu\text{g}/\text{l}$, was reduced by coagulation by 12% to 1090 $\mu\text{g}/\text{l}$. Subsequent GAC filtration was responsible for a further 84% to 47 $\mu\text{g}/\text{l}$.

Oxidation failed to facilitate coagulation. Permanganation increased precursors in the sand filter effluent to 1229 $\mu\text{g/l}$ if compared with control effluent (1090 $\mu\text{g/l}$). The increase of the precursor level amounted to 11%. Similar to permanganation, ozonation increased precursors by 3%.

The main precursors in the Rosenort water may not be humic substances because of three reasons. Firstly, the high TOC level in the raw water, about 11 mg/l, was not parallel with the low color level, about 25 TCU. Humic substances of 4 mg/l TOC may make up color of 100 TCU. Secondly, organics in Rosenort water were not easy to remove by coagulation. Edzwald et al. (1987) reported that more than 40% of TOC and TCMFP in natural water can be expectedly removed by direct sand filtration utilizing a polymeric coagulant. Finally, coagulation of Rosenort water was not facilitated by oxidation. By realizing that the yield is about 1.1% and coagulation could not remove precursors significantly, it is speculated that algal metabolites were the primary organics that composed the precursors.

SDSTCM and TCMFP

SDSTCM was used to estimate the TCM level in Rosenort in the warmest condition. A linear regression was conducted to those data, and a relation between TOC and SDSTCM was determined. Figure 5.3 shows the relation.

A relation between precursor level and TOC also were determined from data of TCMFP. Figure 5.4 shows this relationship.

Figure 5.3 and figure 5.4 show that the data concentrate at TOC levels of 11 mg/l and 1 mg/l for sand and GAC filtered effluents, respectively. Further work should be conducted to fill the TOC levels in between. The TOC levels in between can be interpreted as the TOC levels of GAC filtered effluents when the GAC media are changing from fresh to exhausted.

Order and Rate constant of formation

The reaction order and rate constant were determined from the TCM level at incubation time of 1, 3, and 7 days (see Appendix D). TCM level of 7 days (TCMFP) was used as the precursor level. Using the following equation:

$$dTCM/dt = - dC/dt = k Cl_2 C^n \quad (6)$$

Where TCM is TCM level ($\mu\text{g/l}$)

C is precursor level ($\mu\text{g/l}$)

Cl_2 is chlorine residual (mg/l) and

t is time (day)

it is found that the reaction order, n, varied from 0.97 to 4.43, with the average of 2.6. A reaction order, $n=2.5$, was selected to determine the formation rate constant, k. Table 5.3 lists the reaction orders, n, and rate constant, k, for $n=2.5$. TCM formation equation was constructed as follows:

$$TCM = C_0 - \{ [C_0]^{-1.5} + 1.5 k [Cl_2]_0 t \}^{-0.67} \quad (7)$$

Where TCM is TCM level ($\mu\text{g/l}$)

C_0 is initial precursor level = TCMFP ($\mu\text{g/l}$)

k is rate constant $((\text{mg/l})^{1.5} * \mu\text{g/l} * \text{day})^{-1}$

$[Cl_2]_0$ is chlorine dose (mg/l)

t is reaction time (day)

THM Level Prediction

THM prediction was obtained by developing models. The first model is a linear regression as shown in Figure 5.3. This model is used to estimate the highest THM level in Rosenort drinking water. The highest THM level ever recorded was 379 $\mu\text{g/l}$. If it is assumed that the associated TCM level was 300 $\mu\text{g/l}$ (about 80% of the THM level), using this model, the TOC level would be 7.3 mg/l . This figure seems too low because measurements during summer indicated that the average TOC level was about 11 mg/l . The high chlorine dosage in the laboratory treatment (about 30 mg/l) might cause this model to be unsuitable.

