Abstract

Michael T. Dowd. Assessment of THM Formation with MIOX. (Under the direction of Dr. Philip C. Singer).

Current regulations on trihalomethane (THM) concentrations have led many utilities to explore the use of other oxidants and disinfectants to partially or completely replace chlorine in their treatment schemes. A mixed oxidant solution, generated electrolytically from brine, by the "MIOX" system, appears to be an attractive alternative to chlorine with respect to disinfection and THM formation. However, little is known about the chemical composition of this mixed oxidant solution except that which is based on electrochemical theory. The primary objective of this investigation was to evaluate the formation of THMs by MIOX and to compare the results with those obtained in control experiments using equivalent amounts of sodium hypochlorite (NaOCl). The secondary objective of this investigation was to characterize the mixed oxidant solution as to its chemical composition.

Model waters of well-known chemical composition as well as several real waters of varying quality were treated with MIOX and with NaOCl under identical experimental conditions, and the extent and rate of THM formation was examined.

The results showed that THM formation in MIOX-treated waters was essentially the same as that in NaOCl-treated waters. Little insight as to the chemical composition of the mixed oxidant solution was gained in this investigation.

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Michael T. Dowd

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Chapter 1 - Introduction

Chlorine has been used as a disinfectant and an oxidant for water supplies for over 100 years and is still the most commonly used disinfectant in the U.S.(Water Quality Division Disinfection Committee, 1992). The appeal of chlorine, however, is diminishing due to the formation of trihalomethanes (THMs), a class of halogenated disinfection by-products (DBPs) first discovered in finished drinking water by Rook (1974). THMs were linked to the practice of water chlorination by the National Organics Reconnaissance Survey conducted by the U.S. Environmental Protection Agency (USEPA) in 1975 (Symons et al. 1975). THMs have been linked to gastrointestinal cancer and urinary tract cancer (Clark et al. 1986). THMs are currently regulated by the USEPA at a maximum contaminant level (MCL) of 0.10 mg/L total trihalomethanes (TTHMs) based on a running annual average of four quarterly samples per treatment plant (U.S. EPA, 1979).

There are several strategies for controlling THM formation. These strategies include source water control, and THM precursor removal processes, i.e. granular activated carbon (GAC) adsorption and membrane filtration. Another THM control strategy, air stripping, removes THMs from water after they have been formed. This report addresses yet another THM formation control strategy, the use of alternative disinfectants/oxidants. Two commonly used alternative disinfectants/oxidants are chlorine dioxide (ClO_2) and ozone (O_3). Both ClO_2 and O_3 are effective for oxidation and disinfection, yet neither produce THMs.

The primary objective of this study was to assess the formation of THMs by "MIOX", an electrolytic mixed oxidant generation system developed by the Los Alamos Technical Associates (LATA) of Albuquerque, New Mexico. The MIOX system produces a mixed oxidant solution by electrolyzing brine and separating the resulting products. The anodic product, termed "SCOLA" (solution coming off LATA's anode), is acidic and is presumed to contain chlorine, ozone, chlorine dioxide, hydrogen peroxide, and possibly some radical species. The cathodic product is a mild base that contains sodium hydroxide and hydrogen. The anodic and cathodic products are separated within the electrolysis cell. A secondary objective of the investigation was to characterize the mixed oxidant stream, SCOLA.

The primary objective was met by treating a series of waters with SCOLA and measuring THM concentrations and residual oxidant concentrations under a set of controlled treatment conditions. Both model waters of well-known chemical composition as well as several real waters from locations in the U.S. and Canada were used. The results were compared to those obtained using an equivalent amount of NaOCl. This study also evaluated the effects of total organic carbon (TOC) concentration and pH on THM formation in SCOLA-treated waters.

Chapter 2 - Background

2.1 THM Formation and Control

2.1.1 THM Formation

THMs are volatile, halogenated DBPs that are formed from the reaction of chlorine and bromide with natural organic matter (NOM) that is present in all water supplies. A general reaction that illustrates THM formation is the following:

$$\mathrm{HOCl} + \mathrm{Br}^{-} + \mathrm{NOM} \text{ ----> } \mathrm{THMs} + \text{other halogenated DBPs} \qquad (1)$$

More specifically, THMs are formed from substitution reactions in which three of the hydrogen atoms of a methane structure are replaced by a chlorine or a bromine atom (see Figure 2-1).

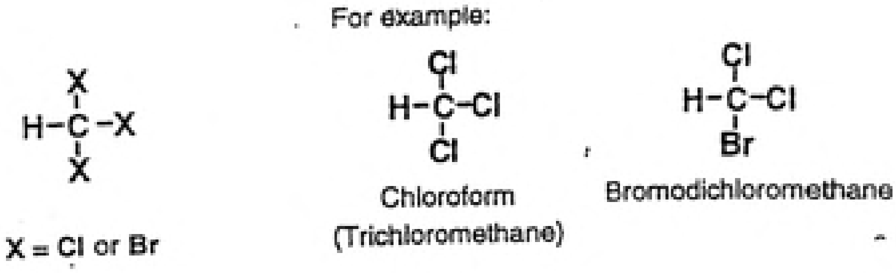

Figure 2-1 Trihalomethane Chemical Structures

In the absence of bromide ion, only chloroform ($CHCl_3$) will be formed. When bromide is present, it can be oxidized by chlorine to hypobromous acid (HOBr), which in turn will react with NOM to form the brominated species bromoform ($CHBr_3$). The action of both chlorine and hypobromous acid leads to the formation of the mixed bromo-chloro species, bromodichloromethane ($CHBrCl_2$) and dibromochloromethane ($CHBr_2Cl$).

Parameters that influence the level of THM formation include the following:

- pH
- Temperature
- Nature and concentration of NOM
- Contact time
- Chlorine dose and residual
- Bromide concentration

THM formation is a base-catalyzed reaction that has been shown to increase with increasing pH (Johnson and Jensen, 1986). The nature of the NOM has a significant impact on the level of THMs formed in chlorinated waters. Work done by Reckhow, Singer, and Malcolm (1990) showed a good correlation between THM formation and the activated aromatic content of NOM. However, the hydrophilic fraction may also contribute significantly to THM formation (Owen et al., 1992). Total Organic Carbon (TOC) and UV-254 absorbance are two surrogates for DBP precursors that have been reported; correlations between these parameters and THM formation have been developed (Edzwald et al., 1985; Singer and Chang, 1989).

The relationships between the aforementioned parameters and THM formation has been studied by several researchers in an effort to develop predictive models of THM formation. One such model is that developed by Amy et al. (1987):

$$\mathrm{TTHM} = 0.00309[(\mathrm{TOC})(\mathrm{UV\text{-}254})]^{0.440}(\mathrm{Cl_2})^{0.409}(t)^{0.265}(T)^{1.06}$$
$$\times\ (\mathrm{pH}-2.6)0^{.715}(\mathrm{Br}+1)^{0.036} \qquad (2)$$

where TTHM is the total trihalomethane concentration (umol/L), TOC is the total organic carbon concentration (mg/L), UV-254 is the absorbance at 254 nm ($\mathrm{cm^{-1}}$), Cl_2 is the chlorine dose (mg/L), t is time (hours), T is temperature ($^{\circ}$C), and Br is bromide concentration (mg/L).

2.1.2 THM Control

Since the regulation of THMs by the EPA in 1979 (U.S. EPA, 1979), a considerable effort has been made to identify means of controlling the formation of THMs as well as other DBPs. Several strategies were developed based on what was known about DBPs and how they are formed. These strategies include:

1. Source control
2. Precursor removal strategies
    - Enhanced coagulation
    - Granular activated carbon (GAC) adsorption
    - Membrane filtration

3. DBP removal strategies
    - Air stripping
4. Alternative disinfectants/oxidants
    - Ozone
    - Chlorine dioxide
    - Combined chlorine, i.e. chloramines
    - Permanganate
    - Advanced oxidation processes (AOPs)
    - UV irradiation

The first two strategies are preventive in nature in that they attempt to reduce the concentration of NOM, the principal precursor of THM formation, prior to chlorination. These two strategies, although very useful, lie outside the scope of this project and therefore will not be discussed further. The third strategy, like the first two, is not within the scope of this project and will also not be discussed further. The fourth strategy, alternative disinfectants/oxidants will be addressed in the following sections dealing with the chemistry of disinfectants and oxidants.

2.2 Chemistry of Disinfectants and Oxidants

Disinfectants are a class of compounds that, due to their chemical characteristics, are biocidal agents capable of inactivating microbial contaminants in water. The most commonly used disinfectants in water treatment are free chlorine, combined chlorine (i.e. chloramines), ozone and chlorine dioxide. The disinfecting strength of these species is typically evaluated for regulatory purposes in terms of "CT" values as a result of the Surface Water Treatment Rule (U.S. EPA. 1989). CT represents the product of the concentration of a disinfectant and the contact time. Disinfectants are ranked according to the CT value required to achieve a certain level of inactivation for a particular microorganism. CT values for several microorganisms for disinfectants commonly used in water treatment are given in Table 2-1.

Table 2-1 C*t Values (mg*min/L) for 99 Percent Inactivation of Microorganisms with Disinfectants at 5°C

	Disinfectant			
Microorganism	Free Chlorine (pH 6 to 7)	Preformed Chloramine (pH 8 to 9)	Chlorine Dioxide (pH 6 to 7)	Ozone (pH 6 to 7)
E. coli	0.034–0.05	95–180	0.4–0.75	0.02
Polio 1	1.1–2.5	770–3740	0.2–6.7	0.1–0.2
Rotavirus	0.01–0.05	3810–6480	0.2–2.1	0.006–0.06
Phage f2	0.08–0.18	–	–	–
G. lamblia cysts	47–>150	–	–	0.5–0.6
G. muris cysts	30–630	1400	7.2–18.5	1.8–2.0

Source: Hoff (1987).

Chlorine, chlorine dioxide, and ozone are also used in water treatment as chemical oxidants. Their uses include oxidation of reduced iron and manganese, oxidation of hydrogen sulfide, control of taste and odor-causing compounds, and removal of color. Table 2-2 lists the half reactions and corresponding electrode potentials of the chemical oxidants commonly used in water treatment.

Table 2-2 Standard Electrode Potentials for Chemical Oxidants Used in Water Treatment (after Glaze, 1990)

Oxidant	Reduction half-reaction	E, °V
Chlorine	$Cl_2(g) + 2e^- \rightarrow 2Cl^-$	1.36
Hypochlorous acid	$HOCl + H^+ + 2e^- \rightarrow Cl^- + H_2O$	1.49
Hypochlorite	$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$	0.90
Chloramines, basic		
Monochloramine	$NH_2Cl + H_2O + 2e^- \rightarrow Cl^- + NH_3 + OH^-$	0.75
Dichloramine	$NHCl_2 + 2H_2O + 4e^- \rightarrow 2Cl^- + NH_3 + 2OH^-$	0.79
Chloramines, acidic		
Monochloramine	$NH_2Cl^+ + H^+ + 2e^- \rightarrow Cl^- + NH_4^+$	1.40
Dichloramine	$NHCl_2 + 3H^+ + 4e^- \rightarrow 2Cl^- + NH_4^+$	1.34
Ozone, acidic	$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$	2.07
Ozone, basic	$O_3 + H_2O \rightarrow O_2 + 2OH^-$	1.24
Hydrogen peroxide		
Acidic	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78
Basic	$HO_2^- + 2e^- + H_2O \rightarrow 3HO^-$	0.85
Chlorine dioxide	$ClO_2 + 2H_2O + 5e^- \rightarrow Cl^- + 4OH^-$	1.71
Permanganate		
Acidic	$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68
	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.49
Basic	$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4HO^-$	0.58
Oxygen		
Acidic	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23
Basic	$O_2 + 2H_2O + 4e^- \rightarrow 4HO^-$	0.40

The following sections describe the chemistry of the three most commonly used oxidants/disinfectants in water treatment: chlorine, ozone, and chlorine dioxide.

2.2.1 Chlorine Chemistry

Chlorine is employed by water treatment plants either as a gas or as a sodium hypochlorite solution. When chlorine gas is dissolved in water, it hydrolyzes rapidly:

$$Cl_2 + H_2O \text{ ----> } HOCl + H^+ + Cl^- \qquad (3)$$

Complete hydrolysis occurs within only a few tenths of a second at 18 C (White, 1992). When a hypochlorite solution is added to water, the following reaction occurs:

$$NaOCl + H_2O \text{ ----> } HOCl + Na^+ + OH^- \qquad (4)$$

HOCl is a weak acid and therefore exists in equilibrium with its deprotonated form OCl^-, with HOCl being the more effective disinfectant of the two. This relationship is shown by Eq. 5:

$$HOCl = H^+ + OCl^- \quad Ka = 2.6 \times 10^{-8} \ @25\ C \qquad (5)$$

The extent of dissociation can be determined by rearranging Eq. 5:

$$Ka = [(H^+)\ (OCl^-)\ ]/\ (HOCl) \qquad (6)$$

The dissociation constant, Ka, is temperature-dependent and increases with increasing temperature. The effect of pH on the distribution of the chlorine species can be illustrated most clearly by Figure 2-2.

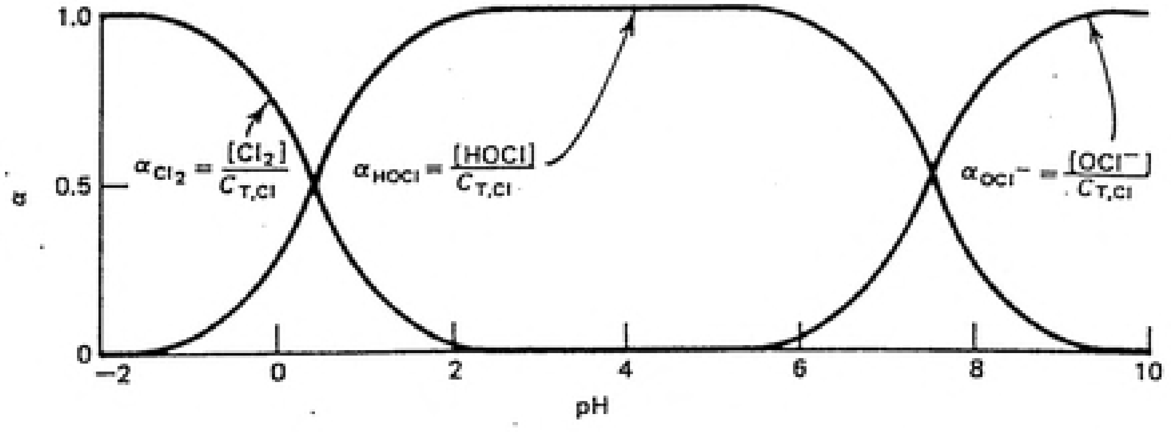

Figure 2-2 Effect of pH on Chlorine Species Distribution at 25°C (after Snoeyink and Jenkins, 1980)

Chlorine is used in water treatment at both an oxidant and a disinfectant. Chlorine oxidation involves a 2-electron transfer (see Table 2-2).

Chlorine is also a potent and versatile biocide. It can be used to inactivate a variety of microorganisms (see Table 2-2). Because HOCl is a more potent biocide than OCl^-, the efficacy of chlorine is pH sensitive and decreases with increasing pH.

As noted previously, chlorine reacts with NOM to produce THMs and other halogenated DBPs. Chlorine dose and free chlorine residual are two parameters that determine the rate and extent of THM formation (see Eq. 2). Increasing chlorine doses result in faster rates of chlorine consumption with correspondingly faster rates of THM formation (Kavanaugh, 1980). THM formation will continue as long as there is a free chlorine residual present (Singer, 1989).

2.2.2 Ozone Chemistry

Ozone is an unstable gas that must be generated on-site. It is the most powerful single oxidant and disinfectant used in water treatment today. Ozone oxidizes inorganic substances, i.e. sulfides, ferrous iron, and manganese, completely and rapidly.

Ozone also oxidizes organic substances. Of particular importance is the oxidation of humic substances which are the principal precursors of THMs (Stevens et al, 1976; Babcock and Singer, 1979; Christman et al, 1983). Ozone oxidation occurs via two different pathways, one being a direct reaction with molecular ozone, the other consisting of indirect reactions with radical species (e.g. $OH^{\bullet}$) formed from the decomposition of ozone in water (Hoigne and Bader, 1976). The direct reaction is more selective and is often slower than the radical pathway (Hoigne and Bader, 1976). The radical pathway is initiated by hydroxide ions and, therefore, molecular ozone is less stable at elevated pH. However, the presence of species that scavenge $OH^{\bullet}$ radicals, such as carbonate and bicarbonate ions, increases its stability. The oxidation potential of ozone is shown in Table 2-2.

The effect that ozone has on THM precursors has been studied by several researchers. Ozonation has been shown to both increase and decrease the trihalomethane formation potential (THMFP) of raw waters and humic extracts (Trussell and Umphres, 1978). Most researchers, however, have found that at practical ozone doses of 0.5 - 1.0 mg O_3/mg TOC, the THMFP of a water is only reduced by 10-20% (Trussell and Umphres, 1978; Jacangelo et al, 1989; Chang and Singer, 1991). The key parameters that seem to indicate what effect ozone will have are ozone dose, pH, alkalinity, and the nature of the organic matter (Langlais et al, 1991). Reckhow et al (1986) showed that increasing alkalinity had the effect of increasing the percent removal of THMFP by 10 to 30 percent using fulvic acid extracts. This suggests that the direct molecular pathway may be more selective towards THM precursors than the indirect, radical pathway. Reckhow and Singer (1984) also reported increases in THM precursor removal by ozone with increases in alkalinity. Ozonation also has the effect of increasing the assimilable organic carbon (AOC) content or biodegradability of a water (Grasso et al, 1993; Tobiason et al, 1993).

Ozone does not produce THMs on its own, yet it does react with NOM to form various oxidation by-products such as aldehydes, aldo- and ketoacids, organic acids and hydrogen peroxide (Singer 1994). Also, when bromide-containing waters are ozonated, several brominated DBPs may be formed including bromate, bromoform, brominated acetic acids, bromopicrin and brominated acetonitriles (Singer 1994).

