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The Occurrence and Control of Disinfection By-Products (DBPs) in Two Water Treatment Plants Utilizing the Same Source

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THE OCCURRENCE AND CONTROL OF DISINFECTION BY-PRODUCTS (DBPs) IN TWO WATER TREATMENT PLANTS UTILIZING THE SAME SOURCE

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The Graduate Program in Environmental Science

The Occurrence And Control Of Disinfection By-Products (DBPs) in Two Water Treatment Plants Utilizing The Same Source

A Thesis in

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By

Sam George Khoury

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For the Degree of

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ABSTRACT

The Occurrence And Control Of Disinfection By-Products (DBPs) in Two Water Treatment Plants Utilizing The Same Source

By
Sam G. Khoury

The influence of disinfection by-products (DBPs) on the operation and design of water treatment plants has been increasing since the early studies by Rook on trihalomethanes (THMs) (Stevens, 1977). Work conducted in the 1980s identified the existence of nonvolatile halogenated organics (non-THM organics), of which the majority produced by chlorination were haloacetic acids (HAAs), within the HAAs, dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) were the dominant members.

Concern over potential health effect led the U.S. Environmental Protection Agency (USEPA) to set a maximum contaminant level (MCL) for total THMs and HAAs. The disinfectant/disinfection by-product rule (D-DBP Rule) currently proposed by the USEPA will lower the MCL for THMs and HAAs. Past and pending DBP regulations have provided a momentum to seek a better understanding of how these compounds are formed as well as how their production can be controlled.

Drinking water utilities are preparing for these major changes. An investigation was conducted to examine disinfection options that would ensure minimization of DBP formation and conform to disinfectant-disinfection by-product regulations. Primary issues were the types of disinfectants applied (chlorine, chlorine dioxide, chloramines and/or ozone). The study was conducted at two public drinking water treatment plants that derive their water from one source; the Delaware River. Each plant was associated with a different chemical environment that affected DBP formation. The effects of implementing different disinfection options on DBP formation were evaluated at pilot plants for various water conditions. Analyses were conducted for disinfectant residuals, organic by-products (trihalomethanes and haloacetic acids). Promising DBP elimination strategies were also investigated utilizing the pilot treatment facilities. Results have shown that DBP control was accomplished by the focus on removal of the precursors through granular activated carbon (GAC), reverse osmosis and coagulation. After the DBPs had formed it was possible to remove them by subsequent GAC and coagulation treatment.

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CHAPTER 1

INTRODUCTION

1.1 General

Early in the century, chlorine was introduced into drinking water for disinfection against waterborne diseases, a practice that has persisted to date and to which the saving of millions of lives has been attributed.

Historically, chlorine has been the primary disinfectant employed by most water utilities in the United States (Bryant 1996). Chlorine disinfection has produced and continues to produce excellent results in terms of killing or inactivation of pathogenic microorganisms. Chlorine, a strong oxidant, has provided many additional water treatment benefits such as the removal of iron, manganese, and color. Under certain source water quality conditions, chlorination has also been effective in reducing tastes and odors. In treatment plant operation, the practice of prechlorination has provided major benefits in reducing algae blooms in open settling basins and in controlling biological growths in water plant filter media (Gaudy 1980). In addition, where the natural organic content might inhibit or interfere with coagulation, prechlorination has often been effective in enhancing the coagulation process.

Concerns for chlorine By-products began in 1970 as new analytical methods were applied for identifying constituents of drinking water. In 1974, a Dutch Chemist, Johnnes Rook, published results that implicated the use of chlorine in drinking water as the cause of chloro and bromo trihalomethanes (THMs) found in treated drinking waters (Beller

1974). During this same year, Congress passed the Safe Drinking Water Act, which established authority through the EPA for Federal regulation of public water supplies throughout the country. After passage of the Safe Drinking Water Act, the EPA performed the National Organics Reconnaissance Survey in 1975 and the National Organic Monitoring Survey in 1976 and 1977 (Stevens 1977). These investigations confirmed the presence of chloroform in a number of water supplies throughout the country (Rook, 1976). These early disinfection by-products (DBPs), as they are now called, were later joined by several other halogenated organic and non-halogenated organic compounds. In part, these revelations have all come about as the result of improved analytical methods and greater scrutiny directed at the contents of chlorinated drinking waters in the last two decades.

DBPs occur as a result of reaction between a disinfecting chemical and naturally occurring background constituents found in many source waters. These constituents and compounds are known as "precursors." Initial concerns about by-products were mainly related to the possible carcinogenic potential of THMs formed in chlorine reactions. Improved analysis techniques have since detected additional DBPs, and there are now concerns for health effects other than cancer.

1.2 Regulatory Requirements

Beginning in 1992, water utilities, environmental groups, and the EPA began regulatory negotiations on disinfection and DBPs. Due to the complexity of the issue and the amount of information still needed, regulations were proposed to be implemented into two stages (USEPA 1994).

Stage One was to start in 1994, and would provide MCLs for four classes of compounds and maximum residual disinfectant goals for chlorine, chloramines, and chlorine dioxide (Minear 1996a). However, due to political and legal matters Stage One was not implemented until November of 2000. Below are shown MCLs and Maximum residual Disinfection Goals for Stage One of the Disinfection/Disnfection By-Product Rule (USEPA 1990).

Table 1: Maximum contaminant levels for DBPs:

DBP	MCL
THMs	80 µg/l
HAAs	60 µg/l
Bromate	10 µg/l
Chlorite	1.0 mg/l

Table 2: Maximum residual disinfectant level:

Disinfectant	MCL
Chlorine	4 mg/l
Chloramines	4 mg/l
Chlorine dioxide	0.8 mg/l

The regulations were supposed to be revisited in 1998. However, this date was further delayed until 2005. It is anticipated that MCLs will be lowered for the THMs to 40 µg/l and haloacetic acids (HAAs) to 30 µg/l. MCLs may also be developed for other by-products (USEPA 2002). To provide the information necessary for the next stage, the information collection rule (ICR) has been proposed (Bellamy 1994). The rule requires utilities serving a population greater than 10,000 to begin monitoring for microbial contaminants and DBPs (USEPA 1994).

1.3 Disinfection and By-product Formation

Disinfection is defined as the inactivation of pathogenic microorganisms. The major and first disinfection step employed in municipal treatment systems is primary disinfection. The intention is to completely kill pathogens present in the source water and to prevent the introduction of such pathogens into the water distribution network (Miltner 1994).

A supplemental disinfection effect may also be accomplished by the separation and removal of pathogens in the filtration of drinking water. This is reflected in the latest regulation that is discussed in the next section. The filtration system, which often includes coagulation and preliminary solid removal, provides baseline treatment. Disinfection chemicals are usually integrated into this baseline process.

A secondary or final disinfection step is added to the treatment process to maintain a disinfectant residual concentration throughout the water distribution system (Miltner 1994). The role of this disinfectant residual is to provide protection against subsequent microbial growth following treatment. Sufficient disinfectant is added to the flow leaving the treatment facilities to ensure that some residual is available throughout a distribution system. The level of disinfectant addition takes into account the residence time in conveyance and storage elements of the distribution networks as well as the possibility of disinfectant loss by degradation (Miltner 1994).

Common disinfecting chemicals include chlorine, chloramines (chlorine/ammonia), chlorine dioxide, and ozone. These chemicals cause the inactivation of the pathogens in different ways. They react differently under various water quality conditions such as pH, temperature, disinfectant concentration, and the presence of other chemicals. Depending on the particular disinfectant, the basic mechanism for inactivation includes: alteration in the permeability of the pathogen cell wall, interference with its cell enzymes or other key cell components, and oxidative attack (Miltner 1994).

Although chemical reactivity is a desirable trait for achieving disinfection, such reactivity makes disinfectants susceptible to other chemical reactions, some of which can form undesirable by-products. Chemical precursors that react with disinfectants to form DBPs can come from several sources. In most cases, naturally occurring organic matter (NOM) is the predominant source of a diverse group of precursors. Originally, precursors for THMs were observed to be humic substances in the source water supply that occur as a consequence of natural plant matter decay processes. Hydrophilic acids and amino compounds may also produce THMs in reactions with chlorine (Minear 1996a).

Chlorinated DBPs form when free chlorine (Cl_2) is added to water to form (HOCl). Chlorine acts as an oxidant and reacts with the precursors present. Equation 1 is the general equation describing the formation of the halogenated DBPs. (Bryant 1996)

$$HOCl + Br^{-} + NOM \Rightarrow THMs + \text{Other Halogenated DBPs} \qquad (1)$$

Most of the attention on DBPs has focused on regulation of THMs. There has been a growing concern that other DBPs may also be significant. Specific regulatory intent for other disinfection by-products were initially indicated in the first Drinking Water Priority List, published by the EPA in January 1988. A second list, which indicates disinfection by-products for possible future regulation, was developed in 1991 (Table 3). The major halogenated DBPs that are commonly identified from chlorine treatment are THMs, HAAs, HANs, cyanogens halides and halopicrins (USEPA 2002). Below are the major types of DBPs:

Table 3: Disinfectants and DBPs on the U.S. Environmental Protection Agency Drinking Water priority list (USEPA 2002):

Disinfectants:	Chlorine, hypochlorite ion, chlorine dioxide, chlorite ion, chlorate ion, chloramines.
Four Trihalomethanes	Chloroform, bromoform, dibromochloromethane, dichlorobromomethane.
Chlorination/Chloramination By-products (misc.):	Haloacetic acids, haloketones, chloral hydrate, MX-2 (3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone, N-organochloramine
Five Haloacetic Acids:	Monochloroacetic Acid (MCAA), Dichloroacetic Acid (DCAA), Trichloroacetic Acid (TCAA), Monobromacetic Acid (MBAA), Dibromoacetic Acid (DBAA).
Ozone By-products	Aldehydes, epoxides, peroxides, nitrosamines, bromate, iodated
Haloacetonitriles:	Bromochloroacetonitrile, dichloroacetonitrile, dibromoacetonitrile, trichloroacetonitrile.