The other model is TCM formation. For an unoxidized sand filtered water, the TCM formation can be described by this following equation:

$$TCM = C_0 - \{ [C_0]^{-1.5} + 1.5 \cdot 1.15\text{E-}6 [Cl_2]_0 t \}^{-0.67} \quad (8)$$

The C_0 (=TCMFP) is estimated using a linear regression as shown in Figure 5.4. Using the equation (8), the TCM level of 300 $\mu\text{g/l}$ is achieved at C_0 of 1078 $\mu\text{g/l}$ (TOC = 10 mg/l), $[\text{Cl}_2]_0 = 10 \text{ mg/l}$, and $t = 1 \text{ day}$. Using this equation again, the TCM level in Rosenort drinking water under the warmest temperature condition is estimated. The TCM level of 80 $\mu\text{g/l}$ is achieved at TCMFP = 600 $\mu\text{g/l}$ (TOC = 6 mg/l).

Formation Rate

The only parameter that could be reduced by oxidation was the formation rate. Table 5.3 shows that the rate constant was reduced by oxidation from $1.15\text{E}-6$ of the unoxidized to $0.53\text{E}-6$ and $0.60\text{E}-6$ ($(\text{mg/l})^{1.5} \cdot \mu\text{g/l} \cdot \text{day})^{-1}$ for permanganated and ozonated sand filter effluents, respectively.

For the Rosenort distribution system, where detention time is short, the constant rate reduction can be significant. The TCMFP of 1078 $\mu\text{g/l}$ (about 10 mg/l TOC) will form TCM of 293, 164, and 181 $\mu\text{g/l}$ for unoxidized, permanganated, and ozonated water, respectively with the chlorine dose of 10 mg/l at 1 day contact time.

TABLE 5.1

COMPLETE TCM LEVEL ($\mu\text{g/l}$) OF THE SAMPLES 22/10/1990

Sample waters	TOC (mg/l)	DOC (mg/l)	Cl (mg/l)	SDSTCM 3d-TCM	TCMFP	Cl res. 1d 3d 7d
raw	11.31	10.50	30	(546)	845 (1347)	(15) 9 (2)
finished	10.48	9.85	30	(443)	835 (1230)	(11) 9 (5)
control sandf.	10.75	10.34	30	480 (736)	1100	20 (14) 6
permang sandf.	10.52	9.99	30	460 (634)	1300	23 (13) 4
ozonate sandf.	10.97	10.34	30	495 (598)	1150	18 (15) 9
control gacfi.	1.05	1.01	5	17 (28)	52	4 (4) 4
permang gacfi.	0.77	0.73	5	10 (16)	39	4 (4) 4
ozonate gacfi.	0.98	1.02	5	9 (15)	33	4 (4) 4

TABLE 5.2

ORGANICS PRODUCTIVITY

sample water	TOC (mg/l)	TCMFP ($\mu\text{g/l}$)	Yield TCMFP-C/TOC
raw	11.13	1241	0.011
finished	9.56	1008	0.011
control sandf	10.87	1090	0.010
permang sandf	10.58	1229	0.012
ozonate sandf	10.68	1125	0.011
control gacfi	1.51	47	0.003
permang gacfi	1.19	47	0.004
ozonate gacfi	1.28	41	0.003

TABLE 5.3
REACTION ORDER AND RATE CONSTANT

Sample waters	Precursors			Chlorine			n	k for n=2.5
	0-d	1-d	3-d	1-d	1-d	3-d		
	(ug/l)				(mg/l)			
raw	1241	738	503	31	16	10	2.00	0.83E-6
finished	1008	645	373	28	12	11	0.97	1.43E-6
control sandf	1090	621	365	31	18	13	1.56	1.15E-6
permang sandf	1229	747	598	30	20	11	3.51	0.53E-6
ozonate sandf	1125	658	548	30	18	15	4.43	0.60E-6
control gacfi	47	32	21	6	4	4	2.16	3.39E-4
permang gacfi	47	34	26	6	4	4	3.34	2.30E-4
ozonate gacfi	41	30	22	6	4	4	2.65	2.96E-4