The strength of ozone as a disinfectant is evidenced by much smaller CT values than those of the other commonly used disinfectants (see Table 2-1). Despite the superior disinfecting capabilities of ozone, its instability in water requires the use of another disinfectant, such as free or combined chlorine, to provide a residual in the distribution system.

2.2.3 Chlorine Dioxide Chemistry

Chlorine dioxide (ClO_2) is an unstable gas that must be generated on-site. ClO_2 is very soluble in water (approximately 5 times more soluble than Cl_2 at room temperature) (White, 1992). For water treatment applications, it is typically generated by the oxidation of chlorite ion by chlorine under low pH conditions (Glaze 1990) (see Eq. 7):

$$Cl_2 + 2ClO_2^- \text{---->} 2ClO_2 + 2Cl^- \qquad (7)$$

Chlorine dioxide disproportionates to form both chlorite and chlorate (Glaze 1990). This reaction, given by Eq. (8), is base-catalyzed:

$$2ClO_2 + 2OH^- \text{---->} ClO_2^- + ClO_3^- + H_2O \tag{8}$$

ClO_2 oxidation potentially involves a 5-electron transfer [Eq.(9)]:

$$ClO_2 + 2H_2O + 5e^- \text{---->} Cl^- + 4OH^- \quad E^\circ = 1.71\ V \tag{9}$$

Considering that ClO_2 is 52.6% Cl by weight, the equivalent available chlorine content in ClO_2 is 5 (no. of electrons transferred) * 52.6% = 263%. Thus, ClO_2 potentially has approximately 2.63 times the oxidizing power of chlorine (by weight). However, the complete reduction of ClO_2 to Cl^- occurs only under extremely acidic conditions ($pH < 2$). At near neutral pH, only a 1-electron transfer is realized [Eq.(10)]:

$$ClO_2 + e^- \text{---->} ClO_2^- \quad E^\circ = 1.15\ V \tag{10}$$

Thus, under typical water treatment conditions, the principal end-product will be chlorite and not chloride.

Chlorine dioxide is also a potent and versatile biocide. Its efficacy as a disinfectant is equal to or better than free chlorine, yet not as good as ozone (see Table 2-1). ClO_2 is best used as a pre-oxidant and primary disinfectant, with either free or combined chlorine used as a secondary disinfectant.

The reaction products of chlorine dioxide, chlorite and chlorate, as well as chlorine dioxide itself, have all been shown to cause hemolytic anemia in rats and mice when administered via drinking water (Couri et al 1982). As a result, a maximum residual disinfectant level (MRDL) of 0.8 mg/L has been set for ClO_2 by the USEPA as part of the Disinfectants/Disinfection By-Products (D/DBP) Rule (USEPA, 1994). Addtionally, a MCL of 1.0 mg/L has been set for ClO_2^- (USEPA, 1994).

Chlorine dioxide does not react with NOM to form THMs. In fact, chlorine dioxide will oxidize THM precursors and thereby reduce THM formation from subsequent chlorination (Werdehoff and Singer 1987). However, to achieve a significant THM reduction (> 10%), a ratio of ClO_2 dose to TOC concentration of greater than 0.4 (weight basis) is required (Werdehoff and Singer 1987). The implications of this fact are significant when the ClO_2^- MCL is taken into account. Because 60-70% of ClO_2 consumed is converted to ClO_2^- (Werdehoff and Singer, 1987) a ClO_2 dose of 1.2 to 1.4 mg/L appears to be an upper limit in order to comply with the 1.0 mg/L ClO_2^- MCL. Therefore, reductions in THM formation greater than 10% are possible in practice only for waters with TOC concentrations less than 4 mg/L.

2.3 Mixed Oxidant Generation Technology

The electrolytic generation of mixed oxidants is a new technology that has its roots in the electrolytic generation of chlorine. The process of generating chlorine electrolytically is well-understood and has been used since the late 1800s (White, 1992). Despite its advantage over chlorine gas in terms of safety, on-site electrolytic chlorine generation is not a common practice in the water treatment field. Reasons for the lack of interest include the higher cost of electrolytic systems (both capital, and operation and maintenance) as compared to conventional gas chlorination systems, as well as the elevated levels of total dissolved solids (TDS) in the electrolysis product streams (White, 1992). Interest in mixed oxidant generation began in 1982 when the Pan American Health Organization (PAHO) began promoting development of technology for on-site generation of chemicals to disinfect the drinking water supplies of small or remote communities in Latin America and the Caribbean (Reiff, 1988). PAHO concluded, based on a review of the literature and discussions with agencies, institutions, scientists and manufacturers that it was usually simpler and cheaper to generate a mixture of oxidants than a single pure oxidant (Reiff, 1988). As a result of PAHO's promotion, two groups of mixed oxidant generators evolved, one relying on electrolysis and the other on photolysis. The electrolytic devices were further subdivided into gas- and liquid-phase oxidant generators. The device developed by LATA, on which this project focused, is a liquid-phase oxidant generator. A schematic diagram of the LATA's electrolysis cell is shown in Figure 2-3.

These devices differ from their chlorine-generating predecessors primarily in the geometry of the electrolysis cell, the coating used on the anode, the configuration of the anode, and the applied potential. It was speculated that, in addition to chlorine, these devices produced ozone, chlorine dioxide, hydrogen peroxide and radical species (Reiff, 1988). This supposition was based primarily on electrochemical theory.

If these non-chlorine oxidants are indeed being produced, particularly ozone, the mixed oxidant solutions are potentially more potent disinfectants than free chlorine alone. Some

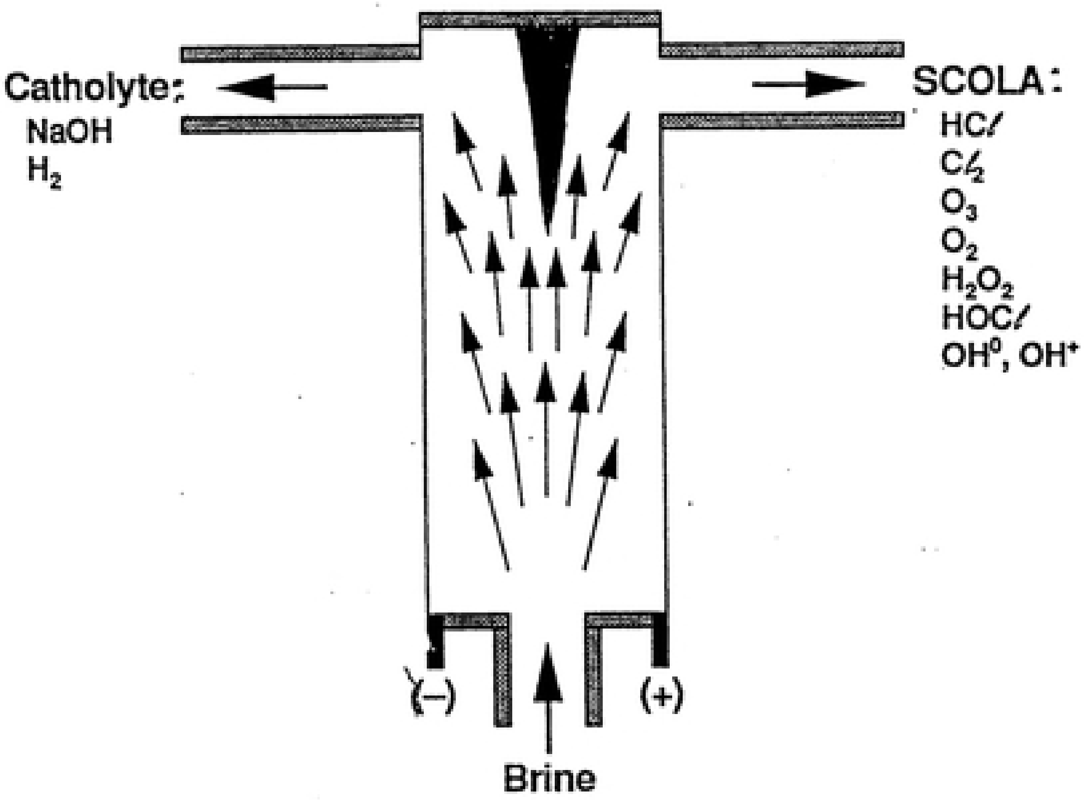

Figure 2-3 Schematic of MIOX System Electrolysis Cell

evidence has been presented which appears to support this theory. Pendergrass et al. (1987), using an electrolysis cell of the Los Alamos Technical Associates (LATA), reported superior kills of *Legionella pneumophila* with the mixed oxidant solution than with free chlorine alone. Other reports on the disinfecting capabilities of mixed oxidants are cited by Reiff (1988), yet little can be concluded from these due to variations in experimental conditions and the lack of controls for some experiments. Current research underway at the University of North Carolina at Chapel Hill (UNC-CH) may help to elucidate some of these early findings (Venczel and Sobsey, unpublished).

In light of the previous discussions on ozone and chlorine dioxide chemistry, specifically their effects on THMFP, the appeal of these mixed oxidant generators to water treatment plant operators is apparent. If ozone and chlorine dioxide are indeed being produced, then they may oxidize a portion of the NOM that would otherwise react with free chlorine to form THMs.

The composition of these mixed oxidant streams is still relatively unknown. This is due in large part to limitations of current analytical techniques used to measure residual disinfectant concentrations. Conventional techniques such as the iodometric titration (Method 408A, Standard Methods, 1989) and the N,N-diethyl-*p*-phenylenediamine (DPD) procedure (Method 408D, Standard Methods, 1989) are not capable of differentiating between chlorine and other oxidants such as ozone and chlorine dioxide, and all three species are capable of interfering with each other to some extent (Gordon et al, 1987). Reliable measurements of free chlorine may be made in the presence of combined chlorine using the amperometric titration procedure (Method 408C, Standard Methods, 1989), and with modifications described by Aieta et al (1984) Cl_2 may be distinguished from $Cl0_2$, ClO_2^-, and ClO_3^-.

2.4 Interactions Between Oxidants

Pertinent to any study of mixed oxidant technology is a discussion of how different oxidants behave in the presence of other oxidants. Little research has been done on the chemistry of mixtures of oxidants, yet some information can be gleaned from the literature. Hoigne et al (1985) investigated the reactions of ozone with both chlorine and chlorine dioxide. They concluded that chlorine could not co-exist with ozone for more than a few minutes at neutral pH when the reactants were present initially in the mg/L range. The stability of chlorine in the presence of ozone is further decreased under alkaline conditions due to the disassociation of HOCl to OCl^- (Hoigne et al, 1985). Under acidic conditions, the reaction between chlorine and ozone is relatively slow, and the half-life of ozone is about 10 minutes when present initially in the mg/L range (Hoigne et al, 1985). Ozone and chlorine dioxide react rapidly over the pH range of 2-9, and chlorine dioxide can not co-exist for more than a few minutes with an excess of ozone when present initially in the mg/L range (Hoigne et al, 1985).

When ClO_2 and Cl_2 are present in the same solution, the following reaction occurs:

$$HOCl + ClO_2 = ClO_3^- + Cl^- + H^+ \qquad (11)$$

This reaction is slow in acid solutions, yet fairly rapid under neutral or alkaline conditions when high reactant concentrations (1500 - 3000 mg/L) are used (Dodgen and Taube, 1949). When concentrations representative of water treatment conditions are used, the reaction occurs slowly in distilled water at pH 7 (White, 1972).

Chapter 3 - Experimental Methods

3.1 Experimental Design

In this study, the effects of TOC concentration, contact time, and pH on THM formation were examined in waters treated with SCOLA and an equivalent amount of NaOCl as a control. Experiments were done on model waters of well-known chemical composition as well as on real waters collected from several locations in the United States and Canada. In addition to these THM formation studies, work was also done with the objective of characterizing SCOLA.

3.1.1 SCOLA Characterization

The composition of the mixed oxidant stream at the onset of the project was speculative at best, based primarily on electrochemical theory. Little information on SCOLA composition was available from LATA. The oxidant species that were considered to be possible constituents of SCOLA were Cl_2, O_3, ClO_2, H_2O_2, and $OH^{\bullet}$. Recognizing that the flow rate of the brine through the cell as well as the concentration of the brine affect the characteristics of SCOLA, it was necessary to first define the operating conditions that produced an acceptable SCOLA according to LATA personnel. Keeping the brine concentration constant at 8 g/L NaCl, the flow rate of the brine through the cell was varied from 4 to 12 gallons per hour (gph), and the SCOLA stream was characterized at each flow rate as to total oxidant concentration, free chlorine concentration, pH, and oxidation reduction potential (ORP). The catholyte was analyzed for free chlorine concentration and pH in order to assess the mixing conditions that existed in the cell. Once the baseline operating conditions had been established, the SCOLA produced was analyzed for ClO_2 and O_3 in addition to the parameters indicated above.

3.1.2 Model Water Studies

The model water studies were designed to examine the effect of varying TOC concentrations and pH on THM formation in waters treated with SCOLA, and to compare the results with those obtained in NaOCl control experiments. The model waters were dosed with sufficient amounts of SCOLA and NaOCl to ensure a 1 mg/L free chlorine residual after a contact time of 24 hours. All solutions were buffered at a constant pH and were held in the dark at room temperature for the designated storage period. After the 24-hour contact period, the residual Cl_2 concentration was measured and samples were taken for THM analysis. These experiments were done at TOC concentrations of 2, 4, and 8 mg/L humic acid (as HA) and at pH 6, 7, and 8. Aldrich Humic Acid (Milwaukee, WI) was used as the source of organic material for these model water studies. Table 3-1 illustrates the test matrix used in the model water studies.

3.1.3 Real Water Studies

To validate the results obtained from the model water studies, several real waters were obtained from a number of locations in the U.S. and Canada. Both raw and settled waters were used and, in all cases, the samples were taken before the application of chlorine to the water. These waters were treated in the same manner as the model waters, i.e. they were buffered at a constant pH, dosed with sufficient amounts of NaOCl and SCOLA to ensure a 1 mg/L free

Table 3-1 Test Matrix for Model Water Studies

TOC concentration mg/L as HA pH	2	4	8
6		X	
7		X	
8	X	X	X

chlorine residual after 24 hours, held in the dark at room temperature, and sampled for THMs and free chlorine after 24 hours.

3.2 Materials and Reagents

3.2.1 High Purity Water

Deionized, organic-free water (Dracor Systems, Durham, NC) that has been determined to be chlorine-demand-free (CDF) was used for dilution water for all of the reagents as well as for the model water test solutions. Distilled water was used to make the brine feed for the MIOX system.

3.2.2 Glassware

All glassware was made chlorine-demand-free by soaking it in a 15 mg/L chlorine solution for at least 24 hours. The glassware was then rinsed thoroughly with CDF water and dried in an oven. After drying, the glassware was either glass-stoppered or covered with aluminum foil. This procedure was repeated every 2 to 3 months. In the time between these rigorous cleanings, glassware that had been used was rinsed copiously with CDF water and oven-dried.

3.2.3 Preparation and Standardization of NaOCl Solutions

NaOCl (Fisher Scientific, Pittsburgh,PA) at a concentration of 4% was used as the stock Cl_2 solution. The stock solution was stored at 4°C in the dark. Working solutions of about 300 mg/L were made by diluting this stock solution approximately 133:1. The dilutions were standardized using the iodometric procedure detailed in Standard Methods (Method 408A, Standard Methods, 1989). Working solutions were kept for 1 week and were standardized prior to each use.

3.2.4 Preparation of Humic Acid Stock Solutions

Humic acid stock solutions were prepared by dissolving appropriate amounts of commercial grade humic acid (Aldrich Chemical Co., Milwaukee, WI) in CDF water to yield a 400 mg/L (as HA) solution. Stock solutions were made fresh prior to each experiment.

3.3 Experimental Procedures

3.3.1 SCOLA Characterization

SCOLA was generated using a 12-volt brine pump system (BPS). The brine feed consisted of appropriate amounts of reagent grade NaCl (Mallinckrodt Specialty Chemicals Co., Paris, KY) dissolved in distilled water. Fresh SCOLA was generated prior to every experiment. The MIOX system was fitted with a flow-through vessel consisting of a 250-mL Erlenmeyer flask connected in line to the anode discharge tubing (see Figure 3-1). Samples were taken from the flow-through cell while the system was running. Table 3-2 lists the oxidant species that were Table analyzed for along with the corresponding analytical method.