In the absence of bromide (Br^-), only chlorinated by-products are formed. In the presence of (Br^-), free chlorine rapidly oxidizes (Br^-) to hypobromous acid (HOBr), which then reacts along with (HOCl) and NOM to produce the mixed chloro-bromo DBPs.

As analytical methods have been developed and improved, an increasing number of by-products (other than THMs and HAAs) have been identified. In spite of such analytical improvement, limitations still exist. Although new by-products continue to be detected, evidence suggests that potentially significant groups of by-products still remain to be identified (Glaze 1993). In addition, areas of uncertainty still exist with respect to evaluation of health effects of already identified DBPs. As health effect evaluation methodologies improve, it is possible that the level of scientific concern for DBPs may change. Such changes may result in either an increase or a decrease of currently established maximum contaminant levels (MCLs) of various DBPs. As a result, there is a significant opportunity for change in scientific views of these issues over time.

Because of much of the original concern was for chlorinated DBPs rather than DBPs of other disinfectants, chlorine first appeared to be the least attractive disinfection alternative. As knowledge of other DBPs develops, it is possible that additional, potentially harmful constituents may be disclosed. Therefore, some flexibility is appropriate in planning for water system disinfection and the management of DBPs. We must allow for possible changes in understanding of the by-products of all disinfectants (Miltner 1994).

Most water treatment plants must achieve two disinfection goals: disinfection to remove source-related pathogens (primary disinfection) and provision of disinfection residual in the distribution system to prevent subsequent re-growth of harmful microbes (secondary disinfection). Among the available disinfecting agents, only chlorine is widely proven for achieving both primary and secondary disinfecting goals (Miltner 1990). If it becomes necessary to use alternative disinfecting agents to control the formation of DBPs, it is possible that the overall disinfection process may become significantly more complex. This may require separate disinfecting agents to meet specific primary and secondary disinfection goals.

1.4 Chemical Reaction Characteristics of Disinfectant Chemicals

1.4.1 Chlorine

Chlorine can occur in several different chemical forms. As an example, chlorine gas, which is in the form of molecular chlorine, Cl_2 (g), rapidly reacts in water to form hypochlorous acid, HOCl, and chloride, Cl^- (Gordon 1994):

$$Cl_2(g) + H_2O = HOCl + Cl^- + H^+ \qquad (2)$$

In normal practice, the initial Cl_2 form of chlorine is not present except for the brief period of time required for this reaction. Reaction products such as HOCl and Cl^- are the most prominent forms remaining. In the reaction shown above, the portion of chlorine that is transformed to Cl^- is relatively inert and does not significantly contribute to the disinfection or to further chemical reaction. Instead, the active portion of chlorine is the portion that is transformed to HOCl. This form of chlorine can be further transformed by other reactions so that the overall disinfecting effectiveness and reactivity of chlorine may actually result from a composite effect of several different forms. As an example, HOCl can form OCl^- by the following reaction: (Jacangelo 1987)

$$HOCl = H^+ + OCl^- \qquad (3)$$

The reaction is driven to the right with increasing pH and reaches a point at which OCl^- becomes the dominant chlorine form at pH>8. At pH<7, HOCl is the dominant form; a transition region occurs between pH 7 and 8. This phenomenon has a significant impact both on disinfection in particular and chemical reactivity in general; OCl^- is much less effective than HOCl as a disinfectant and is less reactive. (Sawyer 1963)

Chlorine gas represents just one of several chlorine sources from which HOCl and OCl^- may be formed and ultimately become the active disinfecting agents. Other examples include sodium hypochlorite, NaOCl, which is also used as household bleach, and calcium hypochlorite, $Ca(OCl)_2$. Reactions of these chemicals with water are as follows: (Severin 1987)

$$NaOCl + H_2O = HOCl + Na+ + OH^- \qquad (4)$$

$$Ca(OCl)_2 + 2H_2O = 2HOCl + Ca^{+2} + 2OH^- \qquad (5)$$

In both instances, HOCl and OCl^- become the active end products. Therefore, disinfection and chemical reaction characteristics of these approaches are generally similar in all chlorine systems in spite of differences in the original form of chlorine. The distribution of HOCl and OCl^- is determined by pH. Some differences in pH control, however, may be required since gaseous chlorine reacts as an acid, whereas hypochlorite solutions tend to be slightly alkaline. (Richardson 1999)

A common characteristic of HOCl and OCl^- is that chlorine exists within both of these chemical forms in a ($^{+1}$) oxidation state:

$(H^{+1}\,O^{-2}\,Cl^{+1})^{\circ}$

$(O^{-2}\,Cl^{+1})^{-1}$

Although chlorine is a strong oxidizing chemical, reactions can also occur in which chlorine remains in the $Cl(^{+1})$ form and without the occurrence of oxidation. These are reactions in which chlorine is added or substituted into the structure of another molecule in the form of $Cl(^{+1})$. Reactions of this type are responsible for the formation of chloramines as well as the chlorinated organics that are the DBPs of concern. Oxidation reactions that involve chlorine result in a modification of the oxidation state of chlorine to the inert chloride ion form (Cl^-) and do not result in the formation of chlorinated compounds (Richardson 1999).

Oxidation by-products that do not contain chlorine are also significant and are receiving increasing attention. The complete oxidation of a simple organic compound by oxygen to produce carbon dioxide and water. However, intermediate organic products can also be formed prior to complete oxidation, which results in a sequence of oxidations illustrated below by the following equation (Sawyer 1963):

$$\underset{\text{Hydrocarbon}}{CH_4} \rightarrow \underset{\text{Alcohol}}{CH_3OH} \rightarrow \underset{\text{Aldehyde}}{H_2C{=}O} \rightarrow \underset{\text{Acid}}{HCOOH} \rightarrow H_2O + CO_2 \qquad (6)$$

Intermediate oxidation products such as aldehydes and acids and others can exist in most chlorine reaction circumstances since complete oxidation does not normally take place. The chlorine reaction may stop before complete oxidation can occur, a condition that leaves intermediate products. Molecular structures and other factors can also influence chemical reactions and pathways as shown by the following equations (Sawyer 1963):

$$\text{Benzene} + HOCl \nrightarrow \text{No Reaction} \qquad (7)$$

$$\text{Phenol} + HOCl \rightarrow \text{Phenol Chloride (Slow Reaction)} \qquad (8)$$

$$\text{Resorcinol} + HOCl \rightarrow CHCl_3 + \text{Others (Fast Reaction)} \qquad (9)$$

In the case of reactions occurring along nonoxidation substitution pathways, several factors can also influence the type of chemical reaction. For example, the tendency for the reaction to occur can be affected by what appear to be relatively small differences in molecular structure. This is illustrated in the reactions above between HOCl and benzene-type compounds. The benzene itself does not readily react with

HOCl. However, if an electronegative group is present, such as OH, the benzene ring is activated and chlorine substitution is allowed to occur at either the adjacent or the opposite carbon site (Miltner 1994). Additional modification of the benzene ring by the introduction of OH groups on either side of the reaction site, as is the case for resorcinol, activates the reaction site to such an extent that the benzene ring can be broken, yielding chloroform ($CHCl_3$) and other by-products (Minear 1996b). This type of reaction is considered to be important in the formation of chloroform and other THMs in spite of the fact that the resorcinol structure is considerably different from the basic structure of chloroform.

1.4.2 Chloramines:

Chloramines are formed by the following substitution reactions in which $Cl(^{+1})$ is substituted for a hydrogen component, $H(^{+1})$, in ammonia (NH_3):

$$HOCl + NH_3 \rightarrow H_2O + NH_2Cl \text{ (Monochloramine)} \tag{10}$$

$$HOCl + NH_2Cl \rightarrow H_2O + NHCl_2 \text{ (Dichloramine)} \tag{11}$$

$$HOCl + NHCl_2 \rightarrow H_2O + NCl_3 \text{ (Nitrogen Trichloride)} \tag{12}$$

The distribution among these forms of chloramines depends on other influences such as pH, temperature, the ratio of chlorine to ammonia, and the presence of other compounds. In disinfection applications, reaction conditions are typically controlled through the chlorine-to-ammonia ratio to ensure that monochloramine is the dominant form. This is because the other two produce taste and odors (Lykins 1991).

The reactivity of Cl^+ is modified by its incorporation into the ammonia forms. Although the NH_2^- component of the monochloramine, NH_2Cl, has a net charge of -1 and appears to be similar to the HO^- component of HOCl. In that regard, differences occur with respect to charge distribution within the molecules. In the case of NH_2Cl, nitrogen in the $N(^{-3})$ form exerts a much more intense electronegative center than $O(^{-2})$. As a result of these differences, the $Cl(^{+1})$ is strongly bound in chloramines and is much less reactive than in HOCl. As a consequence of this reduced reactivity, chloramines do not readily engage in oxidation reactions and also have lower disinfection efficiency. Although chloramines can take part in some substitution reactions and can form a number of chlorinated DBPs, the overall extent of such formation is less than for HOCl. They are not readily involved in substitution reactions that result in the formation of THMs or HAAs. However, some pathways have been identified under laboratory conditions using a synthetic organic compound (Lykins 1991).