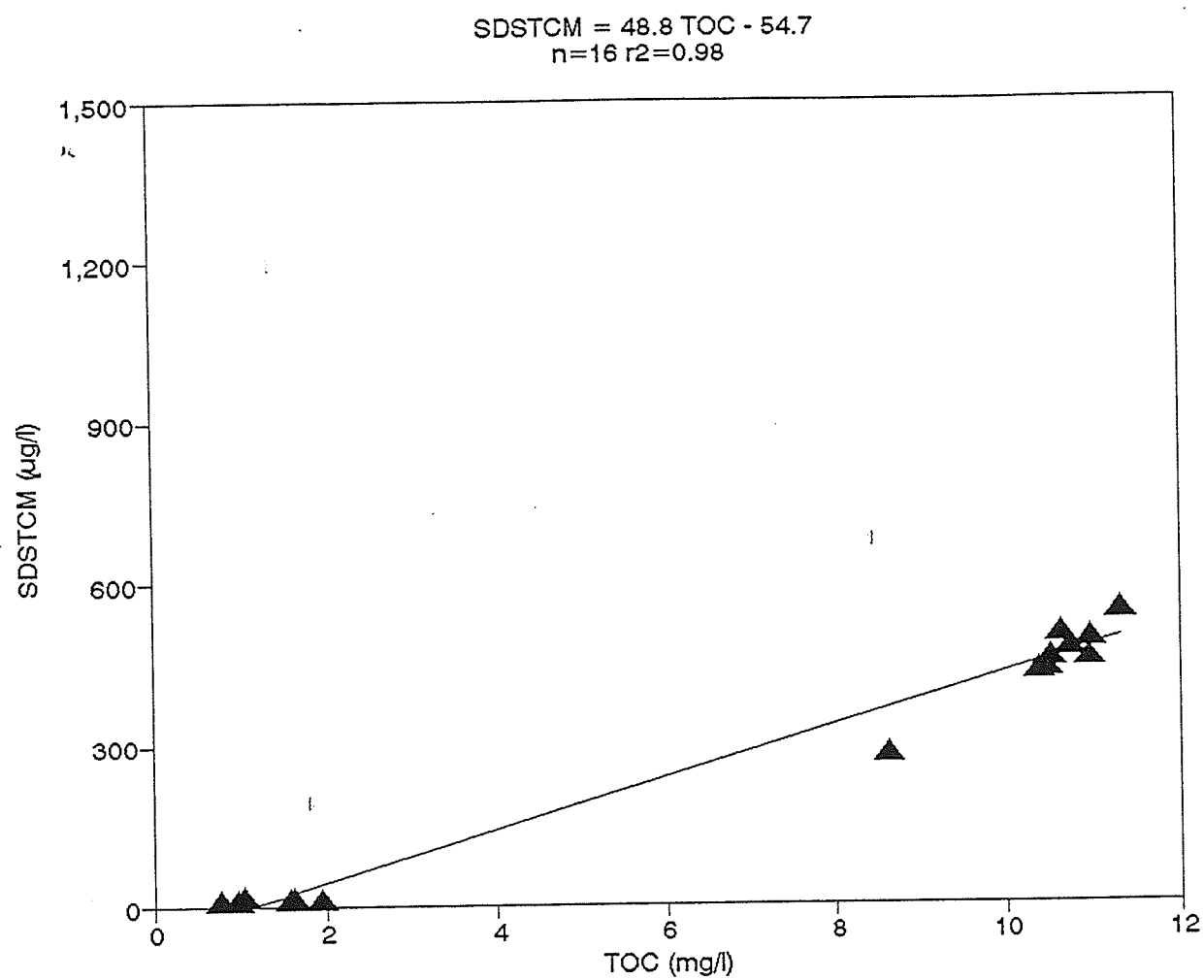


Figure 5.3: SDSTCM as function of TOC

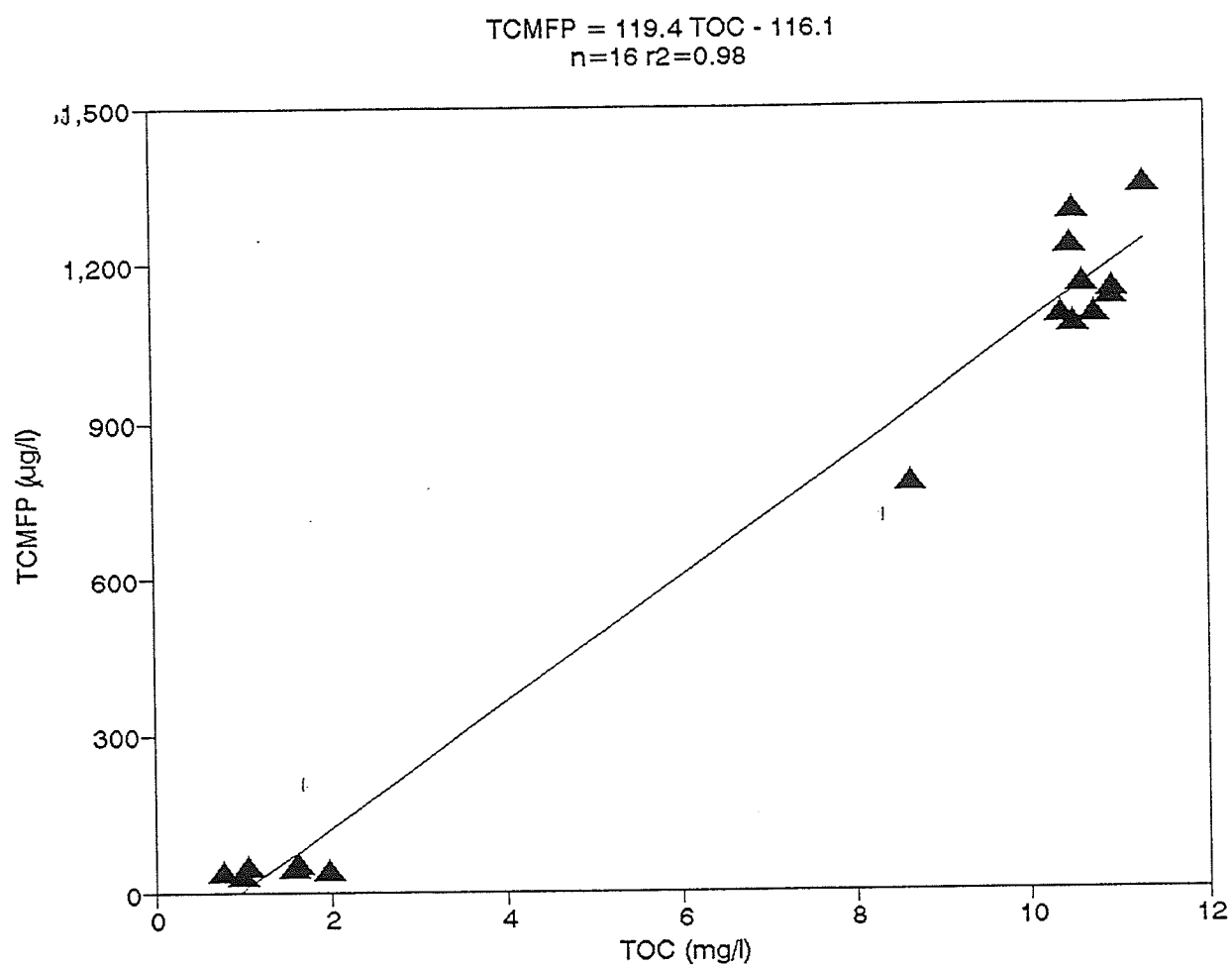


Figure 5.4: TCMFP as function of TOC

Chapter VI

SUMMARY AND CONCLUSIONS

The study was conducted based on a laboratory experiment utilizing treatment trains that were operated using the following parameters: preoxidation detention time 1 hour with ozone dose 2 mg/l or potassium permanganate dose 1.5 mg/l, flash mixing 20 seconds with Nalcolyte coagulant dose 1.0 mg/l, sand filtration overflow rate 90 l/m²/minute and GAC filtration EBCT 10 minutes.