Table 3-2 Oxidant Species Analyzed and Corresponding Analytical Methods

Oxidant Species	Analytical Method
Total oxidants	Iodometric Method I (Method 408A, Standard Methods, 1989)
Free chlorine	Amperometric titration (Method 408C, Standard Methods, 1989)
Chlorine dioxide	Differential amperometric titration (Aieta et al, 1984)
Ozone	Indigo decolorization procedure (Method 4500-O_3 B, Standard Methods, 1989)

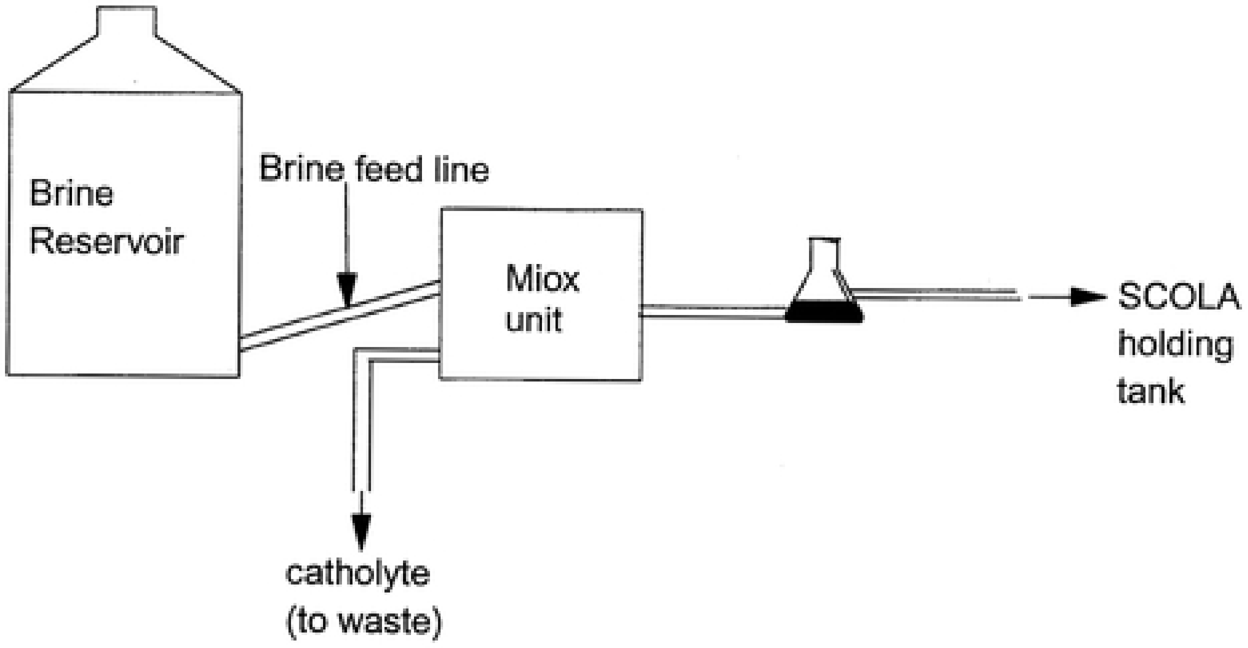

Figure 3-1 Miox System Configuration

3.3.2 Model Water Studies

Figure 3-2 illustrates the procedures used in the model water studies and real water studies. The reaction vessels used in these experiments were 300-mL BOD bottles. BOD bottles were chosen because they could be conveniently made head space-free and therefore prevent the loss of any THMs due to volatilization during storage. The solutions were buffered at the appropriate pH using 15 mL of a 1 M phosphate buffer stock solution. The stock buffer solution was prepared by dissolving an appropriate amount of Na_2HPO_4 in CDF water. The pH of the buffer solution was adjusted using concentrated HCl added drop-wise. Humic acid was added to the BOD bottles from a 400 mg/L (as HA) stock solution in sufficient quantities to yield a 2, 4, or 8 mg/L HA solution (as HA). The bottles were then filled to 2/3 capacity with CDF dilution water, and the buffer was added. Chlorine in the form of NaOCl was added to a series of bottles in incrementally larger amounts. After being dosed with NaOCl, the bottles were filled completely with CDF dilution water and the tops were inserted. The bottles were then placed in a cabinet and stored in the dark at room temperature for 24 hours.

SCOLA was generated as described in Section 3.3.1, and characterized as to total oxidant concentration, free chlorine concentration, pH and ORP. Various volumes of SCOLA were then added to another series of bottles containing the same amounts of humic acid, phosphate buffer and CDF dilution water. After filling with CDF water, these bottles were capped and placed in a storage cabinet.

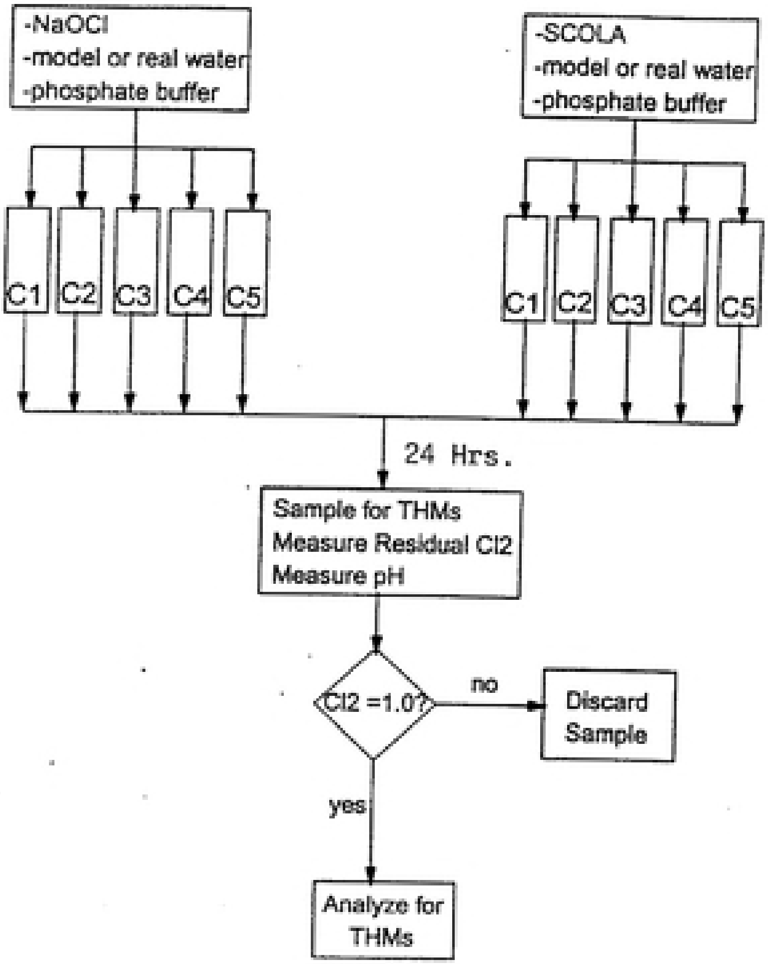

Figure 3-2 Experimental Procedures for Model and Real Water Studies

After the 24-hour contact period, the NaOCl- and SCOLA-dosed solutions were analyzed for residual free chlorine (by amperometric titration) and pH. For THM analysis, two 40-mL Pierce vials were filled to overflowing prior to any analysis of residual chlorine. To these vials, either NH_4Cl or $(NH_4)_2SO_4$ was added to quench the residual Cl_2. Only the test solutions containing residual chlorine concentrations approximately equal to the target residual of 1.0 mg/L were saved for THM analysis while the others were discarded. Samples collected for THM analysis were stored at 4°C for no longer than 2 weeks prior to analysis.

3.3.3 Real Water Studies

Table 3-3 Sources Used in Real Water Studies

Source	Level of Treatment	TOC mg/L
Chapel Hill/Carrboro, NC (OWASA)	raw	4.4
	settled	2.6
Cincinnati, OH	raw	2.1
	settled	1.9
Hackensack, NJ	raw	3.7
E. St. Louis, IL	raw	5.1
Boston Bar, BC, Canada	raw	0.6

Table 3-3 lists the sources of water used in the real water studies. Samples were collected at the utilities by utility personnel and shipped by overnight carrier to UNC-CH. Upon arrival, the TOC concentrations of the waters were analyzed by other UNC-CH graduate students using a Shimadzu TOC-5000 total organic carbon analyzer (Shimadzu Scientific Instruments, Columbus, MD).

The real water studies were conducted in the same manner as the model water studies. All of the real waters were buffered at pH 8 using the same phosphate buffer procedure prior to the addition of NaOCl or SCOLA. A model water consisting of 4 mg/L humic acid (as HA) and buffered at pH 8 was also tested concurrently with each of the real waters as a control.

3.4 Analytical Methods

3.4.1 Iodometric Method

A 20-mL aliquot of either SCOLA or the NaOCl working solution was added to a 125-mL Erlenmeyer flask containing approximately 0.1 g of potassium iodide crystals and 1 mL of concentrated glacial acetic acid. The solution was titrated immediately, while being stirred, with 0.1 N sodium thiosulfate (NTS) until the yellow color of the liberated iodine was almost discharged. One mL of starch solution was then added and the solution was titrated with NTS until the blue color was gone. The total oxidant concentration was then calculated by the following:

$$[\text{total oxidant}],\ \text{mg/L as } Cl_2 = [\text{vol. of NTS} * N_{NTS}\ (\text{eq/L}) * 35{,}450\ (\text{mg/eq})\ ]\ /\ \text{sample vol. (mL)} \qquad (12)$$

3.4.2 Amperometric Titration - Free Chlorine

A 200-mL sample was placed in a 250-mL beaker containing 3 mL of pH 7 phosphate buffer. The sample was then titrated with 0.00564 N phenylarsine oxide (PAO) to the amperometric end-point using a Fisher CL titrimeter, Model 397 (Fisher Scientific, Pittsburgh, PA). The free chlorine concentration was then determined via Eq. 13:

$$[Cl_2],\ \text{mg/L} = [\text{vol. of PAO (mL)} * N_{PAO}\ (\text{eq/L}) * 35{,}450\ (\text{mg/eq})\ ]\ /\ \text{sample volume (mL)} \qquad (13)$$

3.4.3 Amperometric Titration - Total Oxidants

A 200-mL sample was placed in a 250-mL beaker containing 2 mL of 2.5 N HCl. The sample was then stirred and approximately 1 g of potassium iodide crystals was added. Next, the sample was titrated with 0.00564 N PAO to the amperometric end-point. The total oxidant concentration was calculated as follows:

$$[\text{total oxidant}],\ \text{mg/L as Cl2} = [\text{vol. of PAO (mL)} * \text{NPAO (eq/L)} * 35{,}450\ (\text{mg/eq})\ ]\ /\ \text{sample vol. (mL)} \qquad (14)$$

3.4.4 Differential Amperometric Titration

A 5-mL aliquot of SCOLA was taken from the flow-through vessel and diluted 100:1. From this dilution, a 400-mL aliquot was placed in a graduated cylinder and the initial volume was recorded. Approximately 200 mL of the aliquot was then poured into a 250-mL beaker containing 3 mL of pH 7 phosphate buffer and the volume remaining in the cylinder was recorded. After mixing the sample in the beaker, approximately 1 g of KI granules was added and the sample was titrated with 0.00564 N PAO to the amperometric endpoint and the results were recorded as A = mL of PAO/mL of sample. To the same sample, 2 mL of 2.5 M HCl was added to lower the pH to 2, after which the sample was once again titrated with PAO to the amperometric endpoint, and the results recorded as B = mL PAO/mL of sample. The remainder of the 400-mL aliquot was then purged with nitrogen gas to remove any ClO_2. The nitrogen gas was passed through a 5% KI solution prior to passage through the sample to reduce any oxidants that might have been present. After purging for 20 minutes, the two titrations described above were repeated for the purged sample and their results were recorded as C and D = mL PAO/mL of sample. Oxidant concentrations were then calculated using Eqs. 15 and 16:

$$[Cl_2]\text{, mg/L} = [A - (B - D) / 4] * N_{PAO} \text{ (eq/L)} * 35{,}450 \text{ (mg/eq)} \qquad (15)$$

$$[ClO_2]\text{, mg/L} = (5/4)*(B - D) * N_{PAO} \text{ (eq/L)} * 35{,}450 \text{ (mg/eq)} \qquad (16)$$

This procedure (after Aieta et al, 1984) distinguishes between Cl_2, ClO_2, and ClO_2^-. In titration A, all of the free chlorine is reduced to Cl^-, and 1/5 of the ClO_2 is reduced to ClO_2^-. The second titration reduces all of the ClO_2^- to Cl^-. The ClO_2^- titrated in this step consists of that formed by the reduction of ClO_2 in titration A, as well as that which was present initially in the sample. In titration C, all the chlorine that was not volatilized by the purge step is reduced to Cl^-, and in titration D, any ClO_2^- initially present in the sample is reduced to Cl^-.

3.4.5 Indigo Decolorization Procedure

A 1- to 5-mL aliquot of SCOLA was taken from the flow-through vessel and added to a 100-mL volumetric flask containing 10 mL of Indigo Reagent II, 15 mL of malonic acid (to mask the free chlorine), and CDF dilution water to 2/3 capacity. The flask was then filled to the mark with CDF water. The absorbance of the sample at 600 nm was then measured using a Spectronic 1201 spectrophotometer (Milton Roy Co., Rochester, NY). The absorbance of a blank sample containing only the Indigo Reagent II, malonic acid, and CDF water was also measured, and the ozone concentration was determined by the difference in absorbance between the two solutions as given by Eq. 17:

$$[O_3]\text{, mg/L} = [(A_{blank} - A_{sample}) * 100]/(0.42 * \text{sample vol.}) \qquad (17)$$

3.4.6 THM Analysis

THMs were determined by extraction into hexane and analysis of the hexane layer by gas chromatography with electron capture detection (GC/ECD). This procedure is based on the methods reported by McGuire et al (1989). The THM analyses were conducted by another graduate student and UNC-CH.

3.4.7 Measurement of pH and ORP

Solution pH was measured using a Fisher Accumet digital pH/mV meter (Model 13-635-10) and a Fisher Accumet polymer-body, liquid-filled, combination electrode with a Ag/AgCl reference (Model 13-620-287) (Fisher Scientific, Pittsburgh, PA). ORP measurements were made using a Fisher Accumet pH/mV meter (Model 610A) and a Fisher Accumet platinum/Ag/AgCl combination electrode (Model 13-620-82) (Fisher Scientific, Pittsburgh, PA).

Chapter 4 Results and Discussion

4.1 SCOLA Characterization

The first step in the characterization of SCOLA was to determine the operating conditions that produced a representative SCOLA solution according to LATA personnel. A constant brine concentration of 8 g/L NaCl was used, producing a current of about 6 amps, at the recommendation of LATA personnel, and the flow rate was varied from 2 gph/side to 7 gph/side. Recognizing that good separation of anodic and cathodic products is essential, the percentage of free chlorine in the catholyte relative to that in the anolyte was used as a decision variable. An upper limit of 10% was recommended by LATA.

Table 4-1 presents the results of all of the SCOLA generation experiments conducted at different flow rates. The table shows the flow rate measured for both the anode and the cathode, the pH of the anolyte and the catholyte, the total oxidant concentration in the anolyte, the free chlorine concentration in the anolyte and in the catholyte, and the relative and absolute ORP of the anolyte. Inspection of Table 4-1 reveals that poor separation occurred at flow rates of 2, 6, and 7 gph/side as evidenced by cathodic free chlorine concentrations in excess of 10% of the anodic free chlorine concentrations. Another indication of poor separation is unbalanced anodic and cathodic flow rates. LATA recommends that the anodic and cathodic flow rates should be within 10% of one another. Unbalanced flow was a problem only with the two highest flow rates tested, 6 and 7 gph/side. Based on these considerations, three candidate flow rates were chosen for further investigation, 2, 3, and 4 gph/side (termed SCOLA2, SCOLA3, and SCOLA4,

Table 4-1 Summary of SCOLA Generation Experiments

12 volt unit; [NaCl] = 8 g/L

Date	Flowrate gph anode	Flowrate gph cathode	Current amps	pH anode	pH cathode	Total Oxidants* mg/L as Cl2 anode	Free Chlorine** mg/L anode	Free Chlorine** mg/L cathode	ORP(rel)*** mV	ORP(abs)**** mV
7/12/94	1.9	1.8	6.4	2.0	12.1	347	238	53	1127	1415
7/15/94	2.1	2.4	6.4	2.0	12.4	267	224	38	1124	1412
7/19/94	2.1	1.8	6.3	2.2	12.4	302	233	37	1124	1412
mean						**305**	**232**	**43**	**1125**	**1413**
standard deviation						**40**	**7**	**9**	**2**	**2**
7/12/94	2.7	3.0	6.3	2.0	12.0	239	145	16	1123	1411
7/14/94	2.9	3.0	6.0	2.1	12.1	239	185		1124	1412
7/15/94	2.9	2.9	6.4	2.1	12.3	227	177	17	1124	1412
7/19/94	3.0	3.0	6.4	2.1	12.3	195	142	10	1120	1408
7/25/94	3.0	3.3	6.1	2.2	11.9	208	142	15	1120	1408
8/10/94	3.0	3.2	6.1	2.2	11.8	260	199		1120	1408
8/11/94	2.9	3.2	6.1			213	143		1120	1408
8/16/94	3.0	3.3	6.3	2.1	11.9	266	212		1118	1406
8/24/94	2.9	3.0	6.0	2.2	11.9	266	167		1119	1407
9/6/94	3.0	3.0	6.3	2.1	12.0	284	202		1120	1408
mean						**240**	**171**	**15**	**1121**	**1409**
standard deviation						**29**	**28**	**3**	**2**	**2**
7/12/94	4.0	4.0	6.1	2.1	11.9	160	119	8	1117	1405
7/20/94	4.1	4.1	6.4	2.1	12.2	152	97	6	1115	1403
7/26/94	4.1	4.2	6.3	2.3	11.8	153	99	5	1114	1402
7/28/94	4.0	4.1	6.3	2.2	11.8	158	110	5	1113	1401
8/10/94	4.0	4.0	6.2	2.3	11.8	200	155		1116	1404
8/16/94	4.0	4.1	6.1	2.2	11.8	188	119		1114	1402
8/24/94	4.0	4.0	6.0	2.2	11.7	177	124		1114	1402
9/6/94	4.0	4.0	6.2	2.2	11.9	203	150		1116	1404
9/12/94	4.0	4.0	6.3	2.2	11.9	215	177		1115	1403
9/18/94	4.1	4.1	6.0			197	158			
9/19/94	4.0	4.0	6.0			186	151			
9/19/94	4.0	4.0	5.9			177	150			
9/26/94	4.1	4.0				186	158			
10/19/94	4.0	4.0				207	172			
mean						**183**	**139**	**6**	**1115**	**1403**
standard deviation						**21**	**26**	**1**	**1**	**1**
7/12/94	4.9	4.9	6.0	2.3	11.8	129	93	5	1114	1402
7/12/94	6.2	5.1	6.4	2.4	11.8	92	58	8	1107	1395
7/12/94	6.8	4.8	6.4	2.4	11.8	89	71	13	1106	1394

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* determined by thiosulfate titration

** determined by amperometric titration

*** relative to Saturated Calomel Electrode (SCE)

**** relative to Normal Hydrogen Electrode (NHE) respectively). The 2 gph/side flow rate was considered despite evidence of excessive mixing due to the relatively high concentration of total oxidants and free chlorine produced.

In order to compare the SCOLAs produced at each of these flow rates, a chlorine demand study was run using a 4 mg/L humic acid (as HA) solution buffered at pH 8. Various amounts of the SCOLA solutions produced at each of the candidate flow rates were added to humic acid solutions and the residual free chlorine concentration was measured after 24 hours. Table 4-2 and Figure 4-1 show the results of this study. Both the free chlorine doses and the free chlorine residual concentrations were determined by amperometric titration with PAO. All three SCOLAs performed better than NaOCl in their ability to maintain a similar free chlorine residual with smaller chlorine doses. The suggests that the other oxidant species that make up the difference between the free chlorine concentration and the total oxidant concentration in the SCOLA solution are consuming some of the oxidant demand and therefore allowing the free chlorine to persist for a longer period of time. Both SCOLA3 and SCOLA4 performed measurable better than SCOLA2, with SCOLA4 exhibiting marginal superiority over SCOLA3. It was decided to continue the study using both SCOLA3 and SCOLA4.