1.4.3 Chlorine Dioxide

The reactivity of chlorine in chlorine dioxide is substantially different from its reactivity in the other forms. In this case, chlorine no longer occurs as $Cl(^{+1})$, but is in the form of Cl $(^{+4})$, an entirely different oxidation state with distinct reaction pathways (Richardson 1999). Although chlorine dioxide may react with organic material to form some chlorinated substitution products, there is more of a tendency for the formation of unchlorinated oxidation products. Chlorine dioxide also undergoes changes in oxidation state that can form the intermediate inorganic degradation products, chlorite (ClO_2^-) and chlorate (ClO_3^-), prior to degradation to chloride. Unlike chloride, which is the primary degradation product for both free and combined chlorine, these intermediates are still reactive forms of chlorine DBPs (Miltner 1990).

1.4.4 Ozone

Ozone (O_3) is a highly reactive and relatively unstable form of oxygen that is derived from the more common O_2 or diatomic form. The actual formation occurs in the following two steps:

$$O_2 + \text{energy} = 2O\cdot \qquad (13)$$

$$2O\cdot + 2O_2 = 2O_3 \qquad (14)$$

The first step in the reaction cleaves two pairs of electrons that are shared between the two oxygen atoms in O_2, leaving two unpaired electrons in the outer shell of the individual atoms. This is an unstable condition since outer shell configurations tend to be stabilized by maintaining four paired sets of electrons to achieve a full complement of eight electrons for each atom. In the single atom configuration, each atom provides only six electrons, two of which are unshared, resulting in a very unstable condition. The unpaired electron configuration is termed as a free radical (Singer 1996).

The introduction of free radical chemistry into ozonation can have a significant effect on its overall chemistry. For example, ozone can form uncharged hydroxyl radicals (OH·), which are even more reactive than ozone itself. Formation of these radicals tends to be encouraged as pH is increased and leads to a more rapid rate of ozone degradation because of the higher reactivity. Therefore, pH has a significant effect on the capability for maintaining ozone residual over a specified period of time.

Products of ozone reactions are the result of oxidation reactions. However, the formation of varying degrees of halogenated products has also been observed (Singer 1996). This is probably as a result of indirect reaction pathways involving ozone oxidation of naturally occurring bromides, which substitute into organic material to form brominated DBPs.

Reactions with ozone (O_3) fall into two general categories:

1. Direct reactions with dissolved ozone.
2. Reactions with hydroxyl free radical, OH•, an important ozone degradation product whose formation is promoted by hydroxide ions (OH^-) in the alkaline pH range.

Free radicals are more reactive than dissolved ozone, and the reaction pathways that lead to their formation can possibly oxidize a wide range of organic compounds using ozone. Ozone can also react with bromide to form bromate, an important inorganic DBP. Bromate has been identified as a carcinogen and has become a significant concern for ozonation of bromide containing waters (Bailey 1978).

1.5 Disinfection By-product Control Strategies

Regulatory concerns for DBPs have resulted in consideration of several alternative water treatment approaches. These strategies fall into one of the following categories: (1) Use of alternative disinfectants that minimize the formation of regulated By-products. Alternatives to free chlorine include chlorine dioxide, ozone, chloramines, potassium permanganate, and ultraviolet radiation. (2) Removal of organic precursors prior to addition of disinfecting agents. Varying degrees of removal are possible with processes that employ coagulation, activated carbon, and oxidation with chemical agents (i.e. Chlorine). (3) Processes such as activated carbon to remove by-products once they are formed (Minear 1996a).

Locations of the disinfectant feed, special precursor removal technologies, and methods to limit contact times with disinfectant should all be considered to minimize by-product formation. Reducing precursors and disinfectant demand prior to the disinfectant feed could be an important method for meeting otherwise difficult concentration goals for DBPs.

Among the general approaches, removal of DBPs following their formation is often the most expensive approach and normally would be used only if all other techniques would not work. If the combination of disinfection and precursor removal techniques fail to keep the DBPs within EPA requirements, it may be necessary to include some form of DBP removal such as granular activated carbon (GAC) contact.

1.5.1 Coagulation

Coagulation is used for the control of particulates in drinking water, and its role in the control of organic carbon has been documented (Minear 1996b). With the inclusion of DBP control as part of the EPA's drinking water regulatory requirements, the role of coagulation has expanded to include control of DBP precursors.

During conventional coagulation, the concentration of NOM is reduced. One of the strategies for control of DBP formation is removal of the NOM by coagulation prior to disinfection. Because the NOM is largely unidentified and not directly measurable, total organic carbon (TOC) serves as an indicator for the DBP precursors. Typically, about 90% of the TOC is dissolved organic carbon (DOC) (Minear 1996b).

Aluminum and iron salts are used for coagulation. For metal salts, two mechanisms for removal of NOM are accepted (Miltner 1994). The first, the negatively charged NOM is neutralized by positively charged metals forming insoluble complexes (Al or Fe humates and fulvates), followed by precipitation of NOM with the floc. In the second, NOM adsorbs into metal hydroxide ($Al(OH)_3$ floc or $Fe(OH)_3$) floc- precipitates. The effectiveness of coagulation is strongly dependent on pH and the dose of the coagulant. At higher coagulant doses, more metal for floc or complex formation is available. Coagulation of NOM is most effective in the pH range of 5 to 6, as charge neutralization tends to be more effective at lower pH. At lower pH, the charge density of humic and fulvic acids is reduced, making them more hydrophobic and adsorbable. Lower pH can be achieved by acidification and/or by higher coagulant dosing. More metal hydroxide ($Al(OH)_3$ floc or $Fe(OH)_3$) is formed at higher coagulant doses, therefore more H^+ in solution lowers the pH. Therefore, TOC removal and DBP precursor removal can be enhanced by decreasing pH and/or by increasing coagulant doses (Miltner 1994).

1.5.2 Carbon and Membrane Processes

Activated carbon and membrane processes are considered higher-price options for DBP precursor removal and control. For both processes, it is more economical to remove the DBP precursor material than the formed DBPs. DBP precursors are more readily adsorbed into activated carbon than DBPs (Bryant 1996). Precursor materials have larger molecular sizes than DBPs; therefore, it is easier for membranes to reject precursor materials. Also, both activated carbon and membranes have problems handling chlorinated water. Activated carbon quickly reduces free chlorine. This lowers the capacity of the carbon, makes the carbon more brittle, and increases the amount of dioxins formed upon regeneration (Bryant 1996). Also, because activated carbon reduces the disinfectant, post-filter chlorination will be needed, which will form additional DBPs from the precursor material that was not adsorbed into the carbon. Free chlorine attacks membrane material through oxidation pathways, and failure quickly occurs for many of these chlorine-sensitive thin-film membranes. Thin-film membranes are commonly used today because they have better flux and biodegradation characteristics than chlorine-resistant membranes.

Activated Carbon is commonly applied as powdered activated carbon (PAC) or in granular activated carbon (GAC) form. PAC is applied at or before the coagulation/flocculation step. The powdered carbon adsorbs contaminants and NOM until it is removed down stream in the sedimentation and filtration processes. However the adsorption residence time is too short to remove a significant amount of the NOM, which generally adsorb slowly. With regard to pre-chlorinated waters, the PAC adsorption capacities for DBPs are too low for significant removal. Therefore, PAC should only be used for taste and odor control rather than NOM control (Bryant 1996).

GAC is utilized in a filter mode, it can be used as part of a multi-media filter to remove particulates or as a post-filter to remove specific contaminants. Alum coagulation will result in improved GAC removal for TOC and DBP precursor removal because of reduced initial concentration and removal of poorly adsorbed high-molecular-weight organics. Also, enhanced coagulation reduced the concentration of the NOM and increased its adsorbility due to the reduced pH imparted from the increased alum dose (Bryant 1996).

1.6 Characteristics of Precursors

Naturally occurring precursor compounds that can react with chlorine are found in all surface waters. Therefore, the potential for formation of chlorination DBPs is high when chlorine is applied as a disinfectant. The amount of precursor material present depends upon the water quality characteristics. Therefore, wide variation in precursor contents is observed from one source water site to another. Variation in precursor level is also observed in many groundwater supplies where the organic content can result in the formation of DBPs. The potential of DBPs forming in groundwater supplies that have negligible organic content is small (Stevens 1977).

Humic material is the major precursor group found in most waters. Humic material is an end product of biological decay and tends to be relatively stable in comparison with other biological degradation products (Cooke 1989). Other components of naturally occurring NOMs include hydrophilic acids, carbohydrates, carboxylic acids, and amino acids. However, humic materials tend to represent the dominant fraction of dissolved organic carbon, most often present at levels of 50-90% (Cooke 1989). Humic materials have shown significant potential for formation of THMs, HAAs and other chlorinated by-products.

Humic materials are diverse in nature. Based on the analytical methods used for extracting chemical fractions, general characterizations have been developed that segregate these material into humic acid, fulvic acid, and humin groupings. Under such methods of identification, humic acid has been characterized as the portion of organic matter that is soluble in alkaline solutions but precipitated in acidic solutions. Fulvic acid has been characterized by solubility under both alkaline and acidic conditions. The humins group is not soluble in either acidic or alkaline conditions. Because they are not soluble, the humins' reactivity is minimal and is not considered a significant precursor.

Humic and fulvic acids contain complex polymerized molecular structures that have not been fully characterized. Specific chemical groups within these structures are thought to be responsible for the reactions with disinfecting chemicals that form by-products. For example, carboxyl (-COOH) and hydroxyl (-OH) groups associated with benzene rings are proposed as the reactive sites within humic material for the formation of THMs (Rook 1976). These groups provide the same activating potential provided by resorcinol in the reaction shown in equation (9).

Several researchers (Coleman 1992) associated algae and other biologically active sources with the presence of organic nitrogen compounds, such as proteins and amino acids that lead to the formation of organic chloramines and other products. Organic chloramines can interfere with analysis to determine free chlorine by yielding false-positive results. This would compromise the process control that is maintaining effective levels of disinfection (Coleman 1992). The formation of THMs from algae was studied and it was concluded that THM formation is significant on a seasonal basis when high algal levels are present (Minear 1996b).