The study leads to the following conclusions:

1. Coagulation followed by direct in line sand filtration removed 9% of the organics in term of TOC and 12% of the precursors in term of TCMFP. Permanganation removed 2% of the organics but increased precursors by 11%. Ozonation did not affect organics removal but increased precursors 3%. Subsequent GAC adsorption reduced another 79% of the organics and 84% of the precursors.
2. Based on the proposed kinetic model, a TOC level of 6 mg/l in unoxidized water will result in a TCM level of 80 µg/l after 1 day contact time with 10 mg/l of chlorine. Using the same parameters, the TCM levels will be 43 and 48 µg/l for permanganated and ozonated water, respectively.

3. Oxidation before coagulation (preoxidation) using ozone or potassium permanganate cannot be applied to remove precursors because of the precursor breakthrough in the sand filtered effluent. In addition, preoxidation using potassium permanganate will cause permanganate breakthrough in the finished water.
4. Algal metabolites are speculated to be the main precursors in Rosenort's water.
5. Oxidation did not alter the TCM yield, however, it did reduce the reaction rate of TCM formation.

Chapter VII

RECOMMENDATIONS AND FUTURE RESEACH

Based on the laboratory and plant investigation the following recommendations are made:

1. Preoxidation should not be used to remove THM precursors in Rosenort water because preoxidation will cause THM precursors less coagulable.
2. The selection of GAC for the Rosenort plant should be conducted carefully because the THM precursor removal primarily relies on the GAC adsorption. Investigation during the study found that the plant's GAC was ineffective after 1 month of utilization.
3. The GAC should be replaced at the beginning of July when THM level increases due to the temperature increase.

Future reseach is suggested to verify the kinetic model for THM formation in Rosenort water. Another reseach project is recommended to evaluate the effects of ozonation of the sand filtered effluent.

Suggested reseach regarding TOC-TCMFP relationship and kinetic model are:

1. Use sand filtered water from the plant with various TOC levels. The various TOC levels can be made from about 2 to 10 mg/l using GAC adsorption in the laboratory.
2. Spike the water with a chlorine dose of 3 times of the TOC level and incubate for 6, 12, 18 hours, 1, 2, 3, 4, 5, 6, and 7 days at the conditions of pH = 8.2 and temperature = 30 °C.
3. Determine the TCM level and chlorine residual.
4. Determine the TOC-TCMFP relationship.
5. Determine the reaction order and rate constant.

Suggested reseach regarding the effectiveness of ozonation of the sand filtered water are:

1. Use sand filtered water from the plant and then ozonated at various doses from 2 to 20 mg/l.
2. Pass the water continuously through a GAC filter with an EBCT of 10 minutes.
3. Determine the TOC and 1 day TCM levels in the sand filtered and GAC filtered waters.

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Appendix A

OTHER TEST PARAMETERS OF THE PRELIMINARY EXPERIMENT

TABLE A.1

RAW AND SAND FILTERED EFFLUENT TURBIDITY (NTU)

Date	Raw	Unoxi dized	Sand filtered effluents				Ozone(mg/l)		
			KMnO ₄ (mg/l)	1.0	1.5	0.7	2.0	5.0	10.0
24/07	25	2.6	1.8	2.0		2.0	1.8	1.6	0.6
14/08	40	2.5	3.0	2.4		2.2	1.6	1.0	0.6
22/08	24	4.0	3.0	3.0		1.8	1.3	0.7	0.9
29/08	24	2.4	2.0	2.0		2.0	1.2	0.8	0.8

TABLE A.2

FINISHED AND GAC FILTERED EFFLUENT TURBIDITY (NTU)