The total oxidant concentration of SCOLA3 and SCOLA4, measured as Cl2, was comprised of 71 and 75 percent free chlorine, respectively (see Table 4-1). This percentage remained fairly constant despite changes in flow rate (see Fig. 4-2). All SCOLA solutions were approximately 74% free chlorine and 26% other oxidant species.

Table 4-2 Effect of SCOLA on Chlorine Demand in Model Test Solutions

Conditions: TOC = 4 mg/L humic acid (as HA)
pH = 8.0

NaOCl		SCOLA - Q = 2gph/side (7/19/94)			SCOLA - Q = 3gph/side (7/19/94)			SCOLA - Q = 4gph/side (7/20/94)		
Applied Oxidant Dose*	24 hour Residual Free Cl2**	Applied Oxidant Dose*	Applied Free Cl2 Dose**	24 hour Residual Free Cl2**	Applied Oxidant Dose*	Applied Free Cl2 Dose**	24 hour Residual Free Cl2**	Applied Oxidant Dose*	Applied Free Cl2 Dose**	24 hour Residual Free Cl2**
mg/L as Cl2		mg/L as Cl2			mg/L as Cl2			mg/L as Cl2		
3.7	0.9	4	3.1	1.1	4.2	3.1	1.3	4.6	2.9	1.6
4.2	1.2	5	3.9	2.0	5.5	4.0	2.6	6.1	3.9	2.7
4.7	1.5	6.5	5.0	3.0	6.8	5.0	4.0	7.6	4.9	4.0
		8.1	6.2	4.0	8.5	6.2	4.8	9.6	6.1	5.4

* determined by thiosulfate titration

** determined by amperometric titration

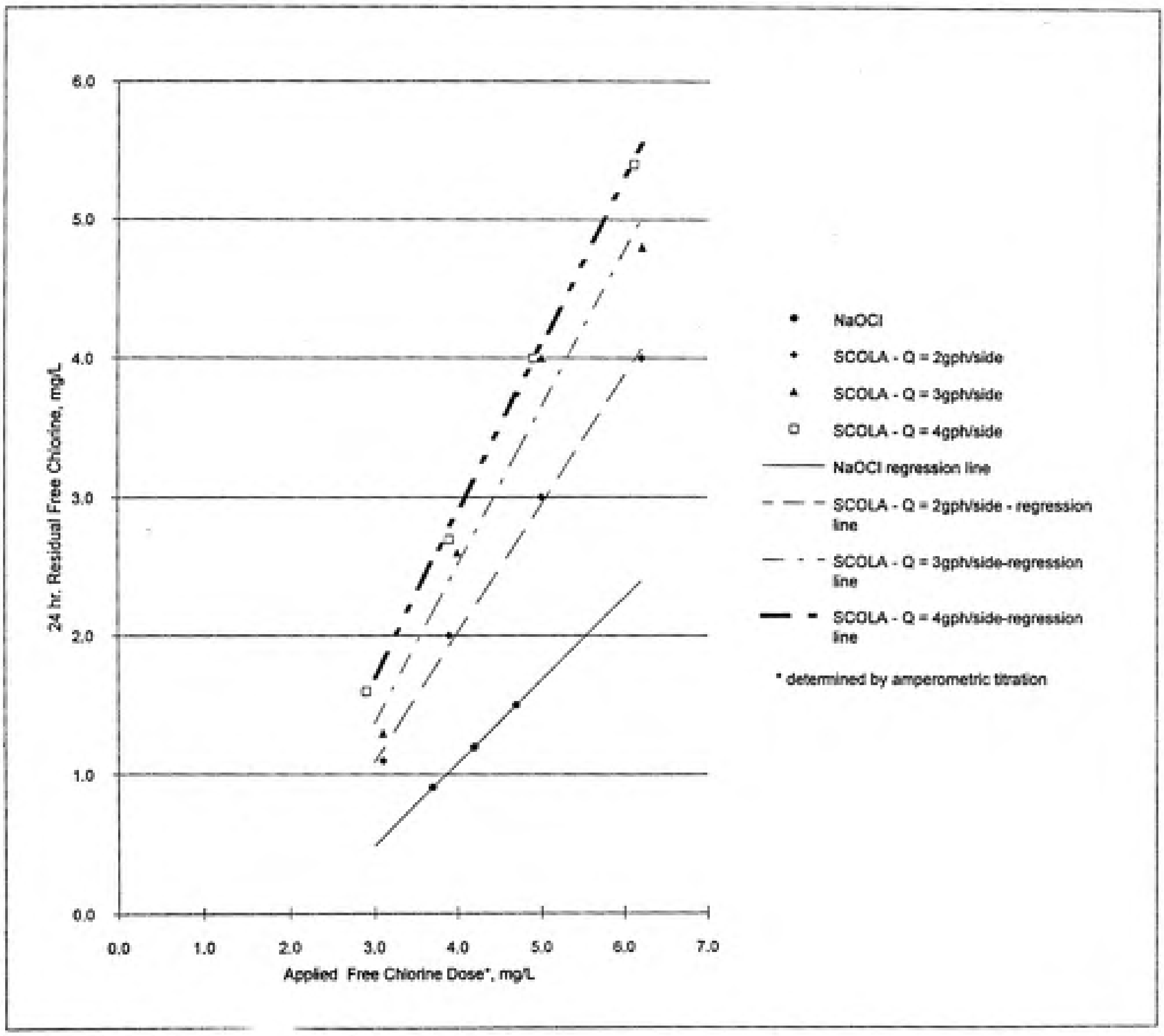

Figure 4-1 Effect of SCOLA on Chlorine Demand in Model Test Solutions

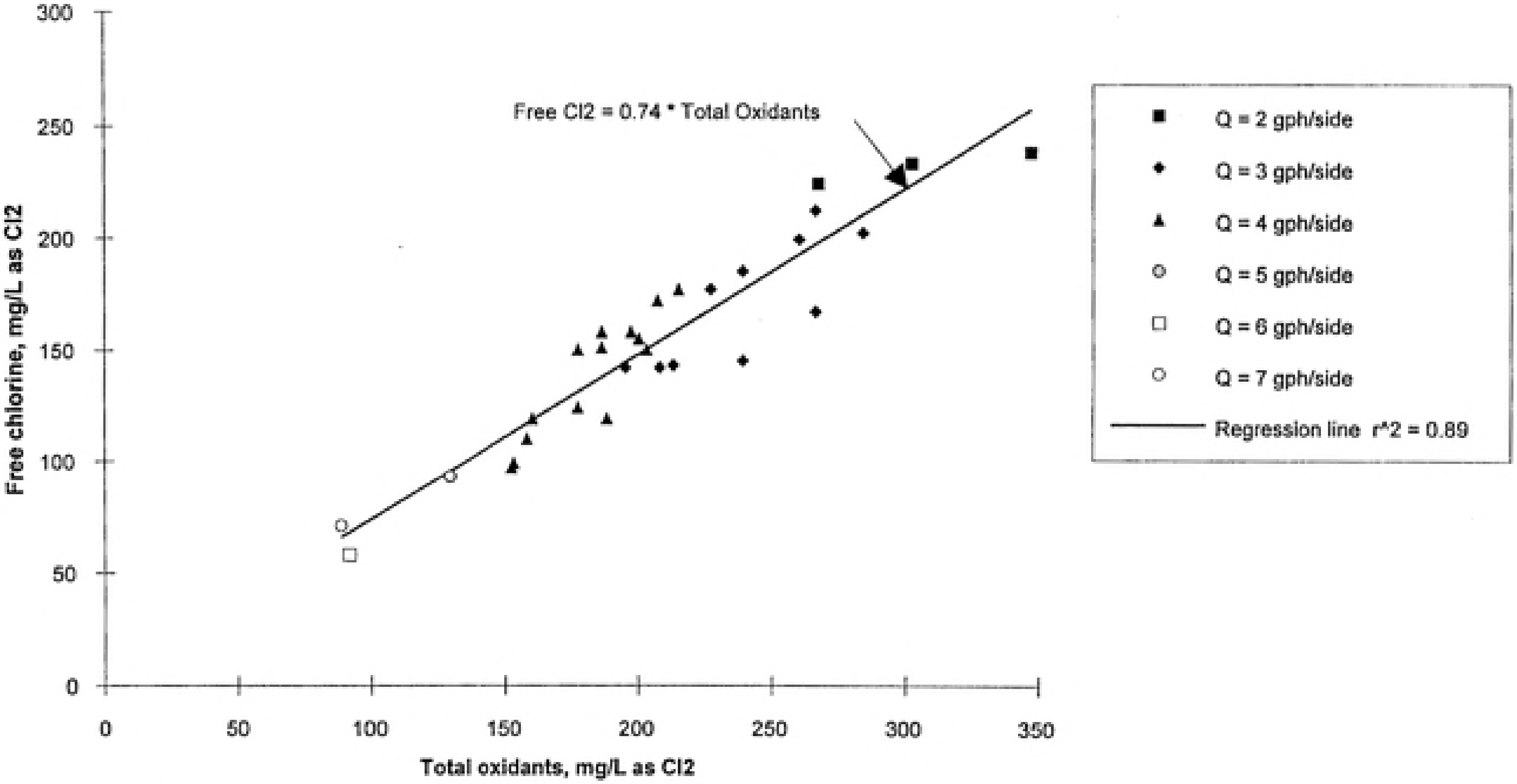

Figure 4-2 Free Chlorine and Total Oxidant Concentrations in SCOLA Solutions for Various Flow Rates

Table 4-3 presents a summary of results from all SCOLA3 and SCOLA4 characterization experiments. Although some ozone was detected in SCOLA4, the effects of an O_3 concentration this small would be negligible when SCOLA is applied to raw or settled water in the typical dilution range of 1:50 to 1:100. ClO_2 was either absent or present in concentrations that were below the detection limit of the titrimeter (< 0.01 mg/L). Other oxidant species that may have accounted for the differential between the free chlorine concentration and the total oxidant concentration include H_2O_2 and radical species. H_2O_2 was not analyzed for, and there is no analytical method that is specific for radical species in the presence of other oxidants.

4.2 Model Water Studies

The results of the model water studies are shown in Tables 4-4 and 4-5 and in Figures 4-3 through 4-6. Figure 4-3 compares the 24-hour chlorine demand exerted in the model waters treated with NaOCl against those treated with SCOLA solutions generated at different flow rates. Only those data which produced comparable free chlorine residuals of about 1 mg/L after 24 hours were compared. The Cl_2 demands of the SCOLA-treated solutions were calculated using the applied free chlorine dose and the residual free chlorine concentration, both determined by amperometric titration with PAO. The chlorine demands of the SCOLA-treated solutions were approximately 70% of the NaOCl-treated solutions.

Based on the information presented in the discussion of factors influencing THM formation in Ch. 2, one would have expected to see a corresponding reduction in the amount of $CHCl_3$ formed in the SCOLA-treated waters. However, as Figure 4-4 illustrates, this was not the

Table 4-3 Summary of SCOLA Characterization Experiments

Parameter	SCOLA Flow Rate	Number of Observations	Mean Concentration	Standard Deviation
mg/L	gph/side		mg/L	mg/L
Total oxidants (as Cl2)	3	10	240	29
	4	14	183	21
Free chlorine	3	10	171	28
	4	14	139	26
Chlorine dioxide	3	1	< 0.01	-------
	4	4	< 0.01	-------
Ozone	3	0	-------	-------
	4	3	1.1	0.1

Table 4-4 Effect of Varying TOC Concentration on THM Formation from SCOLA and from NaOCl

Conditions: pH = 8.0

	NaOCl			SCOLA - Q =3gph/side				SCOLA - Q = 4gph/side			
TOC	Applied Oxidant Dose*	24 hour Residual Free Cl2**	CHCl3	Applied Oxidant Dose*	Applied Free Cl2 Dose**	24 hour Residual Free Cl2**	CHCl3	Applied Oxidant Dose*	Applied Free Cl2 Dose**	24 hour Residual Free Cl2*	CHCl3
mg/L humic acid as HA	mg/L as Cl2		ug/L	mg/L as Cl2			ug/L	mg/L as Cl2			ug/L
2	2.0	0.5		1.4	1.0	0.2		1.5	1.0	0.3	
2	**2.5**	**1.0**	**44**	2.1	1.4	0.6		2.3	1.5	0.8	
2	3.0	1.4	44	**2.8**	**1.9**	**1.2**	**38**	**3.1**	**2.0**	**1.5**	**35**
2				3.5	2.4	1.7	47	3.8	2.5	2.1	
4	3.5	0.8		3.5	1.9	0.3		3.1	2.0	0.5	
4	**4.0**	**1.3**	**89**	4.4	2.4	0.9		3.8	2.5	0.8	
4	4.5	1.7		**5.3**	**2.8**	**1.2**	**84**	**4.6**	**3.0**	**1.2**	**85**
4											
8	6.5	0.8		**7.3**	**5.0**	**0.9**	**185**	**7.7**	**5.0**	**1.4**	**167**
8	**7.0**	**1.4**	**190**	8.7	5.9	1.9	192	9.2	6.0	2.1	
8	7.5	1.7	198	10.4	7.1	3.0		10.7	7.0	3.3	
8				11.8	8.0	4.2		12.2	8.0	4.2	

* determined by thiosulfate titration

** determined by amperometric titration

bold type indicates data presented in figures

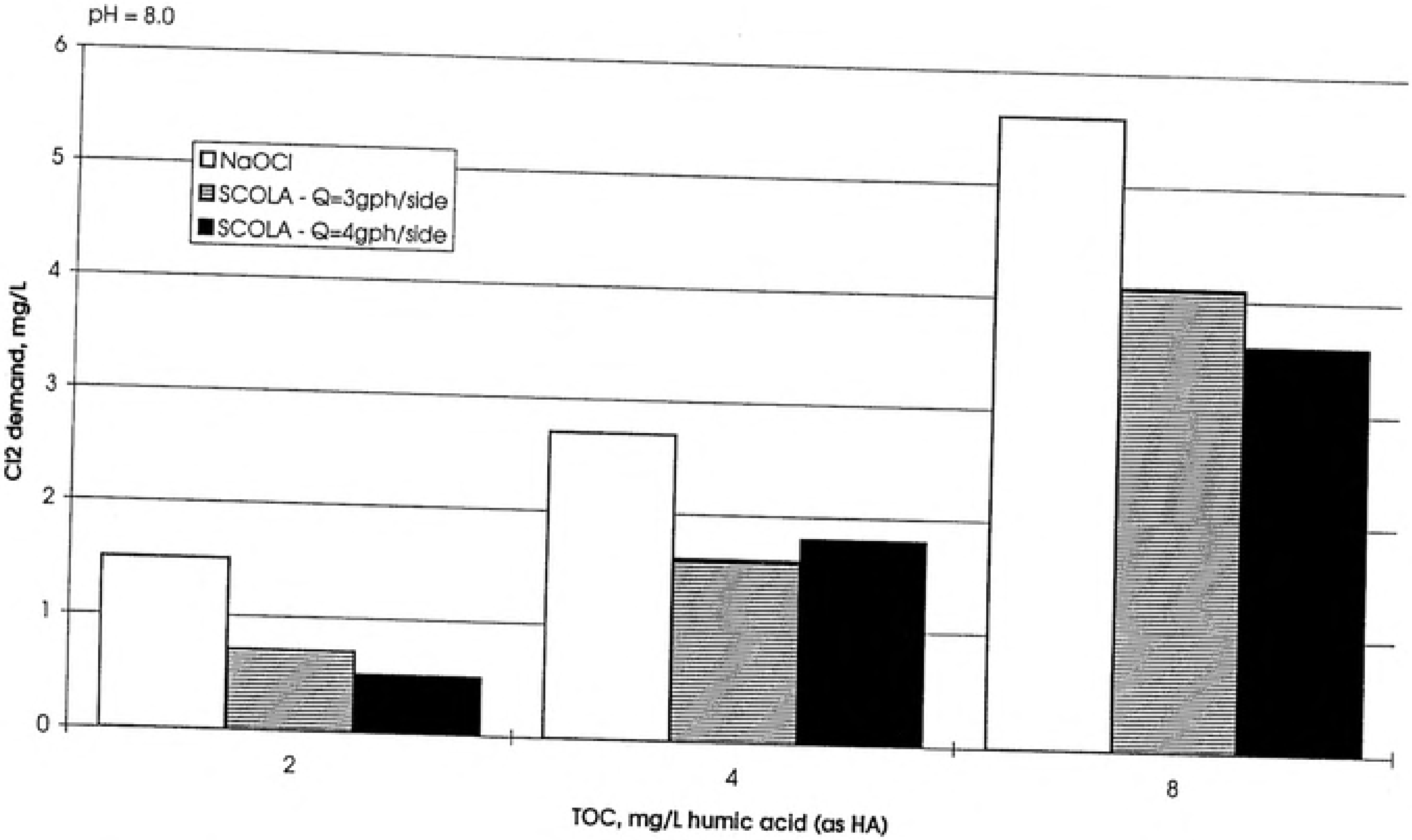

Figure 4-3 Comparison of Chlorine Demand in Model Waters Treated with NaOCl and with SCOLA