High levels of DBP formation are observed in highly colored waters that occur in association with runoff over decaying ground during the spring and early summer periods (Minear 1996a). In other cases, levels are greatest during the hotter summer periods. Peak periods of formation may also occur at times during the fall, in areas where leaf fall and decay is significant. Additionally, higher temperatures tend to increase the rate of DBP formation (Minear 1996a).

1.7 Disinfection Facility Design and Improvement Programs

In the evaluation of the treatment performance of operating water plants, it is essential that the potential and actual efficiency of such operation be determined first. Many existing plants do not perform suitable operating procedures. Such issues must be corrected and optimum performances established before the appropriate design improvements can be selected (Glaze 1993).

The development of a disinfection program for either new or existing plants should include two basic objectives: (1) adequate disinfection. (2) Minimizing the formation of unwanted DBPs.

Each water treatment requirement and disinfection situation will be different. When disinfection options are considered, final water quality goals must meet EPA and finished goods requirements. In most instances, more than one disinfection arrangement will be able to achieve the established quality goals. Cost should determine which alternative is the most advantageous for the particular application.

CHAPTER 2

OBJECTIVES

2.1 Objective

Knowledge of the linkage between Disinfection By-Products (DBPs), DBP precursors, and treatment/disinfection practices by Public Water Utilities would enable these utilities to properly adjust their treatment strategies in order to best control DBP levels. This research would be of interest to the regulatory agencies, water utility systems and consultants.

Carbonated soft drinks (CSD) manufacturing facilities are the "Pilot Treatment Facilities". They are unique in that they purchase water that has already been treated to drinking water standards by the water utilities. Additional disinfection by the pilot treatment facilities, combined with potentially long overall contact times in the treatment system, can lead to increased levels of DBPs in the finished product. Therefore, a better understanding of DBP and precursor occurrence, as related to disinfection practices is needed. This need is further supported by the upcoming Stage 2 D/DBP Rule, which will require an initial distribution system evaluation for public utilities. Treatment changes that may be necessary by the water utilities to meet the new regulation requirements will impact the CSD water treatment systems.

Moreover, the increase of disinfectant contact time for the combination of public water utilities and pilot treatment facilities will allow this project to provide insight into the formation of DBPs in the long distribution systems of some larger water public water utilities. Alternatively, the short term DBP formation trends associated with the pilot treatment facilities will also provide insight into shorter contact time trends in smaller distribution systems. Thus, this research increases the overall understanding of DBP formation and control in distribution systems.

The objectives of this research are to: (1) characterize Disinfection By-Products (DBPs) – Trihalomethanes (THMs) and Haloacetic Acids (HAAs) and DBP precursor occurrence in two public water utilities drawing from the same source; however, utilizing different disinfection and treatment methods; (2) develop an understanding of the changes that occur in DBP levels as related to the disinfection practices employed by both the utilities and industry users; and (3) evaluate and recommend DBP control strategies and treatment technologies for water utility systems.

CHAPTER 3

EXPERIMENTAL TECHNIQUES AND METHODOLOGY

3.1 Scope of Experiment

To meet the objectives, the design of this research involved the study of two water plants; Philadelphia Water Department and Trenton Water Works deriving their waters from one source, Delaware River. The two plants utilize two different treatment and disinfection mechanism. The two distribution systems have different water quality, treatment, and distribution system characteristics. Samples were collected at two points in each location to determine the actual occurrence of DBPs as well as actual occurrence in the distribution system: (1) at the Delaware River (treatment system influent), and (2) at the tap of each treatment system (treatment system effluent).

Since water conditions vary widely during seasonal climate changes (USEPA 1990), DBP data for each location was collected during the winter and the summer months. For each of the utilities, operational information and complementary water analysis were also collected.

DBP precursor concentrations (Total organic compounds, pH, alkalinity, and bromide) were analyzed at the tap to determine a correlation of DBP analytical data and the DBP precursor concentrations.

Cott Corporation owns and operates soft drink plants in both of the utilities service areas. Soft drink plants receive drinking tap water from water utilities. The tap water is further treated to reduce alkalinity, hardness and remove chlorine, off odors and taste. For this thesis purposes, the soft drink plants will be considered "Pilot Treatment Facility A deriving its water from the Philadelphia Water Department and Pilot Treatment Facility B deriving its water from Trenton Water Works" with an average water treatment volume of 100,000 gallons per day per pilot treatment facility.

Water disinfection and treatment practices employed in the Pilot Treatment Facilities A and B varied from one location to another. DBP and DBP precursor concentrations were analyzed after the completion of the water treatment step to determine: (1) any change in DBP and DBP precursors' concentrations that occurred as a result of the Pilot plants disinfection and treatment, (2) The existing DBP control treatment technology in each Pilot plant was evaluated for regulatory compliance purposes with the USEPA Stage 1 and Stage 2 MCL limits for DBPs, and (3) Treatment systems in all locations were evaluated and modifications were researched to facilitate effective DBP control, in accordance with USEPA Stage 2 MCL limits.

3.2 Public Water Plants Operations And Sampling:

On October 30, 2001, February 15, 2002, July 17, 2002, October 16, 2002 and March 19, 2003, water was sampled from two plants (A and B) that operated in parallel from a common source of water. Additional samples were collected from two Pilot Treatment Facilities that purchase Plants A and B effluent and treat it further for CSD production.

The treatment process at plant A – Philadelphia Water Department - includes flocculation, coagulation, sedimentation, and filtration. The settled water is first filtered through a multimedia filter and then through a GAC filter. The raw water is disinfected with free chlorine. After the GAC and at the plant effluent, additional chlorine is added. In addition, chlorine is applied at the end of the sedimentation basin. Ammonia is added to convert the chlorine to chloramines.

The treatment processes at Pilot plant A included flocculation, coagulation, sedimentation, and filtration. The settled water is then treated through a sand/gravel filter and then through a GAC filter. Effluent water did not contain any disinfectants.

The treatment process at plant B – Trenton Water Works - included flocculation, coagulation, sedimentation, and filtration. The settled water is filtered through a GAC filter. Chlorine is applied to the raw and filtered waters and at the plant effluent. Chloramines are not used.

The treatment process at Pilot plant B included a sand/gravel filter, Storage tank - chlorination with chlorine dioxide, cellulose acetate reverse osmosis filtration, GAC and micron filtration. Effluent water also did not contain any disinfectants.

All four plants were sampled at the raw water influent and plant effluent.

3.3 Total Organic Carbon Analysis

TOC was used as a measure of NOM concentrations in the water. TOC of all the samples was measured by a total organic carbon analyzer (EZ TOC II, Isco, Inc.) Sample was drawn into the unit by injection into the manual sample valve to a scrubbing column, where dilute phosphoric acid converts inorganic carbon compounds to CO_2 which was removed by sparging. The scrubbed sample was pumped to the UV reactor where organic carbon compounds were oxidized to CO_2 by interaction of the sample with the UV light, carrier gas, and concentrated persulfate. The CO_2 was dried and measured by a non-dispersive infrared detector (NDIR), and the value is converted to TOC in mg/L.

3.4 pH Analysis

pH analysis was used to determine acidity levels in water. pH for all samples was measured by Orion 720A Meter utilizing selective electrode. Testing procedure involved adding approximately 100 mL of water in a beaker, then placing the pH electrode in the sample and recording the pH reading when prompted by the meter.

3.5 Alkalinity Analysis and Balance

The test for Alkalinity in the water followed the following equation 2P-M=A. Where "P" is the partial measurement of alkalinity resulting from hydrates and carbonates. The "P" value is obtained as the end point for titration with 0.02N sulfuric acid utilizing phenolphthalein indicator. "M" expressed as the total alkalinity of water. "M" is obtained as a continuous reading after "P" where methyl purple indicator is added to the solution after phenolphthalein end point is reached and further titrated with 0.02N sulfuric acid until the methyl purple turns to green. "A" is the chemical balance for a conventional lime coagulation system. As a rule of thumb, the "A" number should be maintained between +2 and +7 to ensure good chemical balance and flocculation in the lime and ferric sulfate systems.

3.6 Bromide Analysis

Bromide Ion-Selective Electrode was used to determine bromide ion levels in water. Bromide content for all the samples was measured by ELIT 8271 Ion-Selective meter. Testing procedure involved adding approximately 100 mL of water in a beaker, then placing the Bromide electrode in the sample. The Bromide reading was recorded when prompted by the meter.

3.7 THM Analysis

THM analysis was determined by utilizing LSC 2000 and Auto Gas Chromatograph XL with Hall Electronic Detector (HED). Samples were collected in duplicates, 2.5-3 mg of crystalline sodium thiosulfate were added to each 40-mL vial prior to sealing to enhance stability of THMs. Samples were injected into the GC for THM measurement.

3.8 HAA Analysis

The determination of Haloacetic Acids in Water was accomplished by utilizing Liquid-Liquid Extraction and Gas Chromatography with Electron Capture Detection (ECD). The method involved measuring 100-mL volume of water in a beaker and adjusting pH to 11.5, extract with methyl-ter-butyl ether (MTBE) to remove neutral and basic organic compounds. The aqueous sample was then acidified to pH 0.5 and the acids were extracted into MTBE. After the extract was dried and concentrated, the acids were converted to their methyl esters with diazomethane (DAM). Excess diazomethane was removed and the methyl esters were determined by the capillary Gas Chromatograph using an electron capture detector (ECD) (Hodgeson, 1990).

3.9 Quality Assurance and Quality Control

To ensure the validity of the results of this investigation and to identify the source of any errors, measurements were repeated twice. Also, in order to verify the accuracy of the in-house laboratory results for THMs and HAAs, additional random samples were collected and sent to Broward Testing Laboratory, LTD in Fort Lauderdale, Florida. The laboratory is an EPA accredited lab. THMs were analyzed by utilizing Method 524.2 - Capillary Column Gas Chromatograph/Mass Spectrometry. HAAs results were obtained by utilizing Method 552.2 - Liquid-Liquid Extraction, Derivatization and Gas Chromatography with electron Capture Detection.