Date	Fin ished	Unoxi dized	GAC filtered effluents				Ozone(mg/l)		
			KMnO ₄ (mg/l)	1.0	1.5	0.7	2.0	5.0	10.0
24/07	0.9	1.5	1.6	1.8		1.8	1.6	1.2	0.6
14/08	0.8	2.3	2.2	2.6		1.9	1.4	1.0	0.6
22/08	2.6	1.8	2.6	2.6		1.7	1.2	0.7	1.2
29/08	1.2	2.4	1.6	2.0		2.0	1.5	1.0	0.8

TABLE A.3
RAW AND SAND FILTERED EFFLUENT pH

Date	Raw	Sand filtered effluents						
		Unoxi dized	KMnO ₄ (mg/l)		Ozone(mg/l)			
			1.0	1.5	0.7	2.0	5.0	10.0
24/07	8.6	8.3	8.2	8.2	8.1	8.2	8.2	8.0
14/08	8.2	8.2	8.2	8.1	8.3	8.3	8.3	8.2
22/08	8.2	8.1	8.4	8.5	8.4	8.4	8.4	8.4
29/08	7.8	8.1	8.1	8.1	8.1	8.1	8.0	8.0

TABLE A.4
FINISHED AND GAC FILTERED EFFLUENT pH

Date	Fin ished	GAC filtered effluents						
		Unoxi dized	KMnO ₄ (mg/l)		Ozone(mg/l)			
			1.0	1.5	0.7	2.0	5.0	10.0
24/07	8.1	8.1	7.4	7.5	8.0	7.3	7.6	7.7
14/08	8.1	7.8	8.0	7.8	7.3	7.4	7.5	7.7
22/08	8.2	7.6	8.1	8.1	7.8	8.1	8.1	8.0
29/08	7.9	7.5	7.7	7.8	7.6	7.7	7.7	7.8

TABLE A.5
RAW AND SAND FILTERED EFFLUENT ALKALINITY (mg CaCO₃/l)

Date	Raw	Sand filtered effluents						
		Unoxi dized	KMnO ₄ (mg/l)		Ozone(mg/l)			
			1.0	1.5	0.7	2.0	5.0	10.0
24/07	138	134	140	140	138	140	140	148
14/08	230	232	240	240	232	230	238	230
22/08	184	180	182	188	190	182	188	184
29/08	184	178	182	184	182	184	184	182

TABLE A.6

FINISHED AND GAC FILTERED EFFLUENT ALKALINITY (mg CaCO₃/l)

Date	Fin ished	Unoxi dized	GAC filtered effluents		Ozone(mg/l)			
			KMnO ₄ (mg/l)		0.7	2.0	5.0	10.0
			1.0	1.5				
24/07	132	140	130	124	130	90	126	120
14/08	236	160	210	224	216	212	214	220
22/08	184	120	180	180	160	170	176	174
29/08	182	130	174	184	160	172	172	176

TABLE A.7

RAW AND SAND FILTERED EFFLUENT TOTAL HARDNESS (mg CaCO₃/l)

Date	Raw	Unoxi dized	Sand filtered effluents		Ozone(mg/l)			
			KMnO ₄ (mg/l)		0.7	2.0	5.0	10.0
			1.0	1.5				
24/07	168	164	172	168	162	168	168	172
14/08	240	252	244	252	252	248	248	242
22/08	250	244	244	250	210	240	250	260
29/08	248	240	248	244	248	240	240	240

TABLE A.8

FINISHED AND GAC FILTERED EFFLUENT TOTAL HARDNESS (mg CaCO₃/l)

Date	Fin ished	Unoxi dized	GAC filtered effluents		Ozone(mg/l)			
			KMnO ₄ (mg/l)		0.7	2.0	5.0	10.0
			1.0	1.5				
24/07	160	180	140	100	160	120	144	160
14/08	240	180	224	240	212	224	232	240
22/08	250	170	240	230	200	220	240	244
29/08	244	180	248	240	220	224	236	240