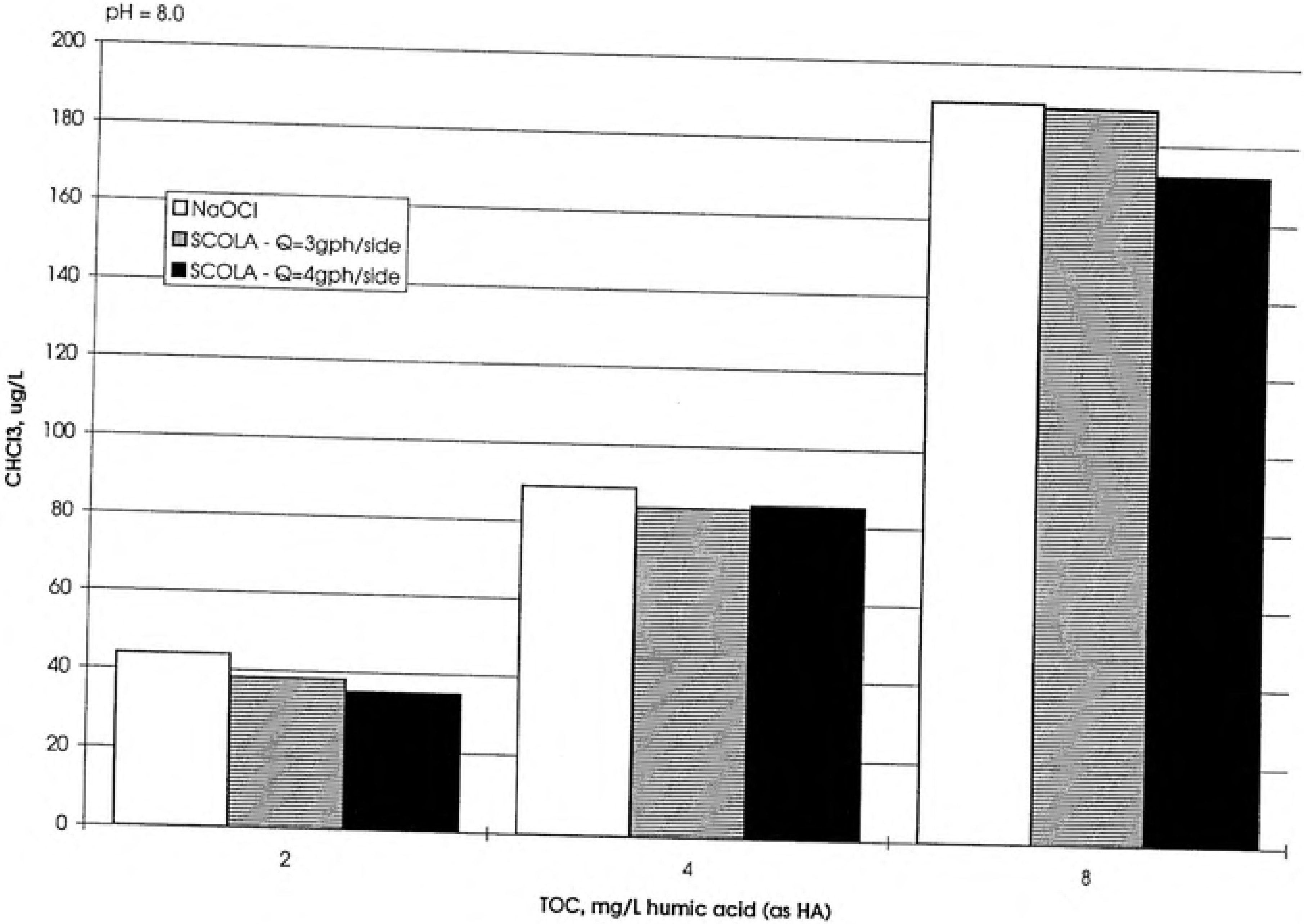

Figure 4-4 Comparison of THM Formation in Model Waters Treated with NaOCl and with SCOLA

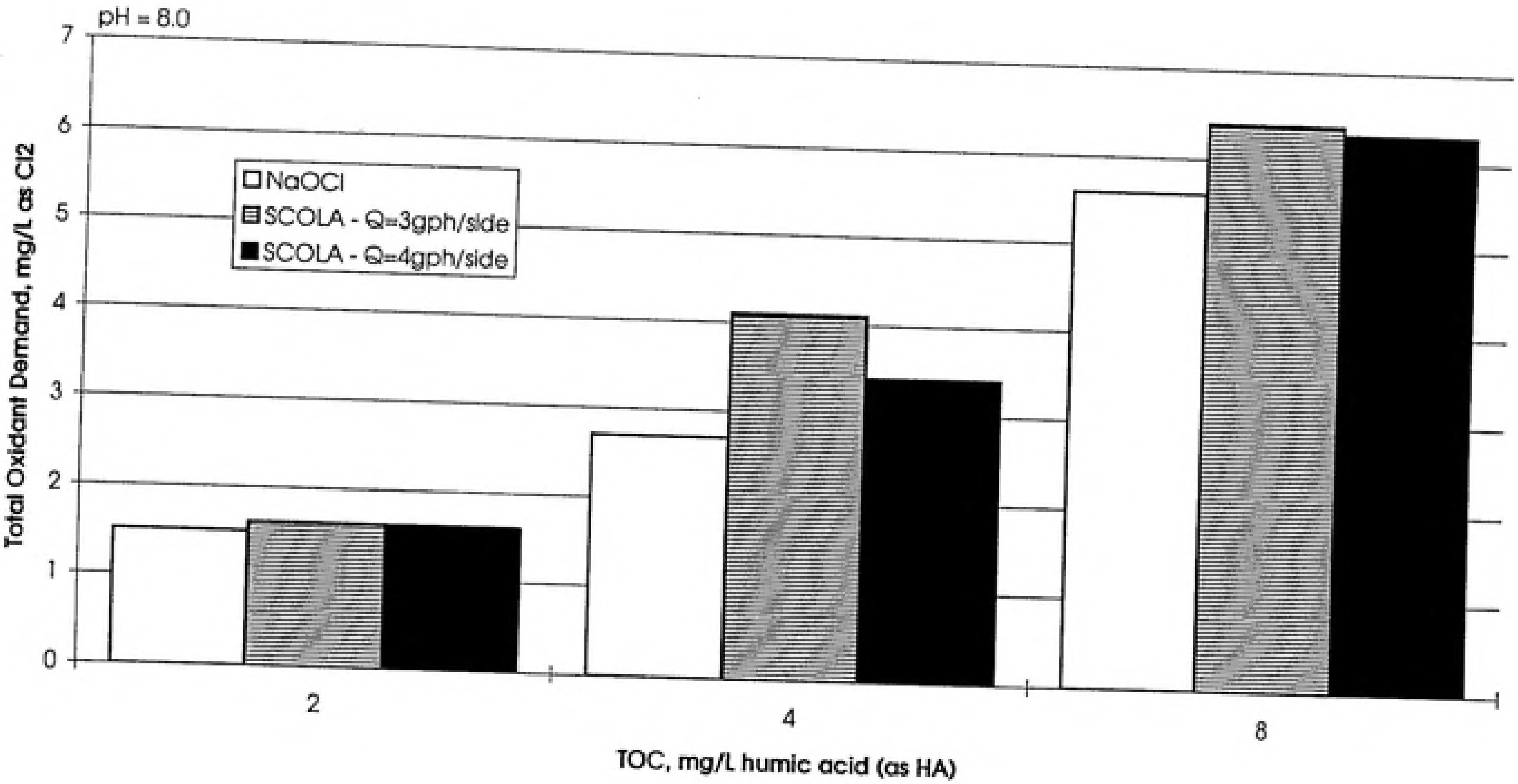

Figure 4-5 Comparison of Total Oxidant Demand in Model Waters Treated with NaOCl and with SCOLA

Table 4-5 Effect of pH on THM Formation from SCOLA and NaOCl

conditions: TOC = 4 mg/L humic acid (as HA)

	NaOCl			SCOLA - Q = 4gph/side			
Chlorination pH	Applied Oxidant Dose*	24 hour Residual Free Cl2**	CHCl3	Applied Oxidant Dose*	Applied Free Cl2 Dose**	24 hour Residual Free Cl2**	CHCl3
	mg/L as Cl2		ug/L		mg/L as Cl2		ug/L
6	3.5	0.9		3.2	2.0	0.5	
6	**4.0**	**1.1**	**51**	**4.0**	**2.5**	**1.0**	**51**
6	4.5	1.4		4.7	3.0	1.5	
7	3.5	0.8		3.2	2.0	0.7	
7	**4.0**	**1.1**	**74**	**4.0**	**2.5**	**0.9**	**80**
7	4.5	1.4	80	4.7	3.0	1.5	88
8	3.5	0.9		3.2	2.0	0.7	
8	4.0	1.4	95	4.0	2.5	1.0	
8	4.5	1.7		4.7	3.0	1.4	85

* determined by thiosulfate titration

** determined by amperometric titration

bold type indicates data presented in figures

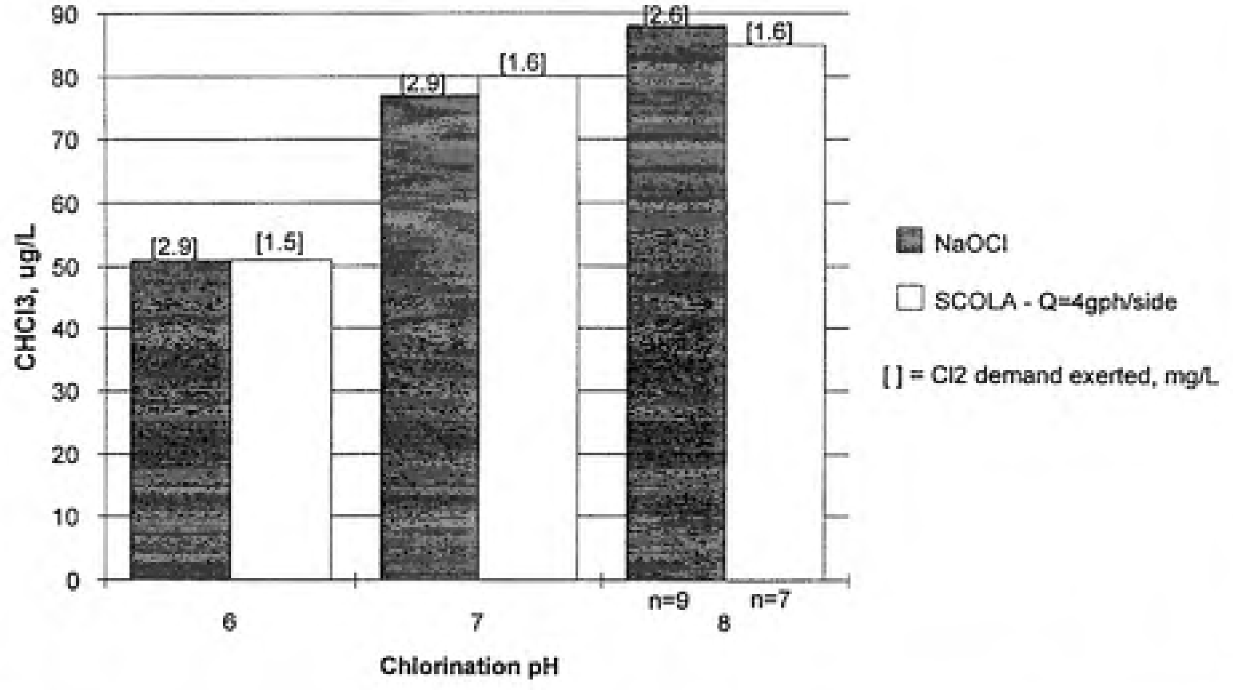

Figure 4-6 Effect of pH on THM Formation from NaOCl and from SCOLA

case. The $CHCl_3$ levels in the NaOCl-treated solutions and the SCOLA-treated solutions were essentially the same. Only $CHCl_3$ data is reported because it was the only THM species formed from NaOCl and essentially all THMs formed from SCOLA consisted of $CHCl_3$.

Figure 4-5 compares the total oxidant demands of the NaOCl- and the SCOLA-treated solutions. The total oxidant demands of the SCOLA-treated solutions were essentially the same as the NaOCl-treated solutions. What these results imply is that the non-chlorine oxidants that are present in SCOLA are behaving like free chlorine in their ability to form THMs. Another possibility is that the Cl^- in SCOLA is being oxidized to Cl_2 by the other oxidant species which is then reacting with the humic material to form THMs.

Table 4-5 and Figure 4-6 illustrate the effect of pH on CHCl3 formation from SCOLA and NaOCl. The data presented for the pH 8 case represents the mean values for all of the model water experiments conducted during the project using 4 mg/L humic acid (as HA) buffered at pH 8.0. As one would expect from the discussion on THM formation in Ch. 2, the extent of THM formation increases as the pH increases. The chlorine demands were essentially the same for both NaOCl- and SCOLA-treated solutions at each pH. Notice how, once again, the chlorine demands of the SCOLA-treated waters were appreciably less than those of the NaOCl-treated waters yet the extent of THM formation was essentially the same.

Similar results were obtained with a 6-volt MIOX unit and a SAL-I MIOX unit (see Appendix A).

4.3 Real Water Studies

In order to test the results obtained in the model water studies, the same experiments were carried out using real water samples collected from several utilities in the U.S. and Canada (see Table 3-3). These samples represent both raw and settled waters of varying quality and composition. All of the water samples examined were collected prior to the addition of any chlorine to the water. The treatment of these waters with NaOCl and SCOLA was the same as for the model waters. They were all buffered at pH 8.0 with a 0.005 M phosphate buffer, and dosed with sufficient amounts of NaOCl and SCOLA to produce a free chlorine residual after 24 hours of about 1 mg/L.

Tables 4-6 through 4-10 and Figures 4-7 through 4-9 show the results of these experiments. Only those data which produced comparable free chlorine residuals of about 1 mg/L after 24 hours were compared. In all cases, the extent of THM formation was the same in the waters treated with SCOLA as in the waters treated with NaOCl (see Figure 4-8). Note that the extent of bromine incorporation was essentially the same for NaOCl- and SCOLA-treated waters (see Tables 4-6 through 4-10). As was the case in the model water studies, the chorine demands of the SCOLA-treated waters were considerably less than for the same waters treated with NaOCl (see Figure 4-7). The average ratio of the chlorine demand exerted in SCOLA-treated waters to that in NaOCl-treated waters was approximately 60%. This reduction in chlorine demand, however, did not result in a corresponding reduction in THM formation. This point is illustrated most clearly by Figures 4-7 and 4-8.

Table 4-6 Comparison of THM Formation in OWASA (NC) Water Treated with SCOLA and NaOCl

conditions: OWASA (NC) raw water - TOC =4.4 mg/L
pH = 8.0

NaOCl

Applied Oxidant Dose* mg/L as Cl2	24 hour Residual Free Cl2** mg/L as Cl2	CHCl3 ug/L	TTHM ug/L
6.0	0.8	138	149
6.5	**1.1**	138	**149**
7.0	1.6		
8.0	2.1		
8.5			

SCOLA - Q = 3gph/side (8/11/94)

Applied Oxidant Dose* mg/L as Cl2	Applied Free Cl2 Dose** mg/L as Cl2	24 hour Residual Free Cl2** mg/L as Cl2	CHCl3 ug/L	TTHM ug/L
5.7	3.8	0.4	136	152
6.4	4.3	0.8		
7.1	**4.8**	**1.1**	144	**161**
7.8	5.3	1.7		
8.5	5.8	2.3		

SCOLA - Q = 4gph/side (8/10/94)

Applied Oxidant Dose* mg/L as Cl2	Applied Free Cl2 Dose** mg/L as Cl2	24 hour Residual Free Cl2** mg/L as Cl2	CHCl3 ug/L	TTHM ug/L
4.7	3.7	0.4	131	146
5.3	4.2	0.8		
6.0	**4.8**	**1.3**	139	**156**
6.7	5.3	1.7		
7.3	5.8			

conditions: OWASA (NC) settled water - TOC = 2.6 mg/L
pH = 8.0

NaOCl

Applied Oxidant Dose* mg/L as Cl2	24 hour Residual Free Cl2** mg/L as Cl2	CHCl3 ug/L	TTHM ug/L
2.0	0.1		
2.5	0.5	32	40
3.0	0.6		
3.5	**1.2**	33	**42**
4.0	1.6		

SCOLA - Q = 3gph/side (8/11/94)

Applied Oxidant Dose* mg/L as Cl2	Applied Free Cl2 Dose** mg/L as Cl2	24 hour Residual Free Cl2** mg/L as Cl2	CHCl3 ug/L	TTHM ug/L
1.3	1.1	0.0		
2.2	1.7	0.2		
2.7	2.0	0.5	37	47
3.5	**2.7**	**1.2**	40	**51**
4.2	3.2	1.5		

SCOLA - Q = 4gph/side (8/10/94)

Applied Oxidant Dose* mg/L as Cl2	Applied Free Cl2 Dose** mg/L as Cl2	24 hour Residual Free Cl2** mg/L as Cl2	CHCl3 ug/L	TTHM ug/L
1.3	1.0	0.0		
2.0	1.6	0.2		
2.7	2.1	0.7	37	48
3.3	**2.7**	**1.3**	40	**52**
4.0	3.2	1.5		

* determined by thiosulfate titration
** determined by amperometric titration
bold type indicates data presented in figures

Table 4-7 Comparison of THM Formation in Cincinnati, OH Water Treated with SCOLA and NaOCl

conditions: Cincinnati, OH raw water - TOC = 2.1 mg/L
pH = 8.0

NaOCl

Applied Oxidant Dose*	24 hour Residual Free Cl2**	CHCl3	TTHM
mg/L as Cl2		ug/L	ug/L
3.0	0.8		
4.0	0.6		
5.0	**1.5**	49	**73**
6.0	2.2		

SCOLA - Q = 3gph/side (8/16/94)

Applied Oxidant Dose*	Applied Free Cl2 Dose**	24 hour Residual Free Cl2**	CHCl3	TTHM
mg/L as Cl2			ug/L	ug/L
3.4	**2.7**	**1.1**	44	**70**
4.0	3.2	0.8		
4.7	3.7	1.5		
5.3	4.2	1.3		
6.0	4.8	2.0		

SCOLA - Q = 4gph/side (8/16/94)

Applied Oxidant Dose*	Applied Free Cl2 Dose**	24 hour Residual Free Cl2**	CHCl3	TTHM
mg/L as Cl2			ug/L	ug/L
4.3	2.7	0.8		
5.1	**3.2**	**1.4**	49	**76**
6.0	3.7	2.3		
6.8	4.2	3.0		
7.6	4.8	3.7		

conditions: Cincinnati, OH settled water - TOC = 1.9 mg/L
pH = 8.0

NaOCl

Applied Oxidant Dose*	24 hour Residual Free Cl2**	CHCl3	TTHM
mg/L as Cl2		ug/L	ug/L
3.0	0.5		
4.0	**1.2**	32	**56**
5.0	2.0		
6.0	2.7		