CHAPTER 4

RESULTS

4.1 Public Water Plants Operations And Sampling

On October 30, 2001, February 15, 2002, July 17, 2002, October 16, 2002 and March 19, 2003, water was sampled from two plants (A and B) that operated in parallel from a common source of water. Additional samples were collected from two Pilot Treatment Facilities that purchase Plants A and B effluent and treat it further for CSD production.

As a result of prior ongoing study the treatment process in Pilot Treatment Facility A was modified by adding a Reverse Osmosis unit after the final GAC filter followed by a storage tank with a chlorine residual of 1-2 mg/l followed by a second large GAC and 10-micron polisher filter.

Figure 1: Pilot plant A modified schematic (2A)

Raw Water (From Philadelphia Water Department)→ flocculation, coagulation, sedimentation → Sand/Gravel filtration → GAC Filtration → Reverse Osmosis → Storage (1-2 mg/l Chlorine) → GAC → Polisher → Plant.

The treatment process in Pilot Treatment Facility B was modified to include a GAC filter at the start of the treatment process. Cellulose Acetate chlorine tolerant reverse osmosis membranes were replaced with TFC – Thin Film Composite - unit that has a higher rejection capability. The disinfection process at the storage tank for RO effluent water was changed to continuous ozonation at 0.1 mg/l, UV light was installed after the storage tank for the ozone destruction when water is pumped to the plant followed by a GAC and 10-micron polisher filter.

Figure 2: Pilot plant B modified schematic (2B)

Raw Water (From Trenton Water Works)→ Sand/Gravel filtration → GAC Filtration → Reverse Osmosis → Storage (0.1 mg/l Ozone) → UV → GAC → Polisher → Plant.

All four plants were sampled at the raw water influent and plant effluent.

4.2 Water Quality

On the days of sampling, information was also collected on the water quality at each of the municipal plants:

Table 4: Water quality information at each municipal plant (Units in mg/l):

	10/30/2001		2/15/2002		7/17/2002		10/16/2002		3/19/2003	
Parameter	**Plant A**	**Plant B**	**Plant A**	**Plant B**	**Plant A**	**Plant B**	**Plant A**	**Plant B**	**Plant A**	**Plant B**
RAW WATER										
PH	7.3	7.2	6.9	6.9	7.3	7.3	7.6	7.3	7.5	7.5
Chlorine	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromide	0.058	0.062	0.022	0.031	0.05	0.041	0.2	0.22	0.023	0.025
TOC	6.44	6.28	6.18	6.17	4.21	4.21	5.87	5.92	4.27	4.5
EFFLUENT WATER										
PH	7.4	6.9	7.2	6.8	7.4	6.9	7.4	7.2	7.5	6.8
Alkalinity	69.0	65.0	27.0	32.0	49.0	42.0	61.0	60.0	38.0	40.0
Chlorine	3.2	1.1	3.5	1.2	3.1	1.2	3.8	1.2	3.3	1.2
Bromide	0.05	0.06	0.01	0.015	0.02	0.02	0.06	0.06	0.012	0.015
TOC	3.46	2.18	3.01	2.59	2.02	2.69	2.39	1.51	1.18	2.45

Raw water TOC ranged from 4.3 to 6.4 mg/l. In both plants the treatment removed 30-60% of the TOC content. In both plants GAC filtration was used to prevent taste and odor problems in the finished water. It was not used for DBP precursor removal.

Bromide was lowest in winter and highest in summer and fall. Since the source of both plants A and B is the Delaware River, it is influenced by the tides and is prone to flow reversal at the intakes (Leary 2002). Tidal influences were the source of bromide.

The source was low in alkalinity, which caused the pH to drop after treatment.

4.3 DBP Formation in Plant A and Plant B

Tables 5 and 6 show results for DBPs that were analyzed at Plant A and Plant B On 10/30/2001, 2/15/2002, 7/15/2002, 10/16/2002 and 3/19/2003.

Table 5: DBP results at plant A (All units are in µg/l)

	Oct '01	Feb '02	July '02	Oct '02	Mar '03
Chloroform	12.00	27.00	16.00	18.00	20.00
Bromodichloromethane	13.00	5.30	7.00	24.00	8.00
Dibromochloromethane	5.00	0.80	2.00	11.00	3.00
Bromoform	0.70	0.10	0.30	2.00	0.00
THMs	**30.70**	**33.20**	**25.30**	**55.00**	**31.00**
Monochloroacetic Acid	0.00	2.30	2.20	0.00	0.00
Monobromoacetic Acid	0.00	0.00	0.00	0.00	1.00
Dichloroacetic Acid	6.70	11.00	6.40	4.60	17.00
Bromochloroacetic Acid	3.00	1.20	2.70	3.40	2.60
Dibromoacetic Acid	1.00	0.00	1.00	2.60	0.00
Trichloroacetic Acid	6.00	19.00	2.20	1.20	21.00
HAAs	**16.70**	**33.50**	**14.50**	**11.80**	**24.90**

Table 6: DBP results at plant B (All units are in µg/l)

	Oct '01	Feb '02	July '02	Oct '02	Mar '03
Chloroform	43.00	29.00	22.00	34.00	20.00
Bromodichloromethane	28.00	4.30	8.00	34.00	8.00
Dibromochloromethane	7.00	0.70	1.00	13.00	3.00
Bromoform	1.00	0.10	0.00	2.00	0.00
THMs	**79.00**	**34.10**	**31.00**	**83.00**	**31.00**
Monochloroacetic Acid	6.40	4.70	8.20	0.00	0.00
Monobromoacetic Acid	0.00	0.00	0.00	0.00	1.00
Dichloroacetic Acid	27.00	25.00	24.00	17.00	17.00
Bromochloroacetic Acid	8.00	1.70	4.50	7.20	2.60
Dibromoacetic Acid	1.00	0.00	0.00	2.80	0.00
Trichloroacetic Acid	32.00	35.00	29.00	20.00	21.00
HAAs	**74.40**	**66.40**	**65.70**	**47.00**	**41.60**

4.4 DBP Results in Pilot Plants A and B

On the days of sampling, information was also collected on the water quality at each of the municipal plants:

Table 7: Water quality as a result of pilot plant A treatment (all units in mg/l)

	10/30/2001		2/15/2002		7/17/2002		10/16/2002		3/19/2003	
Parameter	**Plant A**	**Pilot A**	**Plant A**	**Pilot A**	**Plant A**	**Pilot A**	**Plant A**	**Pilot A**	**Plant A**	**Pilot A**
PH	7.4	6.5	7.2	6.2	7.4	6.2	7.4	6.4	7.5	6.2
Alkalinity	69	20	27	22	49	22	61	28	38	24
Chlorine	3.2	ND	3.5	ND	3.1	ND	3.8	ND	3.3	ND
Bromide	0.05	0.05	0.01	0.01	0.02	0.02	0.06	0.05	0.012	0.01
TOC	3.46	3.52	3.01	2.82	2.02	2.11	2.39	1.10	1.18	0.50

Table 8 show results for DBPs that were analyzed at Plant A and Pilot Plant on 10/30/2001, 2/15/2002, 7/15/2002, 10/16/2002 and 3/19/2003.

Table 8: DBP formation in pilot plant A (all units in µg/l)

	10/30/01		2/15/02		7/17/02		10/16/02		3/19/03	
	Plant A	Pilot A	Plant A	Pilot A	Plant A	Pilot A	Plant A	Pilot A	Plant A	Pilot A
Chloroform	12	18	27	25	16	16	18	17	20	23
Bromodichloromethane	13	9	5	3	7	6	24	22	8	4
Dibromochloromethane	5	3	1	0	2	2	11	10	5	2
Bromoform	1	1	0	0	0	0	2	2	1	0
THMs	**31**	**31**	**33**	**29**	**25**	**24**	**55**	**51**	**34**	**29**
Monochloroacetic Acid	0	0	2	4	2	4	0	0	3	0
Monobromoacetic Acid	0	0	0	0	0	1	0	0	0	0
Dichloroacetic Acid	7	6	11	12	6	4	5	14	8	19
Bromochloroacetic Acid	3	4	1	2	3	2	3	8	2	3
Dibromoacetic Acid	1	1	0	0	1	1	3	4	0	0
Trichloroacetic Acid	6	5	19	18	2	1	1	10	13	20
HAAs	**17**	**16**	**34**	**35**	**15**	**13**	**12**	**35**	**25**	**42**

Table 9: Water quality as a result of pilot plant B treatment (Units in mg/l):

	10/30/2001		2/15/2002		7/17/2002		10/16/2002		3/19/2003	
Parameter	**Plant B**	**Pilot B**	**Plant B**	**Pilot B**	**Plant B**	**Pilot B**	**Plant B**	**Pilot B**	**Plant B**	**Pilot B**
PH	6.9	6.1	6.8	6.0	6.9	6.2	7.2	6.2	6.8	6.5
Alkalinity	65	14	32	15	42	12	60	16	40	14
Chlorine	1.1	ND	1.2	ND	1.2	ND	1.2	ND	1.2	ND
Bromide	0.06	0.06	0.015	0.01	0.02	0.02	0.06	0.05	0.015	0.01
TOC	2.18	2.14	2.59	2.42	2.69	2.60	1.51	1.06	2.45	2.01

Table 10: DBP formation in pilot plant B (Units in µg/l):

	10/30/01		2/15/02		7/17/02		10/16/02		3/19/03	
	Plant B	Pilot B	Plant B	Pilot B	Plant B	Pilot B	Plant B	Pilot B	Plant B	Pilot B
Chloroform	43	40	29	24	22	22	34	26	20	24
Bromodichloromethane	28	26	4	3	8	7	34	27	8	9
Dibromochloromethane	7	7	1	1	1	1	13	10	3	3
Bromoform	1	1	0	0	0	0	2	1	0	0
THMs	**79**	**74**	**34**	**28**	**31**	**30**	**83**	64	**31**	36
Monochloroacetic Acid	6	8	5	5	8	20	0	0	0	2
Monobromoacetic Acid	0	1	0	0	0	0	0	1	1	0
Dichloroacetic Acid	27	24	25	32	24	18	17	23	17	20
Bromochloroacetic Acid	8	7	2	2	5	9	7	6	3	3
Dibromoacetic Acid	1	1	0	0	0	0	3	3	0	0
Trichloroacetic Acid	32	27	35	33	29	20	20	22	21	22
HAAs	74	68	66	72	66	67	47	56	42	48

4.5 Process Modifications in Pilot Plants to Reduce DBP Levels.

During the summer of 2001 both pilot treatment facilities underwent experimental changes to evaluate water treatment alternatives. This was done in order to determine the best treatment schematic that will achieve compliance with Stage II DBP requirements for THMs and HAAs while properly reducing alkalinity and metal content in water for CSD production.