TABLE A.9

RAW AND SAND FILTERED EFFLUENT CALCIUM HARDNESS (mg CaCO₃/l)

Date	Raw	Sand filtered effluents						
		Unoxi dized	KMnO ₄ (mg/l)		Ozone(mg/l)			
			1.0	1.5	0.7	2.0	5.0	10.0
24/07	104	96	68	84	84	100	104	104
14/08	128	160	160	144	152	140	156	148
22/08	140	150	150	150	130	140	150	140
29/08	140	144	148	148	152	148	148	148

TABLE A.10

FINISHED AND GAC FILTERED EFFLUENT CALCIUM HARDNESS (mg CaCO₃/l)

Date	Fin ished	GAC filtered effluents						
		Unoxi dized	KMnO ₄ (mg/l)		Ozone(mg/l)			
			1.0	1.5	0.7	2.0	5.0	10.0
24/07	100	112	68	88	84	64	84	100
14/08	140	104	132	144	128	140	144	148
22/08	150	110	144	148	120	120	140	130
29/08	144	120	148	152	132	132	140	144

Appendix B

OTHER TEST PARAMETERS OF THE TREATMENT EVALUATION EXPERIMENT

TABLE B.1

OZONE RELEASED FROM THE CONTACTOR

Date	Ozone dose (mg/l)	Released (mg/l)	Residual (mg/l)
06/09	2.0	0.50	
17/09	2.0	0.44	
25/09	2.0	0.37	
01/10	2.0	0.43	0.05
05/10	2.0	0.41	0.13
10/10	2.0	0.31	0.10
15/10	2.0	0.42	0.12
22/10	2.0	0.32	0.07
05/11	2.0	0.50	0.12

TABLE B.2

LABORATORY GAC ADSORPTION OF UNOXIDIZED RAW WATER (25/09/90)

Raw water TOC (C_0) = 10.14 mg/l, $k = 1.77$, $1/n = 0.99$

GAC dose(m) (g/l)	Effluent TOC (C_e) (mg/l)	Organics adsorbed x/m	Log(C_e)	Log(x/m)
0.2	10.63			
0.5	5.44	9.40	0.74	0.97
1.0	3.67	6.47	0.56	0.81
1.5	2.31	5.22	0.36	0.72
2.0	2.04	4.05	0.31	0.61
2.5	2.04	3.24	0.31	0.51
3.5	1.96	2.34	0.29	0.37
5.0	0.96	1.84	(0.02)	0.26

$$x = C_0 - C_e$$

TABLE B.3

LABORATORY GAC ADSORPTION OF PERMANGANATED RAW WATER (25/09/90)

Raw water TOC (C_0) = 10.14 mg/l, $k = 1.51$, $1/n = 1.14$

GAC dose(m) (g/l)	Effluent TOC (C_e) (mg/l)	Organics adsorbed x/m	Log(C_e)	Log(x/m)
0.2	7.51	13.15	0.88	1.12
0.5	5.17	9.94	0.71	1.00
1.0	3.49	6.65	0.54	0.82
1.5	2.46	5.12	0.39	0.71
2.0	2.12	4.01	0.33	0.60
2.5	2.00	3.26	0.30	0.51
3.5	1.69	2.41	0.23	0.38
5.0	1.28	1.77	0.11	0.25

$$x = C_0 - C_e$$

TABLE B.4

LABORATORY GAC ADSORPTION OF OZONATED RAW WATER (25/09/90)

Raw water TOC (C_0) = 10.14 mg/l, $k = 1.79$, $1/n = 0.82$

GAC dose(m) (g/l)	Effluent TOC (C_e) (mg/l)	Organics adsorbed x/m	Log(C_e)	Log(x/m)
0.2	8.57	7.85	0.93	0.89
0.5	5.69	8.90	0.76	0.95
1.0	4.06	6.08	0.61	0.78
1.5	2.74	4.93	0.44	0.69
2.0	2.29	3.93	0.36	0.59
2.5	2.16	3.19	0.33	0.50
3.5	1.47	2.48	0.17	0.39
5.0	1.31	1.77	0.12	0.25