SCOLA - Q = 3gph/side (8/16/94)

Applied Oxidant Dose*	Applied Free Cl2 Dose**	24 hour Residual Free Cl2**	CHCl3	TTHM
mg/L as Cl2			ug/L	ug/L
1.3	1.1	0.0		
2.0	1.6	0.0		
2.7	2.1	0.2		
3.4	**2.7**	**0.5**	27	**52**

SCOLA - Q = 4gph/side (8/16/94)

Applied Oxidant Dose*	Applied Free Cl2 Dose**	24 hour Residual Free Cl2*	CHCl3	TTHM
mg/L as Cl2			ug/L	ug/L
1.7	1.1	0.0		
2.6	1.6	0.0		
3.4	2.1	0.7		
4.3	**2.7**	**1.2**	30	**58**

---

* determined by thiosulfate titration

* * determined by amperometric titration

bold type indicates data presented in figures

Table 4-8 Comparison of THM Formation in Hackensack, NJ Raw Water Treated with SCOLA and NaOCl

Conditions: TOC = 3.7 mg/L
pH = 8.0

NaOCl				SCOLA - Q = 3gph/side (8/24/94)					SCOLA - Q = 4gph/side (8/24/94)				
Applied Oxidant Dose*	24 hour Residual Free Cl2**	CHCl3	TTHM	Applied Oxidant Dose*	Applied Free Cl2 Dose**	24 hour Residual Free Cl2**	CHCl3	TTHM	Applied Oxidant Dose*	Applied Chlorine Dose**	24 hour Residual Free Cl2**	CHCl3	TTHM
mg/L as Cl2		ug/L	ug/L		mg/L as Cl2		ug/L	ug/L		mg/L as Cl2		ug/L	ug/L
5	0.3			5.3	3.2	0.1			4.4	3.2	0.1		
6	0.4			6.7	4.2	0.2			5.9	4.2	0.3		
7	0.6			**8.4**	**5.3**	**1.2**	105	**130**	7.7	5.3	1.4	NA	NA
8	**1.0**	105	**127**	10.2	6.4	2.2			8.9	6.4	2.3		
9	1.6	112	133	12.0	7.4	3.3			10.6	7.4	3.6		

* determined by thiosulfate titration
** determined by amperometric titration
bold type indicates data presented in figures
NA = not anlayzed

Table 4-9 Comparison of THM Formation in East St. Louis, IL Raw Water Treated with SCOLA and NaOCl

Conditions: TOC = 5.1 mg/L
pH = 8.0

NaOCl				SCOLA - Q = 4gph/side (9/6/94)				
Applied Oxidant Dose*	24 hour Residual Free Cl2**	CHCl3	TTHM	Applied Oxidant Dose*	Applied Free Cl2 Dose**	24 hour Residual Free Cl2**	CHCl3	TTHM
mg/L as Cl2		ug/L	ug/L		mg/L as Cl2		ug/L	ug/L
6	0.6			5.7	4.2	0.7		
7	0.7			**7.1**	**5.3**	**1.5**	116	**145**
8	**1.5**	123	**148**	8.6	6.4	2.5		
9	2.1			10.0	7.4	3.7		
10	2.9							
11	3.7							

* determined by thiosulfate titration
* *determined by amperometric titration
bold type indicates data presented in figures

Table 4-10 Comparison of THM Formation in Boston Bar, BC Raw Water Treated with SCOLA and NaOCl

conditions: TOC = 0.6 mg/L
pH = 8.0

NaOCl

Applied Oxidant Dose*	24 hour Residual Free Cl2**	CHCl3	TTHM
mg/L as Cl2		ug/L	ug/L
1.0	0.1		
2.0	0.7	26	27
3.0	**1.5**	34	**35**
4.0	2.4		

SCOLA - Q = 4gph/side (9/26/94)

Applied Oxidant Dose*	Applied Free Cl2 Dose**	24 hour Residual Free Cl2**	CHCl3	TTHM
mg/L as Cl2			ug/L	ug/L
1.2	1.0	0.3		
2.5	**2.0**	**1.1**	25	**29**
3.7	3.0	2.2		
5.0	4.0	3.1		

* determined by thiosulfate titration

** determined by amperometric titration

bold type indicates data presented in figures

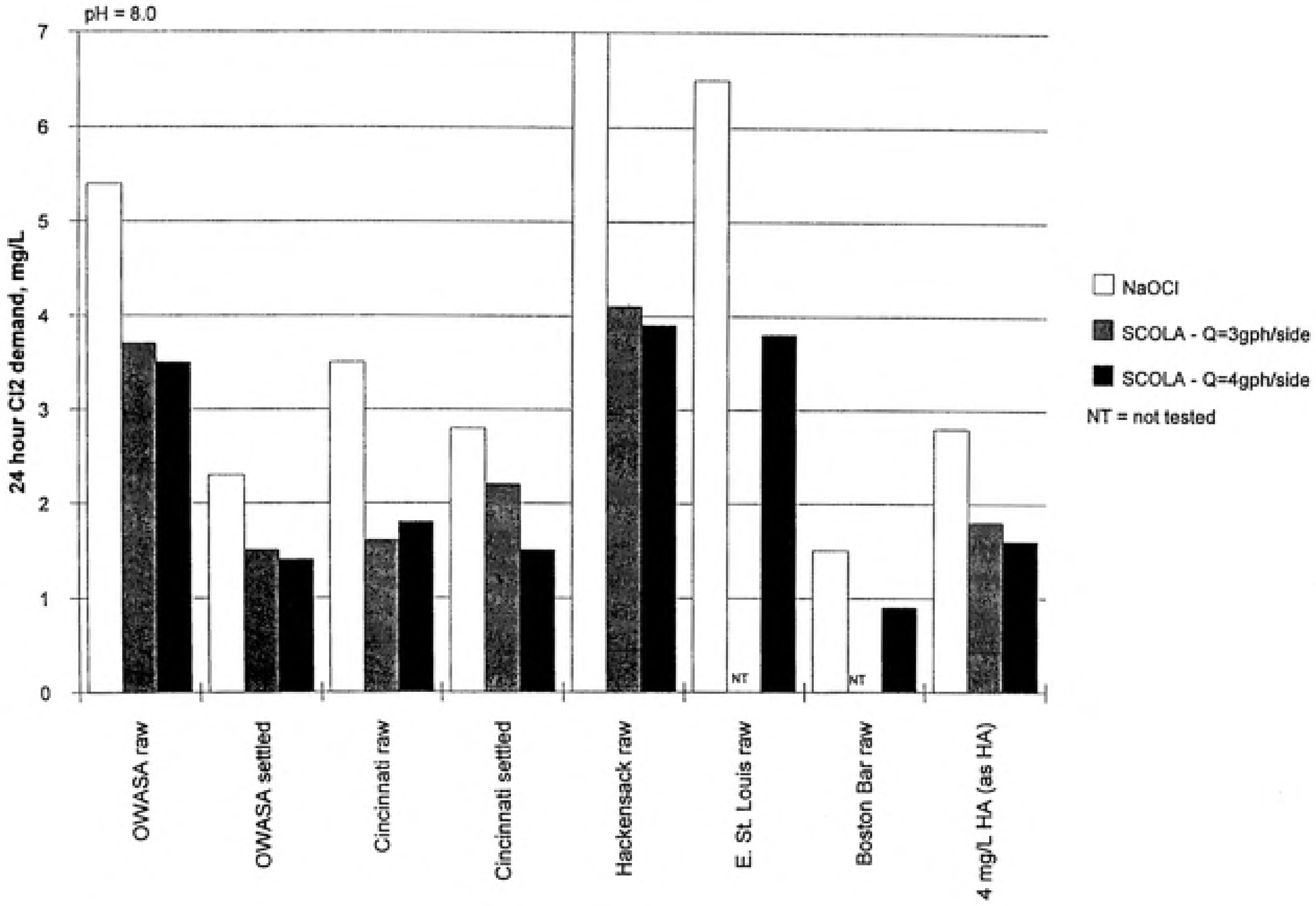

Figure 4-7 Comparison of Chlorine Demand in Test Waters Treated with NaOCl and with SCOLA

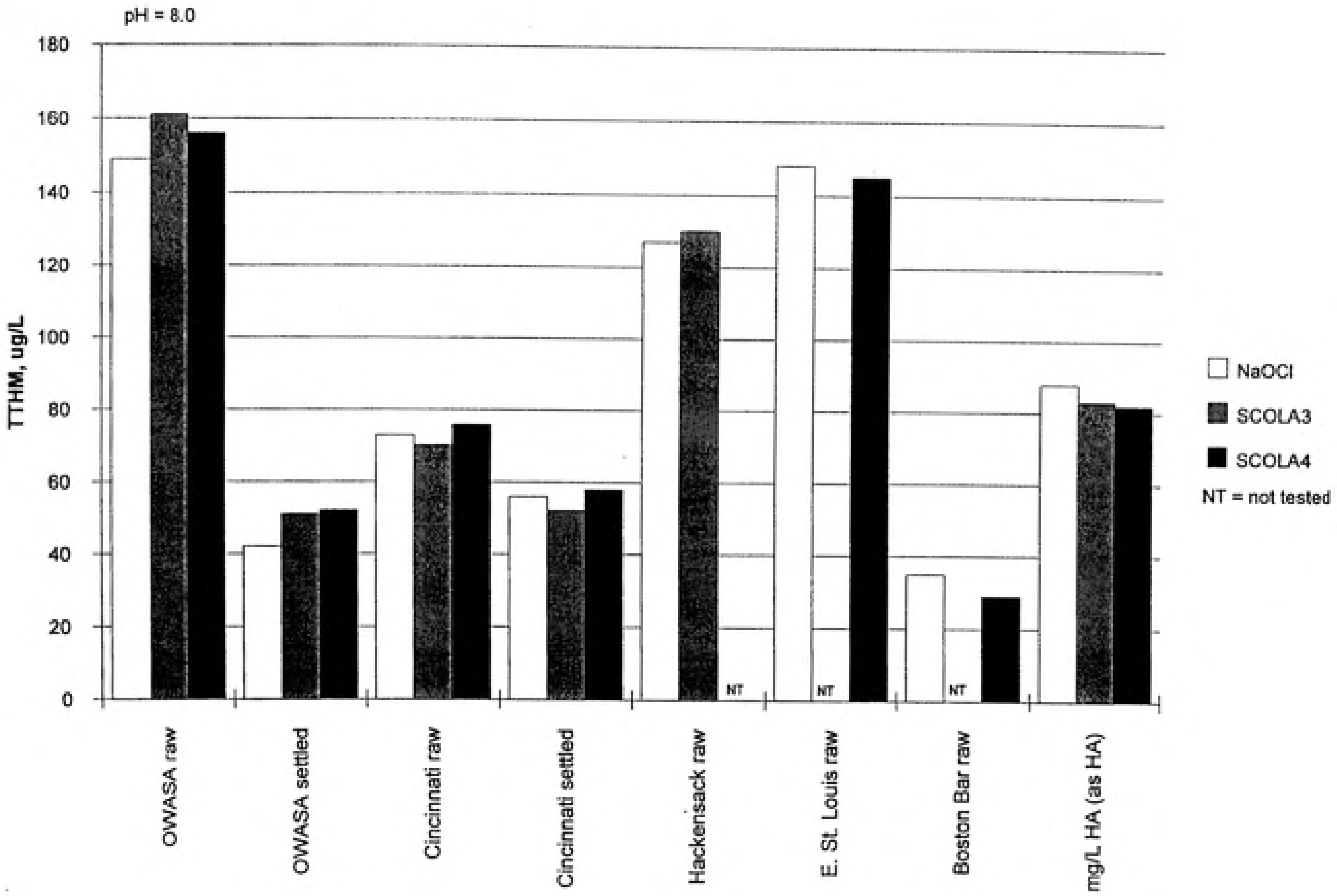

Figure 4-8 Comparison of THM Formation in Test Waters Treated with NaOCl and with SCOLA

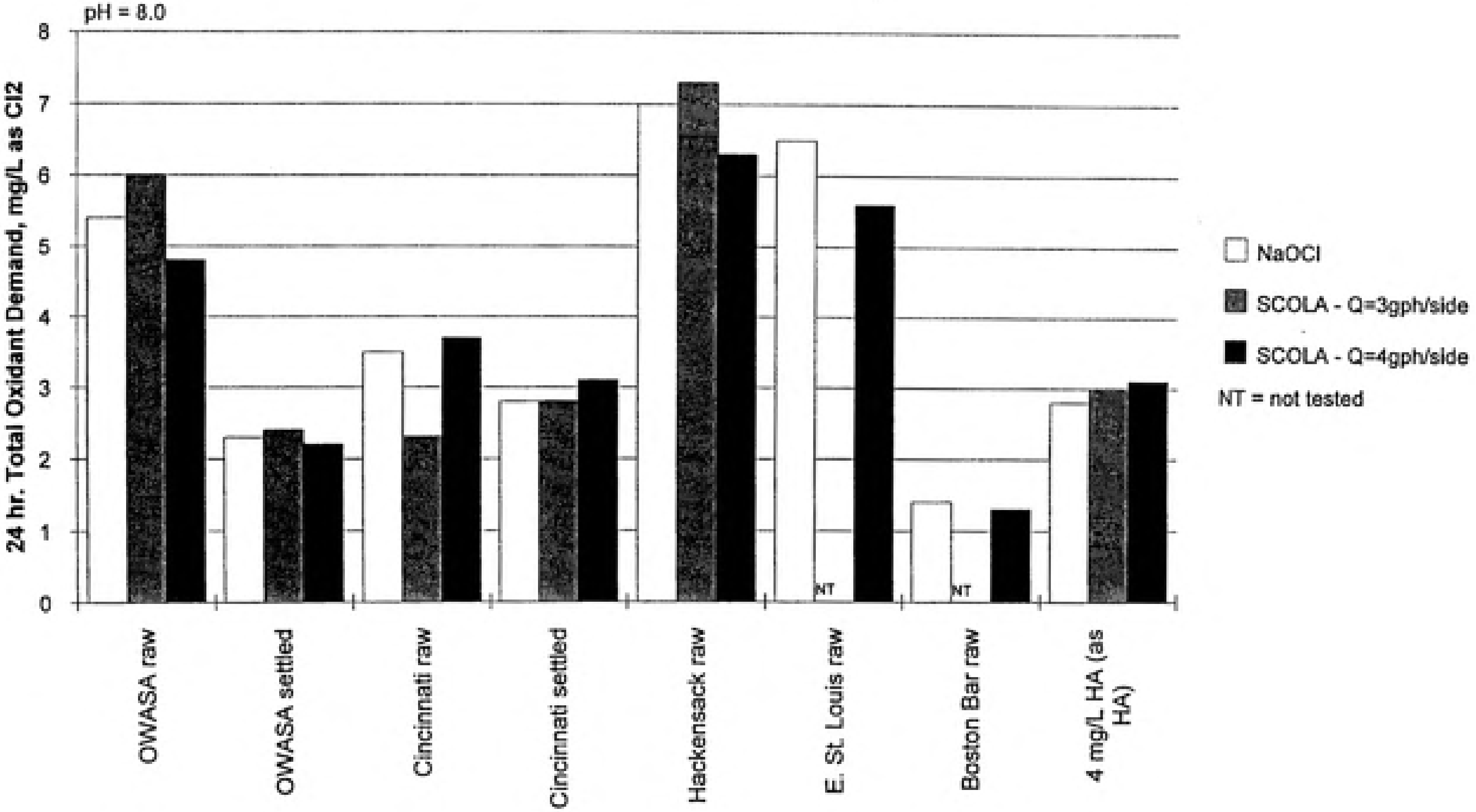

Figure 4-9 Comparison of Total Oxidant Demand in Test Waters Treated with NaOCl and with SCOLA

Figure 4-9 compares the total oxidant demands in all of the waters tested. The similarities between the total oxidant demands exerted in the chlorinated waters and those in SCOLA-treated waters parallels the comparable levels of THM formation from both treatments, suggesting that the non-chlorine oxidant species present in SCOLA are behaving like free chlorine in their ability to form THMs, or that the other oxidant species present in SCOLA are stoichiometrically oxidizing Cl- to Cl_2 which subsequently forms an equivalent amount of THMs.

Figures 4-10 and 4-11 show plots of TTHM formation versus chlorine and total oxidant demand for SCOLA3, and SCOLA4, respectively. Figure 4-12 shows the composite SCOLA results along with the NaOCl results for all of the waters tested. There is a good correlation between TTHM formation and chlorine demand for both SCOLAs ($r^2 = 0.88$) and especially for SCOLA4 ($r^2 = 0.97$), and also for NaOCl ($r^2 = 0.84$). Of particular significance, however, is how the total oxidant demand regression line for the composite SCOLA data collapses onto the NaOCl regression line (see Figure 4-12). This gives credence to the hypothesis that the other oxidant species present in SCOLA are behaving stoichiometrically-equivalent to free chlorine in their ability to form THMs. What is uncertain is the mechanism by which this is occurring. From the discussions in Chapter 2 on ozone and chlorine dioxide chemistry, it is known that neither species reacts with NOM to form THMs.

The oxidation of Cl^- in SCOLA by the other oxidant species present is another possibility. If this is indeed occurring, then the other oxidant species must be creating Cl_2 from Cl^- in amounts that are equivalent to their concentrations expressed as Cl_2.