4.5.1 Pilot Treatment Facility A

The experimental treatment in Pilot Treatment Facility A included the addition of a Reverse Osmosis unit after the final GAC filter. This was followed by a storage tank with a chlorine residual of 1 to 2 mg/l, followed by a GAC and 10-micron polisher filter.

Figure 3: Pilot plant A modified schematic (2A)

Raw Water (Philadelphia Water)→ flocculation, coagulation, sedimentation → Sand/Gravel filtration → GAC Filtration → Reverse Osmosis → Storage (1-2 mg/l Chlorine) → GAC → Polisher → Plant.

The purpose of reverse osmosis was to remove remaining TOCs, bromides and any other NOM material that may still be in the water. New GAC filter was automatically backwashed daily and regenerated with steam weekly. Analysis results for DBPs indicated a major reduction in THMs with a range between 39-63%.

Table 11: Water quality results after pilot plant 2A treatment (Units in mg/l):

	10/30/2001		2/15/2002		7/17/2002		10/16/2002		3/19/2003	
Parameter	**Pilot A**	**Pilot 2A**	**Pilot A**	**Pilot 2A**	**Pilot A**	**Pilot 2A**	**Pilot A**	**Pilot 2A**	**Pilot A**	**Pilot 2A**
PH	6.5	6.2	6.2	6.2	6.2	6.1	6.4	6.2	6.2	6.1
Alkalinity	20	9	22	9	22	5	28	6	24	8
Chlorine	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromide	0.05	0.01	0.01	ND	0.02	0.01	0.05	0.05	0.01	0.01
TOC	3.52	0.11	2.82	0.25	2.11	0.24	1.10	0.14	0.50	0.20

Figures 4 offers a comparison of THMs concentration levels in Plant A – The Philadelphia Water Treatment plant, Pilot A – The private treatment facility purchasing its water from Plant A, and Pilot 2A – The Experimental modification for the treatment system for the private treatment facility.

Figure 4: Impact of pilot plant A modifications on THMs levels (Units in µg/l)

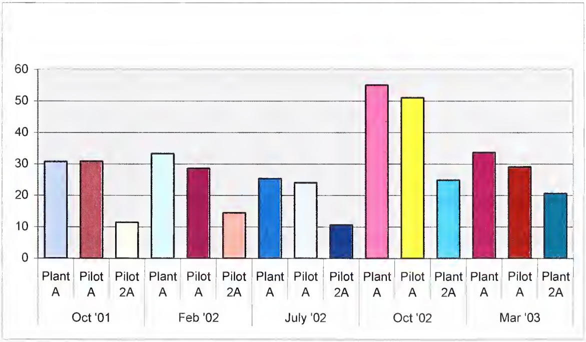


Figure 5: Impact of pilot plant A modifications on HAAs levels (Units in µg/l)

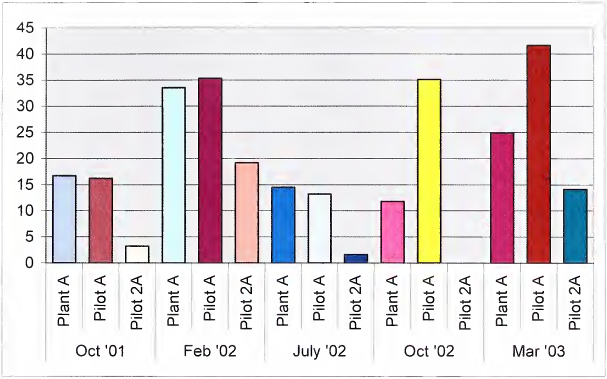


Figure 5 demonstrates the removal efficiency for HAAs utilizing the modified treatment system.

4.5.2 Pilot Treatment Facility B

The experimental treatment in Pilot Treatment Facility B included diverting the water after the initial Sand/Gravel Filtration and installation of a GAC filter at the start of the treatment process. A TFC – Thin Film Composite – Reverse Osmosis unit that has a higher rejection capability than the older unit was leased. A smaller storage tank was purchased and was equipped with continuous ozone injection at 0.1 mg/l. UV light was installed after the storage tank to remove the ozone when water is pumped from the storage tank to the newly installed GAC and 10-micron polisher filter.

Figure 6: Pilot plant B modified schematic (2B)

Raw Water (From Trenton Water Works)→ Sand/Gravel filtration → GAC Filtration → Reverse Osmosis → Storage (0.1 mg/l Ozone) → UV → GAC → Polisher → Plant.

The new initial filter purpose was to reduce DBP load and remove TOCs and chlorine. The TFC Reverse Osmosis purpose was to remove any remaining TOCs, bromides and any other NOM material that may still be in the water. New GAC filter was automatically backwashed daily and regenerated with steam weekly. An ozonated storage tank was brought in to eliminate any potential new formation of HAAs or THMs with chlorine. Analysis results for DBPs indicated a major reduction in THMs. Removal efficiency ranged between 19-52%.

Table 12: Water quality results after pilot plant 2B treatment:

	10/30/2001		**2/15/2002**		**7/17/2002**		**10/16/2002**		**3/19/2003**	
Parameter	**Pilot B**	**Pilot 2B**	**Pilot B**	**Pilot 2B**	**Pilot B**	**Pilot 2B**	**Pilot B**	**Pilot 2B**	**Pilot B**	**Pilot 2B**
PH	6.1	6.1	6.0	6.2	6.2	6.1	6.2	6.2	6.5	6.2
Alkalinity	14	4	15	5	12	2	16	6	14	2
Chlorine	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromide	0.06	0.01	0.01	ND	0.02	0.01	0.05	0.05	0.01	0.01
TOC	2.14	0.11	2.42	0.15	2.60	0.14	1.06	0.21	2.01	0.10

Figures 7 and 8 offers a comparison of DBP concentration levels in Plant B – The Trenton Water Works treatment plant, Pilot B – The private treatment facility purchasing its water from Plant B, and Pilot 2B – The Experimental modification for the treatment system for the private treatment facility.

Figure 7: Impact of pilot plant B modifications on THM levels (All units in mg/l)

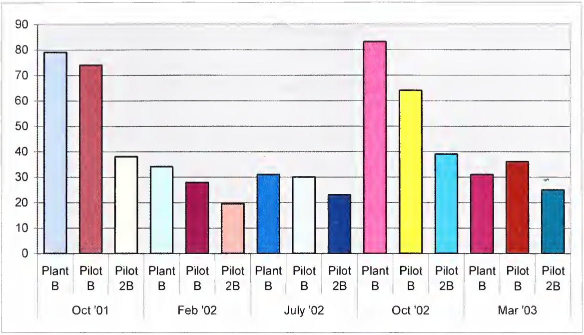
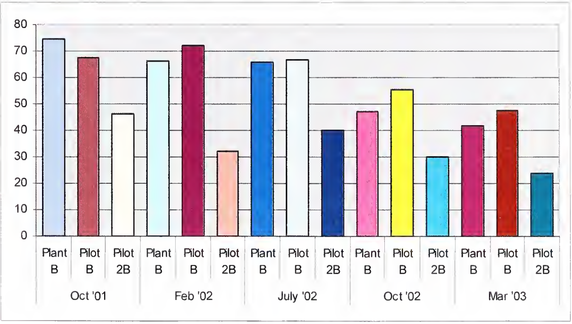


Figure 8: Impact of pilot plant B modifications on HAA levels (All units in µg/l)



CHAPTER 5

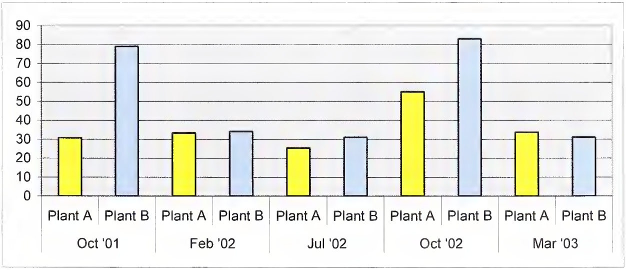
DISCUSSION

5.1 DBP formation in Plants A and B

Figure 9 below shows the seasonal variability in THM formation at plants A and B. The sum of THMs ranged from 31 to 83 µg/l in the plant B effluent. The highest formation was in Oct '02 when the bromide level was the highest.

THMs ranged from 25 to 55 µg/l in the plant A effluent. THM formation in Oct '01 was less than that in Oct '02, most likely due to the difference in bromide concentration between these two periods (0.06 mg/l vs. 0.2 mg/l).