 $x = C_0 - C_e$

TABLE B.5

LABORATORY GAC ADSORPTION OF RAW WATER (22/10/90)

Raw water TOC (C_0) = 11.31 mg/l, $k = 1.69$, $1/n = 1.03$

GAC dose(m) (g/l)	Effluent TOC (C_e) (mg/l)	Organics adsorbed x/m	Log(C_e)	Log(x/m)
0.2	8.05	16.30	0.91	1.21
0.5	6.69	9.24	0.83	0.97
1.0	3.53	7.78	0.55	0.89
1.5	2.73	5.72	0.44	0.76
2.0	2.58	4.37	0.41	0.64
2.5	2.00	3.72	0.30	0.57
3.5	1.99	2.66	0.30	0.43
5.0	1.20	2.02	0.08	0.31

 $x = C_0 - C_e$

TABLE B.6

PLANT GAC ADSORPTION OF RAW WATER (22/10/90)

Raw water TOC (C_0) = 11,31 mg/l, $k = 0.72$, $1/n = 0.85$

GAC dose(m) (g/l)	Effluent TOC (C_e) (mg/l)	Organics adsorbed x/m	Log(C_e)	Log(x/m)
0.2	9.21	10.50	0.96	1.02
0.5	9.05	2.18	0.96	0.34
1.0	6.00	4.14	0.78	0.62
1.5	6.14	2.67	0.79	0.43
2.0	4.71	2.72	0.67	0.43
2.5	4.08	2.42	0.61	0.38
3.5	3.23	1.97	0.51	0.30
5.0	2.42	1.54	0.38	0.19

 $x = C_0 - C_e$

Appendix C

OTHER TEST PARAMETERS AFTER TCM FORMATION
EXPERIMENT

TABLE C.1

ORGANIC AND TCM LEVELS IN ROSENORT WATER

Date	Raw water	Finished water at a point in the dis tribution system	
	TOC(mg/l)	TOC(mg/l)	TCM(μ g/l)
17/01/91	15.59	15.80	
24/01/91		14.92	158
31/01/91	16.34	15.08	152
07/02/91	14.04	14.10	156

Appendix D

KINETIC MODEL OF TCM FORMATION

D.1 REACTION ORDER AND RATE CONSTANT DETERMINATION

Basis of the equation:

1. Precursor disappearance is equal to TCM formation.
2. Reaction rate is first order with respect to chlorine residual.

$$dTCM/dt = -dC/dt = k [Cl_2] C^n$$

Where C is the precursor residual

[Cl₂] is the chlorine residual

t is the contact time

This equation is approximated with the following equation:

$$-\Delta C/\Delta t = k [Cl_2] C^n$$

then, $\log(-\Delta C/\Delta t) - \log[Cl_2] = \log k + n \log C$

Plotting data into a linear regression:

$$Y = A + B X$$

Where $Y = \log(-\Delta C/\Delta t) - \log[Cl_2]$

$$A = \log k$$

$$B = n$$

$$X = \log C$$

the reaction order, n , and the rate constant, k , can be determined.

D.2 FORMATION EQUATION

$$-dC/dt = k [Cl_2] C^n$$

or
$$-dC/C^n = k [Cl_2] dt$$

By an assumption that the chlorine residual will remain constant in the interest period ($t = 1$ day), the equation can be solved as follows:

$$-C_0^{-m} + C^{-m} = m k [Cl_2]_0 t$$

The TCM level is equal to the disappearance of the precursors.

$$TCM = C_0 - C$$

$$= C_0 - \{C_0^{-m} + m k [Cl_2]_0 t\}^{-1/m}$$

where $m = n-1$

C_0 = initial precursor level (=TCMFP)

$[Cl_2]_0$ = chlorine dose