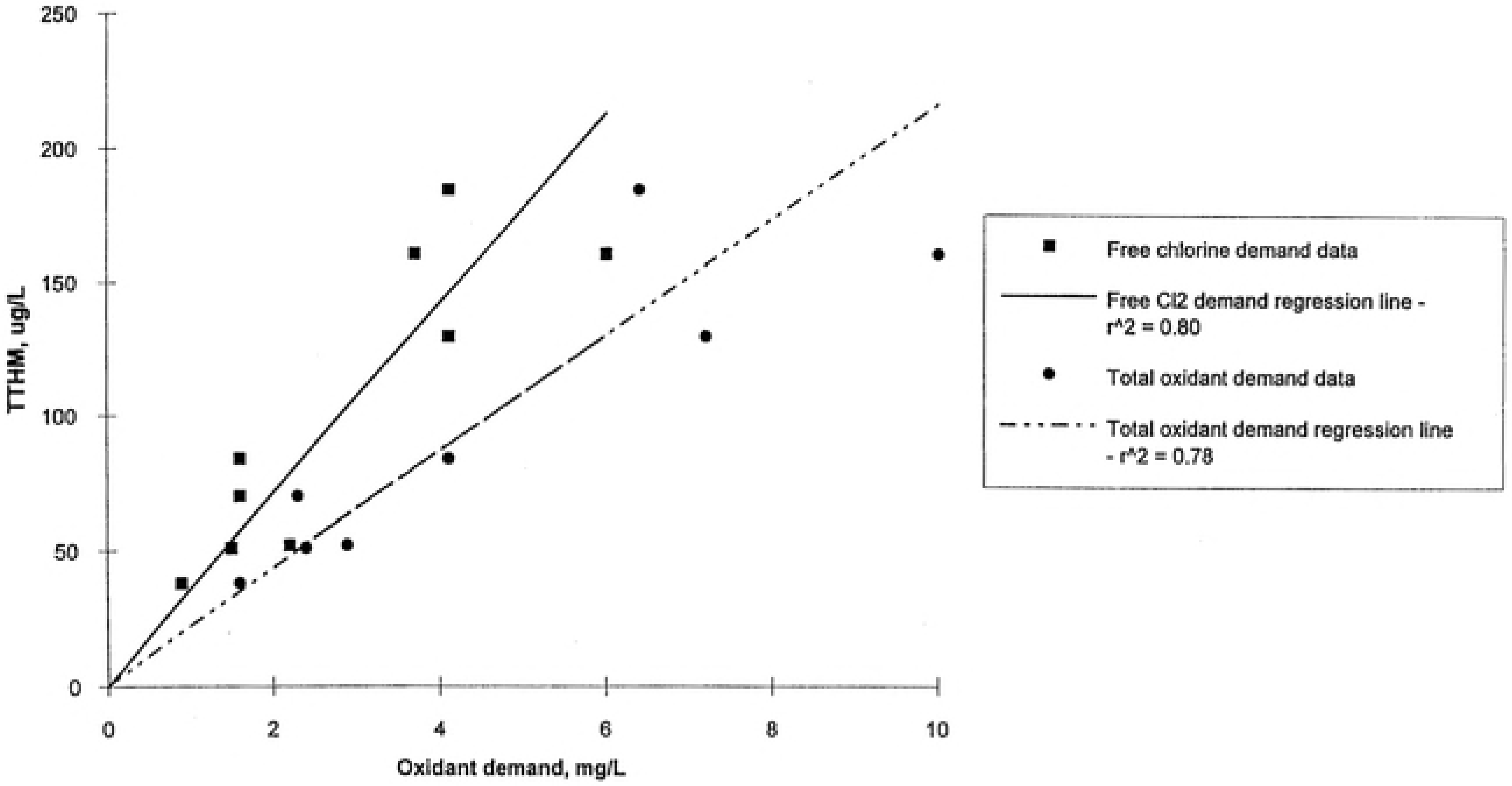

Figure 4-10 TTHM Formation versus Free Chlorine and Total Oxidant Demands in Test Waters Treated with SCOLA3

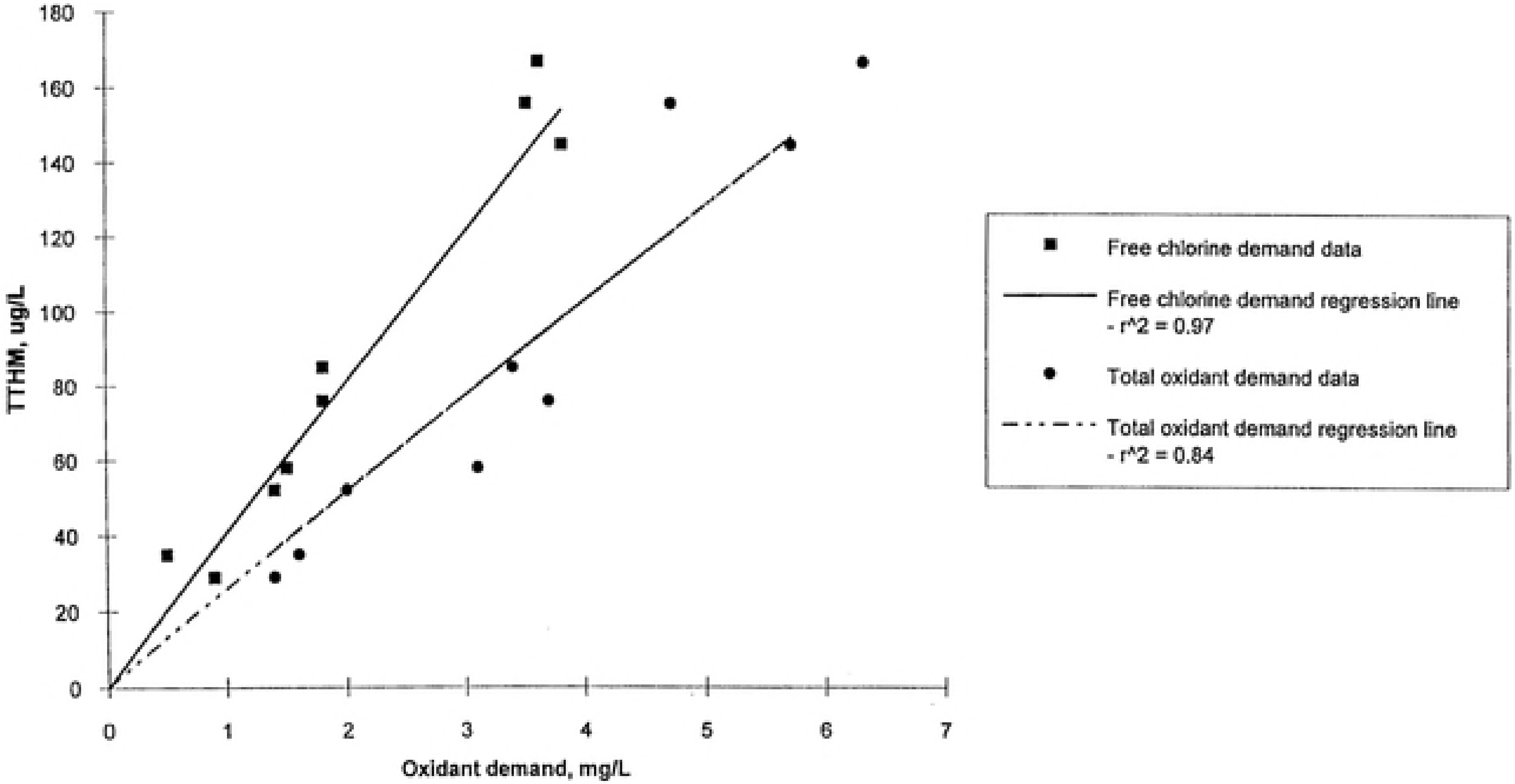

Figure 4-11 TTHM Formation versus Free Chlorine and Total Oxidant Demands in Test Waters Treated with SCOLA4

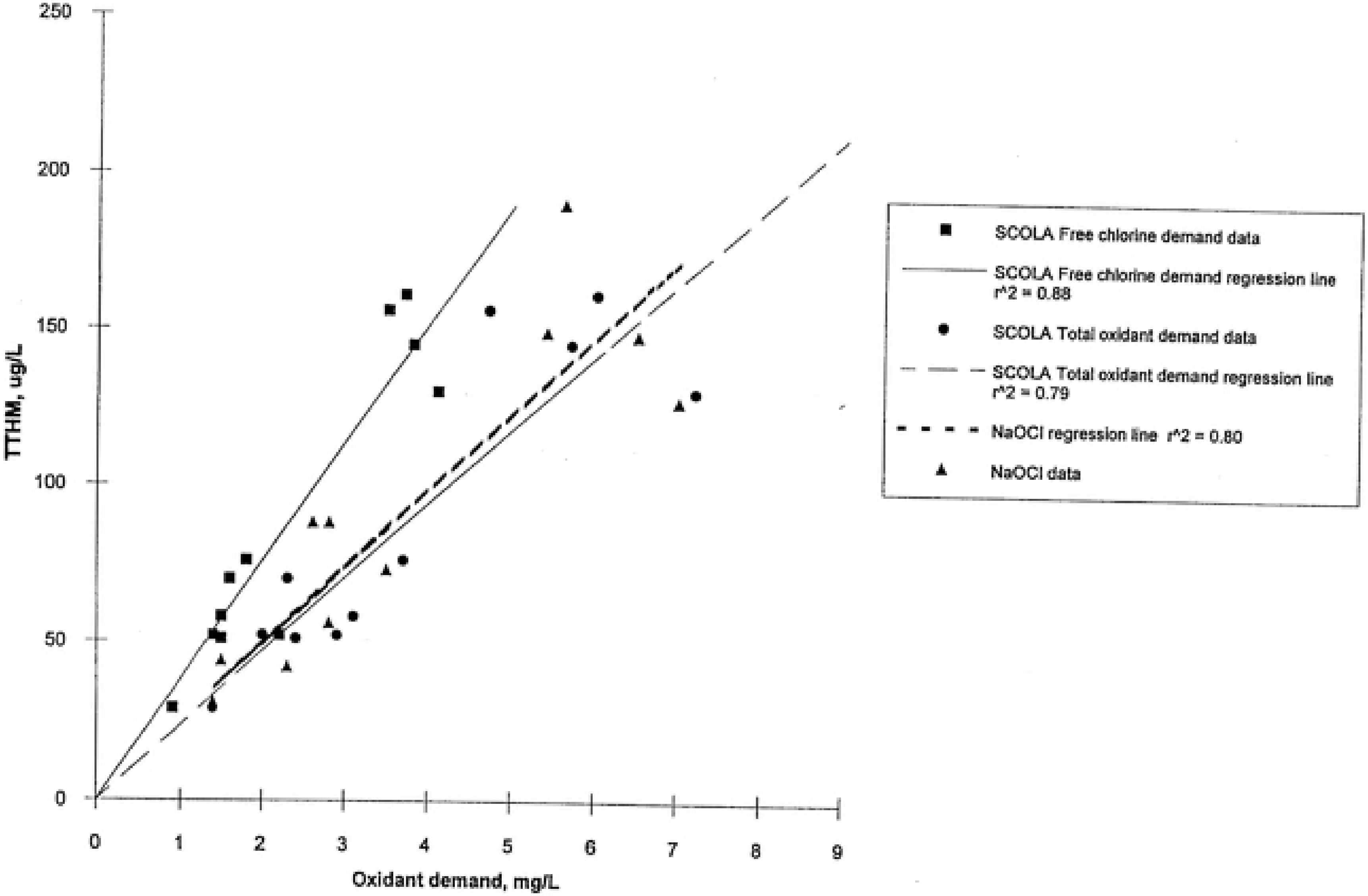

Figure 4-12 TTHM Formation versus Free Chlorine and Total Oxidant Demands in Test Waters Treated with NaOCl and with SCOLA

What this would mean is that the mixed oxidant solution produced by MIOX is stoichiometrically equivalent to a NaOCl solution in terms of its THM formation potential. Although both ozone and the hydroxyl radical are thermodynamically capable of oxidizing Cl^- to Cl_2, kinetically they are not (Langlais et al, 1991; Kang, 1989). At neutral pH, ClO_2 is thermodynamically incapable of oxidizing Cl^- to Cl_2 as is H_2O_2. Perhaps there is a product of ozone decomposition, other than the hydroxyl radical, that is capable of oxidizing Cl^- to Cl_2; if so, it is not known if this will occur at pH 7-8.

4.4 Other Studies

4.4.1 SCOLA Stability Studies

Based on the results of the model water and the real water studies, it was deemed necessary to investigate the composition and stability of SCOLA and the SCOLA species more thoroughly, particularly with regard to changes that might occur in SCOLA composition when the pH is raised from 2 to 8. Another set of experiments was designed with the objective of determining how the SCOLA species behaved, i.e. how stable they were, at pH 2 and at pH 8. Only SCOLA4 was used for these experiments.

Recognizing that ozone decomposes rapidly at elevated pH, the stability of SCOLA4 was investigated at its initial pH of 2.1 as well as at pH 8, the pH value at which most of the THM formation experiments were conducted. The stability of both the total oxidant concentration and the free chlorine concentration were evaluated. The total oxidant concentration of SCOLA4 was measured both iodometrically and amperometrically in these experiments. Free chlorine was measured, as in all cases, by amperometric titration with PAO.

The experiments at pH 2.1 were conducted by filling a series of 40-mL Pierce vials directly from the SCOLA discharge tube. The vials were filled to overflowing and capped. The vials were then analyzed at t = 1, 5, 15, 30, and 60 minutes for total oxidant concentration and free chlorine concentration. The thiosulfate titrations were done using the contents of the vials at full strength, whereas the amperometric titrations were done by first diluting the contents of the vials 100:1 in CDF water, and then titrating a 200-mL aliquot with PAO to the amperometric end-point. Free chlorine measurements were done at pH 7 and total oxidant measurements were done at pH 2 in the presence of excess KI.

The pH 8 iodometric measurements were done by filling another series of 40-mL Pierce vials containing about 0.5 mg of $Na_3PO_4*12H_2O$. The amount of phosphate buffer used was predetermined to yield a pH 8 solution when mixed with 40 mL of SCOLA. The vials were filled to overflowing and capped. Total oxidants were measured by removing a 20-mL aliquot from the vials, adding it to a 150-mL Erlenmeyer flask containing 2 mL of concentrated glacial acetic acid and about 1 g of KI, and titrating with thiosulfate to the iodometric end-point. The pH of the solution remaining in the vials was then measured. This was done at t = 1, 5, 15, 30, and 60 minutes. The pH 8 amperometric measurements, both for free chlorine concentration and total oxidant concentration, were done by taking a 10-mL aliquot of SCOLA from the flow-through vessel, diluting 100:1 in CDF water buffered at pH 8 using a 5×10^{-3} M phosphate buffer, and titrating 200-mL aliquots with PAO to the amperometric end-point. This was done at t = 1, 5, 15, 30, and 60 minutes.

Table 4-11 and Figures 4-13 and 4-14 show the results of the SCOLA4 stability studies. SCOLA4 is stable in terms of its total oxidant concentration and free chlorine concentration both at pH 2.1 and at pH 8. The variation in the free chlorine data at pH 2 is probably due to the fact that each point represents an independent sample and dilution. Therefore, variations in output from the MIOX cell could manifest themselves as apparent changes in concentration over time. Two conclusions can be drawn from the results of this study. First, in organic-free water, no Cl_2 is formed from the oxidation of Cl^- by the other oxidant species present in SCOLA4. Second, because the total oxidant concentration of SCOLA4 is relatively constant at both pH 2.1 and at pH 8, whatever oxidant species in addition to Cl2 that are present in SCOLA4 are stable at pH 8, which is the critical pH value at which most of the THM formation experiments were conducted.

The stability of SCOLA4 oxidant species was also investigated in the presence of humic acid. A 4 mg/L humic acid (as HA) working solution was made by diluting the 400 mg/L humic acid stock solution 100:1. The working solution was buffered at pH 8.0 with 0.005 M phosphate buffer. A series of four 300-mL BOD bottles was filled to 2/3 capacity with the humic acid working solution, dosed with equal amounts of freshly generated SCOLA4, filled with the humic acid working solution, and capped. The SCOLA4 solution was characterized prior to dosing as to its total oxidant concentration, free chlorine concentration, and pH. The contents of the bottles were then analyzed for free chlorine concentration by amperometric titration at pH 7, and for total oxidant concentration by amperometric titration at pH 2 with KI addition. This was done at $t = 2$,

Table 4-11 Results of SCOLA Stabiltiy Study

time, min	Free Chlorine*		Total Oxidants**		Total Oxidants***	
	pH 2	pH 8	pH 2	pH 8	pH 2	pH 8
1	149	149	165	162	168	173
5	149	154	165	162	180	180
15	149	151	163	168	180	174
30	132	149	165	167	175	173
60	132	150	166	168		