Figure 9: THM results at plants A and B (units in µg/l)



Figures 10 and 11 shows the impact of bromide on THM speciation in plants A and B effluent. In Oct '02, when the bromide level was the highest, there was the greatest shift in speciation to brominated THMs. In Feb '02 and Mar '03, when bromide concentration was the lowest, chloroform was the major THM species formed.

Figure 10: Bromide and TOC impact on THM speciation in plant A (Units in µg/l)

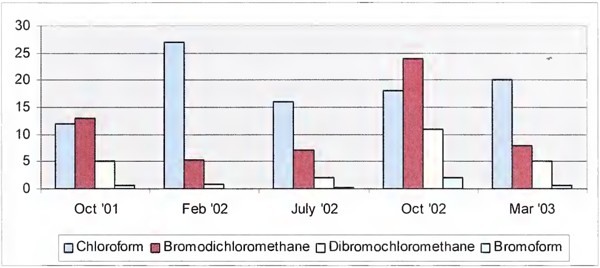


Figure 11: Bromide and TOC impact on THM speciation in plant B (Units in µg/l)

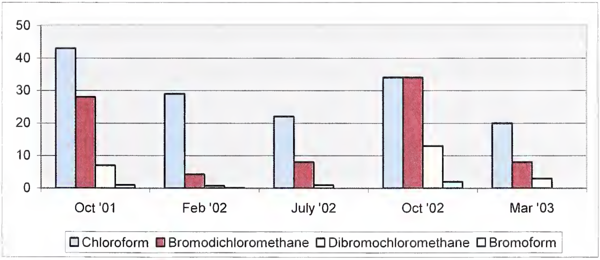


Figure 12 shows the seasonal variability in haloacetic acid (HAA) occurrence at plants A and B. The sum of the five regulated HAAs ranged from 42 to 74 µg/l in the plant B effluent. In plant A HAAs ranged from 12 to 33 µg/l with the highest HAA occurrence during the winter.

Figure 12: HAA results at plants A and B (Units in µg/l)

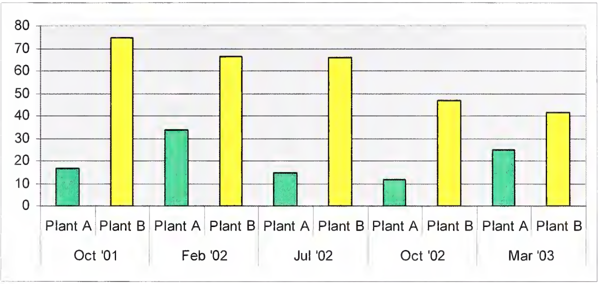
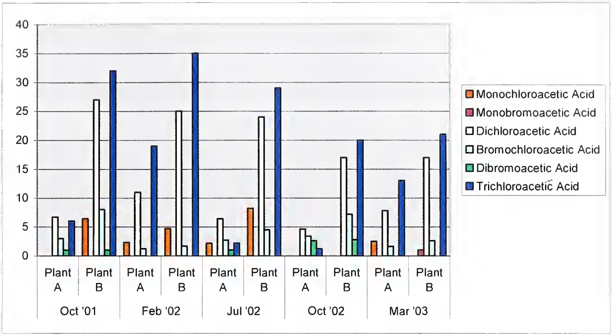


Figure 13 shows the impact of bromide on HAA speciation in plants A and B. In Oct '02, when bromide level was the highest, there was the greatest shift in speciation to brominated HAAs. In Feb '02 and Mar '03, when the bromide concentration was the lowest, dichloroacetic acid and trichloroacetic acid were the major HAA species formed.

Figure 13: HAA speciation at plants A and B (Units in µg/l)



5.2 DBP formation in Pilot Plants A and B

At pilot plants A and B the concentration of HAAs and THMs remained steady or even increased rather than decreased by the treatment methods employed by the plants.

In pilot plant A, the water was chlorinated to 20 mg/l to break the chloramines bond between chlorine and ammonia prior to treatment. GAC filtration was only utilized to remove chlorine. The GAC bed was not properly backwashed and regenerated on daily basis. At times the water was stored for periods exceeding 48 hours with a chlorine residue of 1 to 2 mg/l converting TOCs and bromides into DBPs. As indicated by Table 8, this was observed in Oct '02 and Mar '03 where the water was stored for 48 hours prior to sampling. A significant increase in HAA results for both of those sampling events were observed as a result of extended storage in a disinfection solution.

Figures 14 and 15 illustrate the Impact of Pilot Plant A treatment on the incoming HAAs and THMs loads.

Figure 14: Impact of pilot plant A treatment on THMs formation (Units in µg/l)

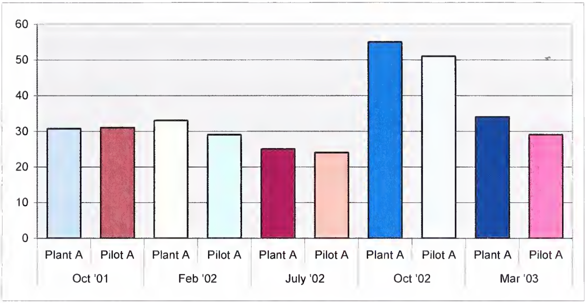
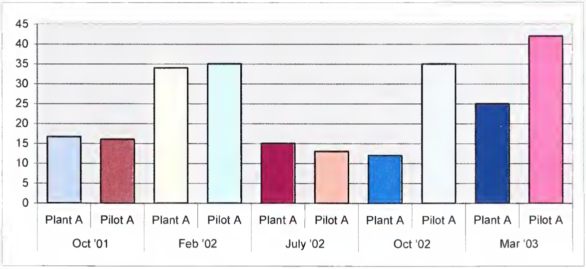


Figure 15: Impact of pilot plant A treatment on HAAs formation (Units in µg/l)



In Pilot Plant B results were similar to Pilot Plant A. The concentrations of HAAs and THMs remained steady. THMs removal was more successful than that for HAAs. The HAAs load actually increased in all sampling periods except Oct '01. This is significant because in Nov '01, the plant changed the chlorine treatment method from Chlorine Dioxide injection to Potassium Hypochlorite. This is a better and more uniformed disinfection method, and the hypochlorite was effective in oxidizing TOCs and bromides. This formed DBPs as indicated by Tables 9 and 10. A drop in TOC concentrations is a result of NOM oxidation, resulting in an increase of DBPs. Inefficient GACs that were not properly maintained, backwashed and regenerated contributed to the system's inefficiency in removing DBPs.

Figures 16 and 17 illustrate the Impact of Pilot Plant B treatment on the incoming THMs and HAAs loads.

Figure 16: Impact of pilot plant B on THMs formation (Units in µg/l)

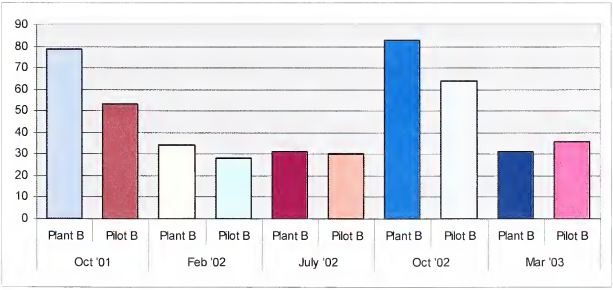
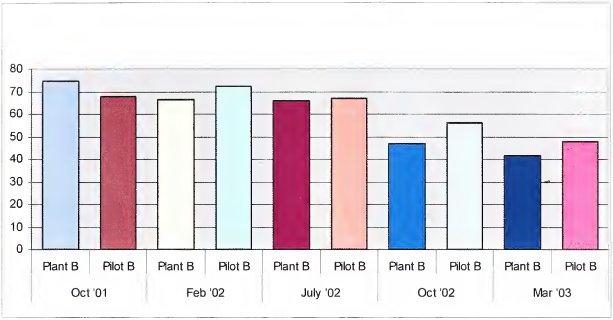


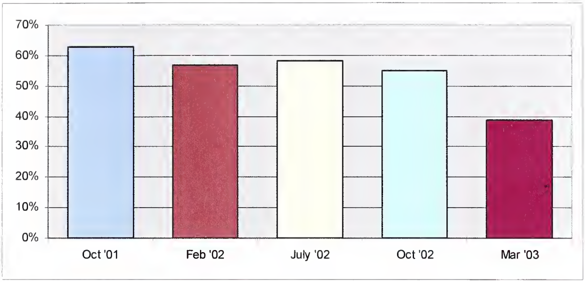
Figure 17: Impact of pilot plant B on HAAs formation (Units in µg/l)



5.3 DBP Removal in Modified Pilot Plant A

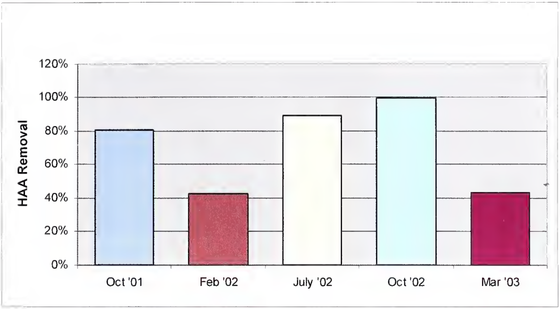
As indicated by figure 18, the removal efficiency for THMs utilizing the modified treatment system ranged from 39% to 63%. THMs removal rate was lowest in Mar '03. This was due to the increased flow of influent water and increase water demand. An increase of water flow through the final GAC filtration unit is inversely proportional to the carbon interaction time with water. Therefore, carbon adsorption of THMs and other organic compounds have decreased.

Figure 18: Removal efficiency of THMs in modified pilot plant A treatment



Removal efficiency ranged from 42% to 100%. HAAs removal rate was also low in Mar '03, which was due to the increased flow of influent water and increase water demand. Figure 18 also shows that when the water temperature was warmer, HAAs were effectively removed. However, when the water was colder, the removal of HAAs was impacted.

Figure 19: Removal efficiency of HAAs in modified pilot plant A treatment



5.4 DBP Removal in Modified Pilot Plant B

As indicated by figure 20, the removal efficiency for THMs utilizing the modified treatment system ranged from 19% to 53%. THMs removal was lowest in Mar '03, as in the case for Plant 2A. This was due to the increased flow of influent water and increase water demand.

Figure 20: Removal efficiency of THMs in modified pilot plant B treatment

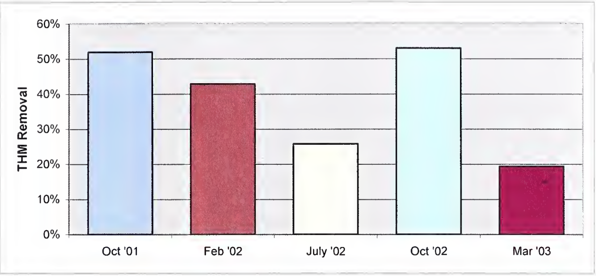
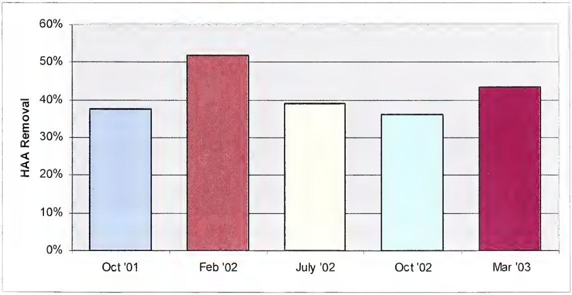


Figure 21 demonstrates the removal efficiency for HAAs utilizing the modified treatment system. Removal efficiency ranged from 36% to 52%. The increase of flow in Mar '03 did not effect the removal of HAAs. Contrary to Pilot Plant A results, the warmer temperature did not increase HAAs removal.

Figure 21: Removal efficiency of HAAs in modified pilot plant B treatment



5.5 Process Modifications Efficiency Comparison

Figure 22: Comparison of THMs removal rate between pilot plants 2A and 2B

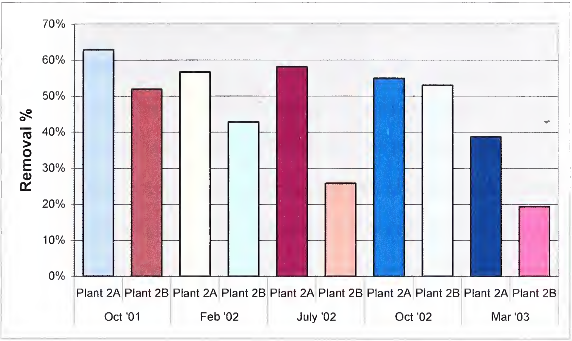
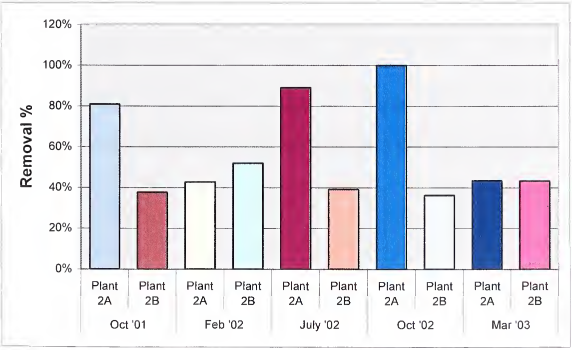


Figure 23: Comparison of HAAs removal rate between pilot plants 2A and 2B



As indicated by the figures 22 and 23 the removal efficiency of THMs and HAAs in the modified pilot plant A are almost consistently at a higher rate than that for the modified pilot plant B. This can be attributed to the different treatment processes of both plants. At pilot plant A, flocculation, coagulation and sedimentation are employed as means for reduction of alkalinity and for the breakup of the chloramines molecules. This also contributed to the removal of NOMs and reduced TOC values. Additionally, the coagulation resulted in an improved GAC removal for TOCs and other DBP precursors. This was because of the reduced initial concentration and the removal of poorly adsorbed highly-molecular weight organics. Also, enhanced coagulation reduced the concentration of the NOMs and increased its adsorbility, due to the reduced pH imparted from the alum dose (Bryant 1996). Pilot Plant B did not employ coagulation. NOMs and TOCs concentrations were not initially reduced and their adsorbility were not enhanced by coagulation. The GAC adsorption residence is too short to remove a significant amount of the NOM matter, especially during high production times. The reverse osmosis system was able to remove the larger precursor material. However, reverse osmosis was not able to reject incoming DBPs and smaller NOMs particles. Ozonation and the final GAC filtration helped eliminate the number of DBPs formed; however, the process in Pilot Plant B was not as effective as that of Pilot Plant A in THMs and HAAs removal.

CHAPTER 6

SUMMARY AND CONCLUSIONS

6.1 Overview

The results obtained from this study give an insight into the nature of THMs and HAAs formation and removal strategies. These results can be utilized for further studies to target problematic compounds like precursors to DBP formation and also for the modification of water treatment plant processes. However, it should be noted that the results obtained are subject to seasonal and climatic variation.

6.2 Impact of TOC and Bromide on DBP formation

Both TOC levels and bromide levels affect DBP formation, but it is chlorine-to bromide ratio and bromide-to-TOC ratio that affects DBP speciation.

As TOC increased or bromide decreased, $CHCl_3$ increased. As bromide increased, bromoform increased. However, as TOC increased, bromoform formation increased. When the bromide level was the highest, there was a shift in speciation to brominated THMs and brominated HAAs. In Feb 2002 and Mar 2003, when bromide concentration was the lowest, chloroform was the major THM species formed and dichloroacetic acid and trichloroacetic acid were the major HAA species formed.

6.3 Precursor Control/Removal

DBP control was accomplished by the focus on removal of the precursors. NOMs, measured as TOCs, and Bromides to a lesser degree.

Techniques utilized to remove NOMs were reverse osmosis membranes, enhanced coagulation, and GAC adsorption. These techniques proved to be very effective. However, they vary in NOMs removal effectiveness, cost, operational complexity, and residuals produced.

The greatest removals were achieved using reverse osmosis membranes, but the process is expensive and residuals are a major issue. The residuals include concentrated brine, which can be difficult to dispose. Reject water from the membrane system can be of concern in some areas, ranging from 10 to 20% of the water entering the facility.

The simplest strategy used was enhancing conventional coagulation through increase in the coagulant dose and lowering the pH. However, the enhanced conditions increased the turbidity in the water.

Initial GAC adsorption added with conventional coagulation, were the most viable options for NOMs removal.

6.4 Removal of DBPs

After the DBPs have formed, it was possible to remove them by subsequent treatment processes (i.e. modified pilot plants 2A and 2B). GAC units that are operated at optimal flows, back-flushed daily and steam-regenerated demonstrated capability to remove THMs in both pilot plants 2A and 2B. However, as pilot plant 2B indicated, GAC proved less efficient for HAAs removal, without the use of conventional coagulation mechanism.

CHAPTER 7

RECOMMENDATION FOR FUTURE RESEARCH

7.1 General

The work presented in this thesis is a part of larger project of investigating the nature and removal of DBPs. This preliminary work should be considered as a basis for future research. The observations and conclusions reached in the analysis of data need to be confirmed through additional tests. Most of the work reported herein included relatively low-TOC source waters. The applicability of the results and conclusions to higher-TOC sources remain to be demonstrated.

7.2 Research Applicability

The research work and experimentation conducted can be applied to minimize DBPs through control of precursors and removal of DBPs. Technologies and treatment methods studied in this thesis can be applied to larger water work systems, especially the two systems that were studied; Philadelphia Water Department and Trenton Water Works.

7.3 Current Methods and Future Directions

While options for removing DBPs after they are formed are needed, the goal should be to minimize the formation of the DBPs in the first place. Through precursor removal, manipulation of water quality parameters, and minimizing the use of oxidants, while still achieving adequate disinfection.

Removal of precursors should be the preferred method for controlling DBPs. Coagulation, GAC, RO membranes, and ozone treatment are currently the best options available. The performance of these options will vary based on water quality and other treatment objectives. Cost, operational complexity, and environmental factors will need to be evaluated for each option. Removing the DBPs after formation, while possible, should be a secondary consideration.

Research continues to be needed. The AWWA Research Foundation has sponsored 72 projects on disinfection and DBPs, with an investment of almost $20 million. At a recent workshop (Bellamy 1994), it was estimated an additional $30 to $50 million would be needed in the next 5 years. Cooperative efforts among water suppliers, research community, and EPA will be needed to address control of DBPs.

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APPENDIX A

ABBREVIATIONS

AWWA	American Water Works Association
CA	Cellulose Acetate
CSD	Carbonated Soft Drinks
DBAA	Dibromoacetic Acid
DBPs	Disinfection Byproducts
DCAA	Dichloroacetic Acid
HANs	Haloacetonitriles
HAAs	Haloacetic Acids
ICR	Information Collection Rule
GAC	Granular Activated Carbon
GC	Gas Chromatograph
MBAA	Monobromacetic Acid
MCAA	Monochloroacetic Acid
MCL	Maximum Contamination Level
NOM	Natural Organic Matter
PAC	Powdered Activated Carbon
RO	Reverse Osmosis
TCAA	Trichloroacetic Acid
TFC	Thin Film Compsite

APPENDIX A
(Continued)

ABBREVIATIONS

TOC	Total Organic Carbon
USEPA	United States Environmental Protection Agency
UV	Ultraviolet Absorbance