* determined by amperometric titration at pH 7

** determined by thiosulfate titration

*** determined by amperometric titration at pH 2 with KI addition

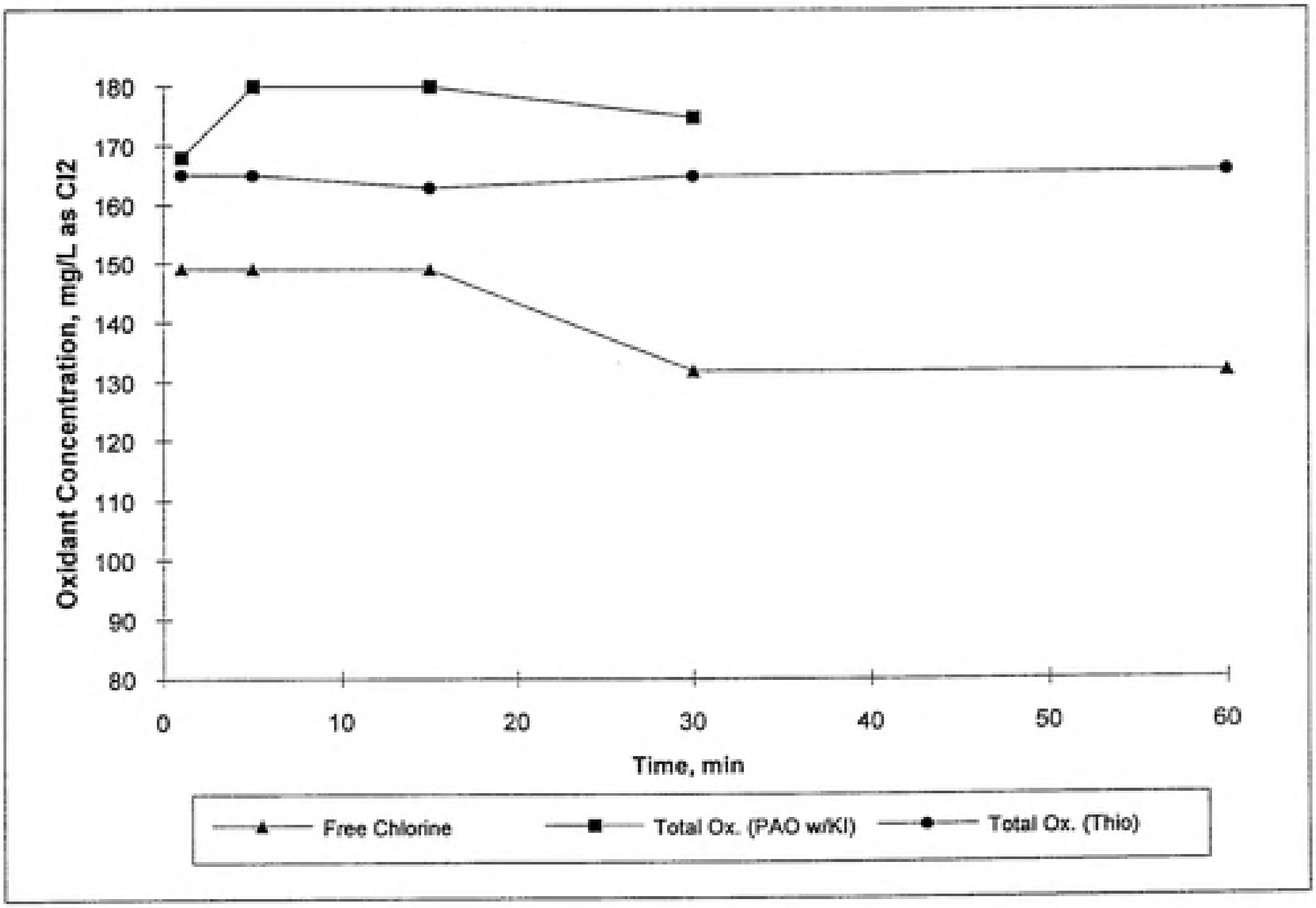

Figure 4-13 Results of SCOLA4 Stability Studies Conducted at pH 2

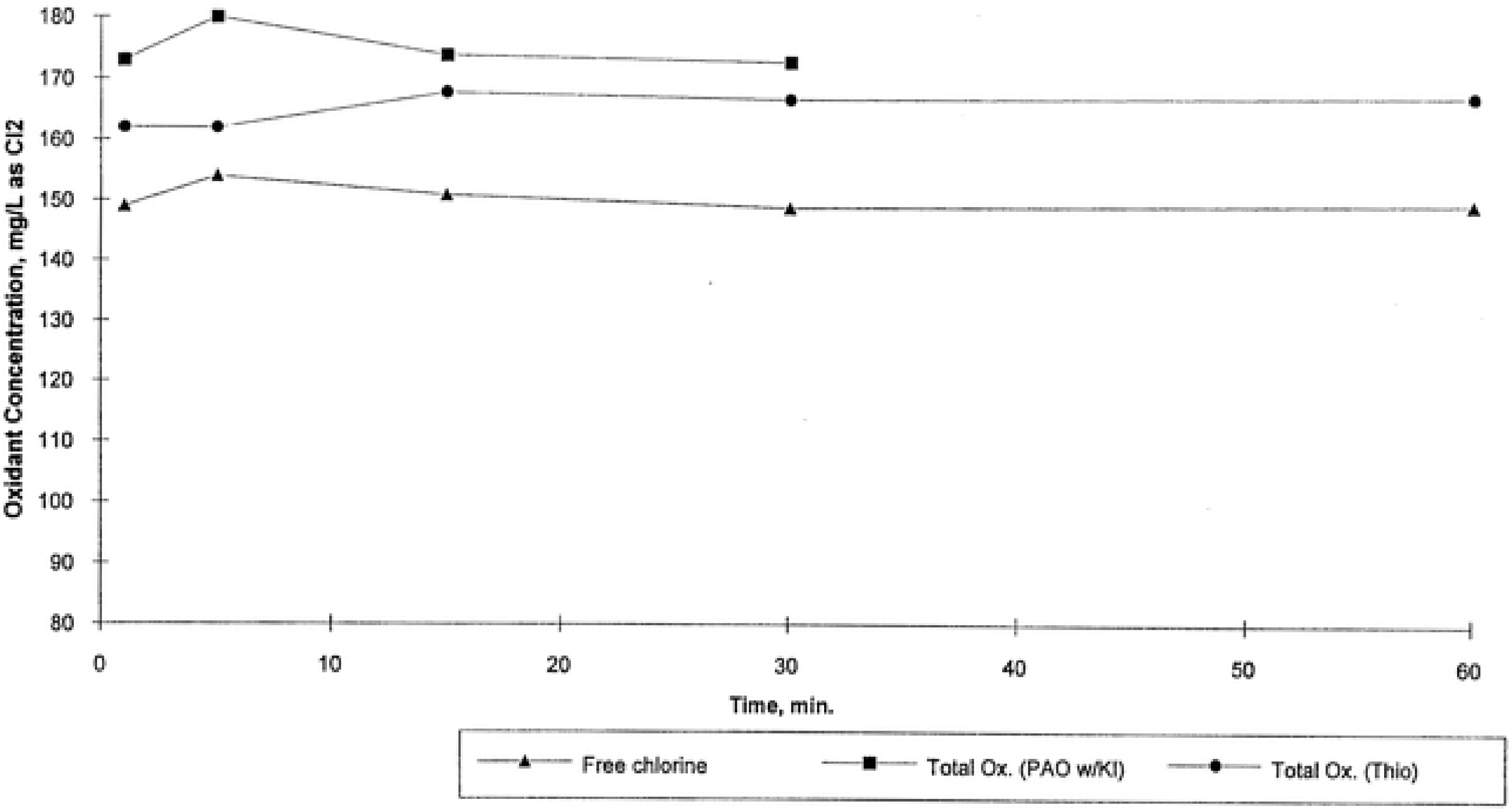

Figure 4-14 Results of SCOLA4 Stability Studies Conducted at pH 8

5, 15, and 30 minutes. The initial measurements of free chlorine concentration and total oxidant concentration, i.e. the concentrations immediately upon dilution with the humic acid solutions, were done by taking a 200-mL aliquot of the humic acid working solution and transferring it to a 250-mL beaker. The solution was then dosed with the same volume of SCOLA4 used in the BOD bottles, stirred, combined with either 2 mL of 2.5 M HCl or 2 mL of pH 7 phosphate buffer, and titrated to the amperometric end-point either with the addition of KI or without. Table 4-12 and Figure 4-15 show the results of this study.

The non-chlorine oxidant species are highly reactive in the presence of NOM and are depleted within 5 minutes. These non-chlorine oxidant species in SCOLA are apparently short-lived in the presence of NOM yet stable in its absence. They are apparently less stable than free chlorine in the presence of NOM. Still, they do persist for up to five minutes in the presence of humic acid. However, without accompanying THM data, nothing can be ascertained from this experiment as to how these other oxidant species are forming THMs.

4.4.2 Short-term THM Formation Studies

A final experiment was designed to investigate the initial oxidant consumption and THM formation in chlorinated and SCOLA- treated model waters. The model water used was a 4 mg/L humic acid (as HA) solution buffered at pH 8. SCOLA was added to the model water in sufficient quantity to provide a 1 mg/L free chlorine residual after a 24-hour contact period. Residual oxidant concentrations were measured and THM samples were taken at t = 15, 30, 60 min. and 24 hours. Two different control experiments using the NaOCl stock solution were done.

Table 4-12 Short Term Oxidant Consumption in Humic Acid Solution Treated with SCOLA4

conditions: DOC = 4 mg/L humic acid (as HA)
pH = 8

Time min.	(Cl2) mg/L*	Total Oxidants mg/L as Cl2**
0***	2.8	3.6
0.25	2.4	2.7
2	2.3	2.4
5	2.1	2.1
15	1.6	1.7
30	1.6	1.7

* determined by amperometric titration at pH 7

** determined by amperometric titration at pH 2 with KI addition

*** concentrations reported at time = 0 are assumed values based on dilution

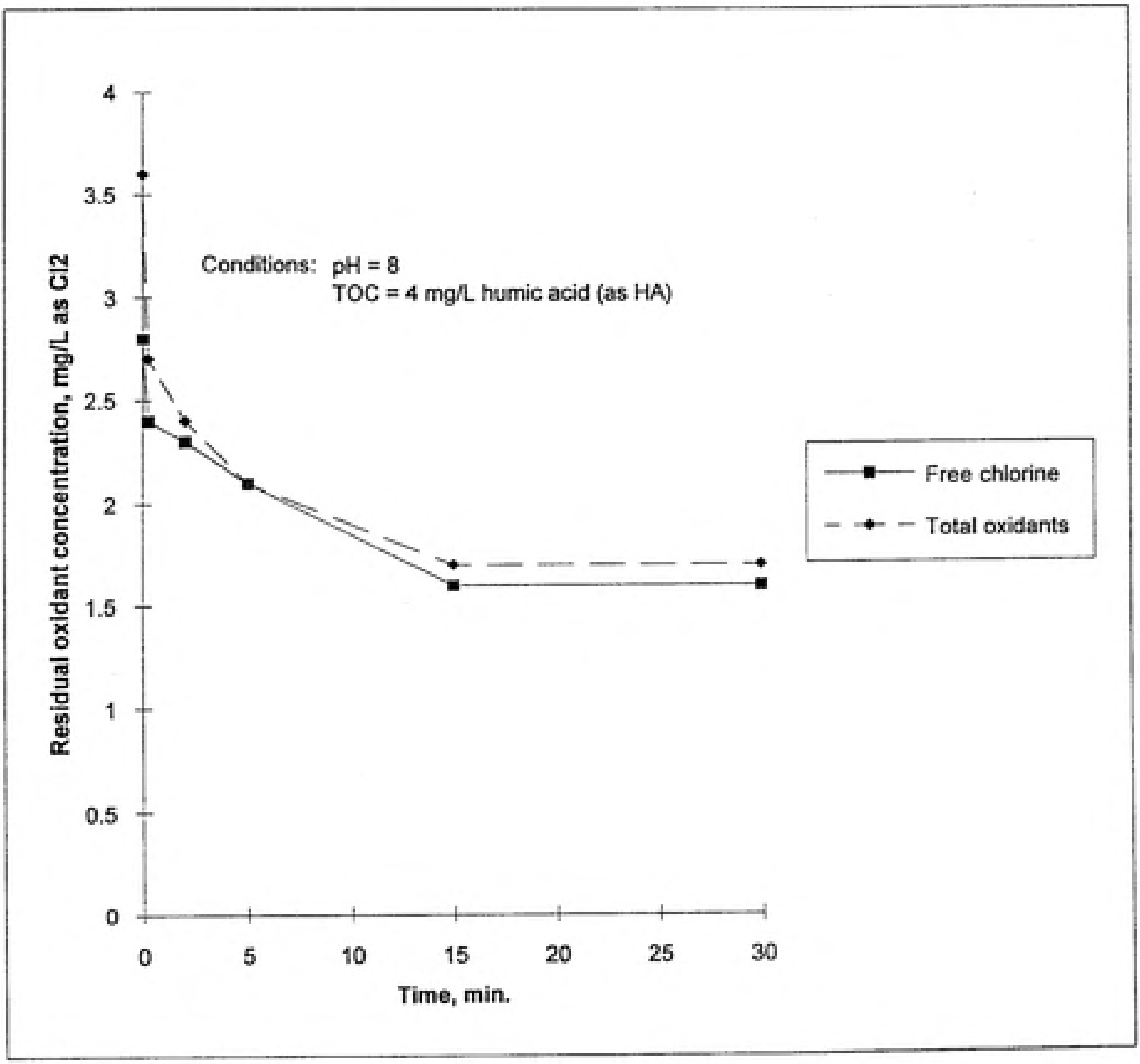

Figure 4-15 Short-Term Oxidant Consumption in Humic Acid Solutions Treated with SCOLA4

In one, the initial chlorine concentration from NaOCl corresponded to the initial free chlorine concentration of the SCOLA-treated water. In the other, the initial chlorine concentration from NaOCl corresponded to the initial total oxidant concentration of the SCOLA-treated water.

Table 4-13 and Figures 4-16 and 4-17 show the results of these experiments. As can be seen in Figure 4-16, the rate of THM formation was essentially the same in all cases. The fast consumption of the non-chlorine oxidant species that was seen in the previous experiment was corroborated by this kinetic study. The non-chlorine oxidant species were essentially gone within 15 minutes. As has been seen throughout the project, the other oxidant species present in SCOLA are behaving like equivalent amounts of free chlorine in their ability to form THMs. However, the reason for this is still unknown, and the results from this study offer no additional insights.

4.5 Discussion

The non-chlorine oxidant species present in SCOLA have consistently had the effect of reducing the free chlorine demand of both model and real waters when compared to equivalent amounts of NaOCl. Yet, identical levels of THM formation in both SCOLA- and NaOCl-treated solutions indicate that these other oxidants are behaving exactly like equivalent amounts of free chlorine in their ability to form THMs. None of the oxidant species suspected to be present in SCOLA, except chlorine, are capable of forming chloroform from reactions with NOM.

Table 4-13 Results of Short-Term Study of Free Chlorine and Total Oxidant Consumption and TTHM Formation in Model Test Solutions

Time, min	SCOLA4 Total oxidants* mg/L as Cl2	SCOLA4 Free chlorine** mg/L	SCOLA4 TTHM ug/L	NaOCl -- (Cl2)o = 3.6 mg/L Free chlorine** mg/L	NaOCl -- (Cl2)o = 3.6 mg/L TTHM ug/L	NaOCl -- (Cl2)o = 3.0 mg/L Free chlorine** mg/L	NaOCl -- (Cl2)o = 3.0 mg/L TTHM ug/L
0	3.6	3.0	0	3.6	0	3.0	0
5			19		17		17
6	2.6	2.2		2.6		2.0	
15			25		23		21
16	2.2	2.1		2.5		1.9	
30			31		26		24
31						1.8	
32	2.1	2.0		2.2			
60			34		32		31
61	2.4	2.2		2.0		1.6	
24 hour	1.2	1.2	91	1.0	87	0.8	88

* determined by amperometric titration at pH 2 with KI addition

** determined by amperometric titration at pH 7

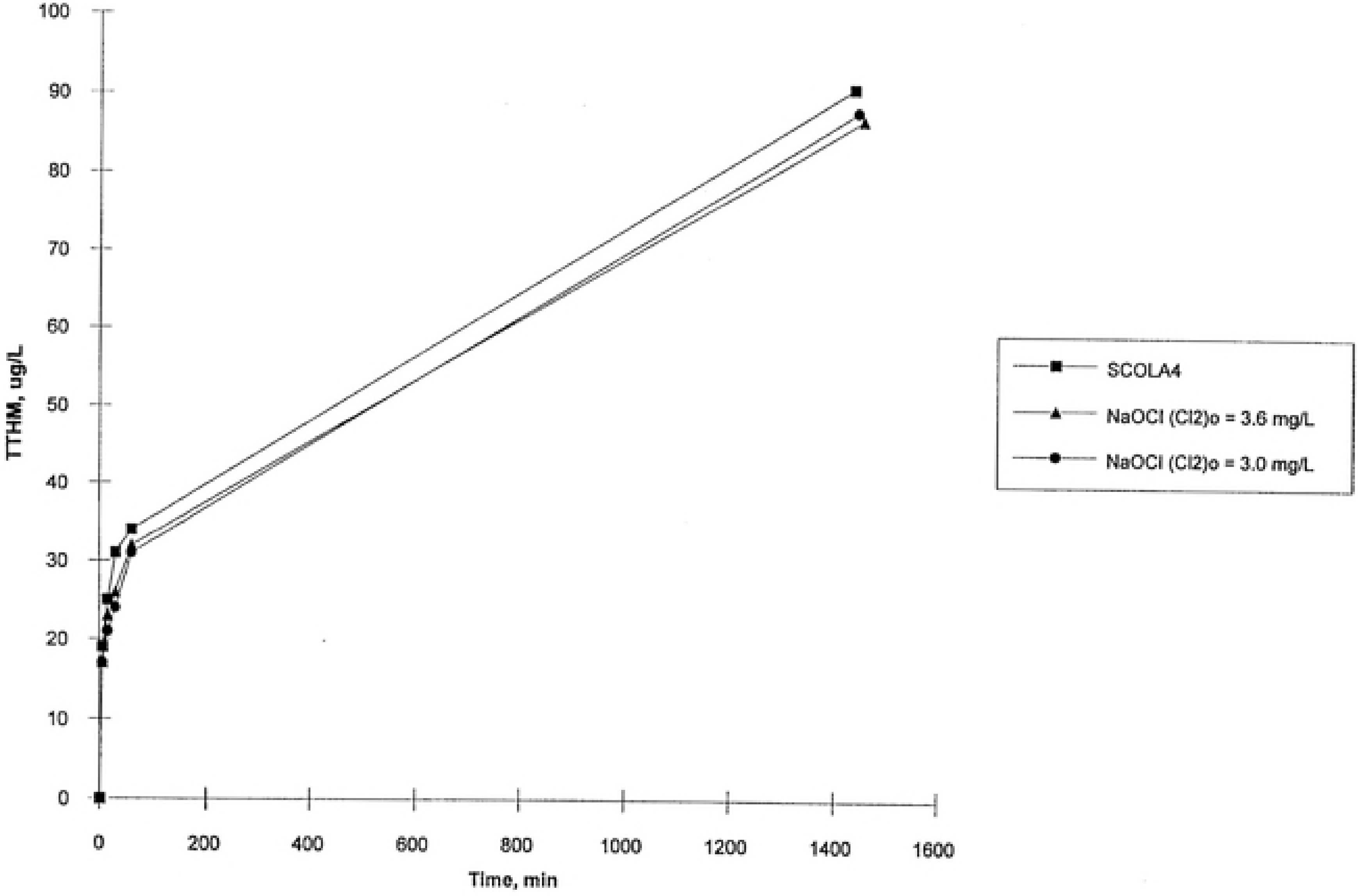

Figure 4-16 Short-Term TTHM Formation in Model Waters Treated with NaOCl and with SCOLA4

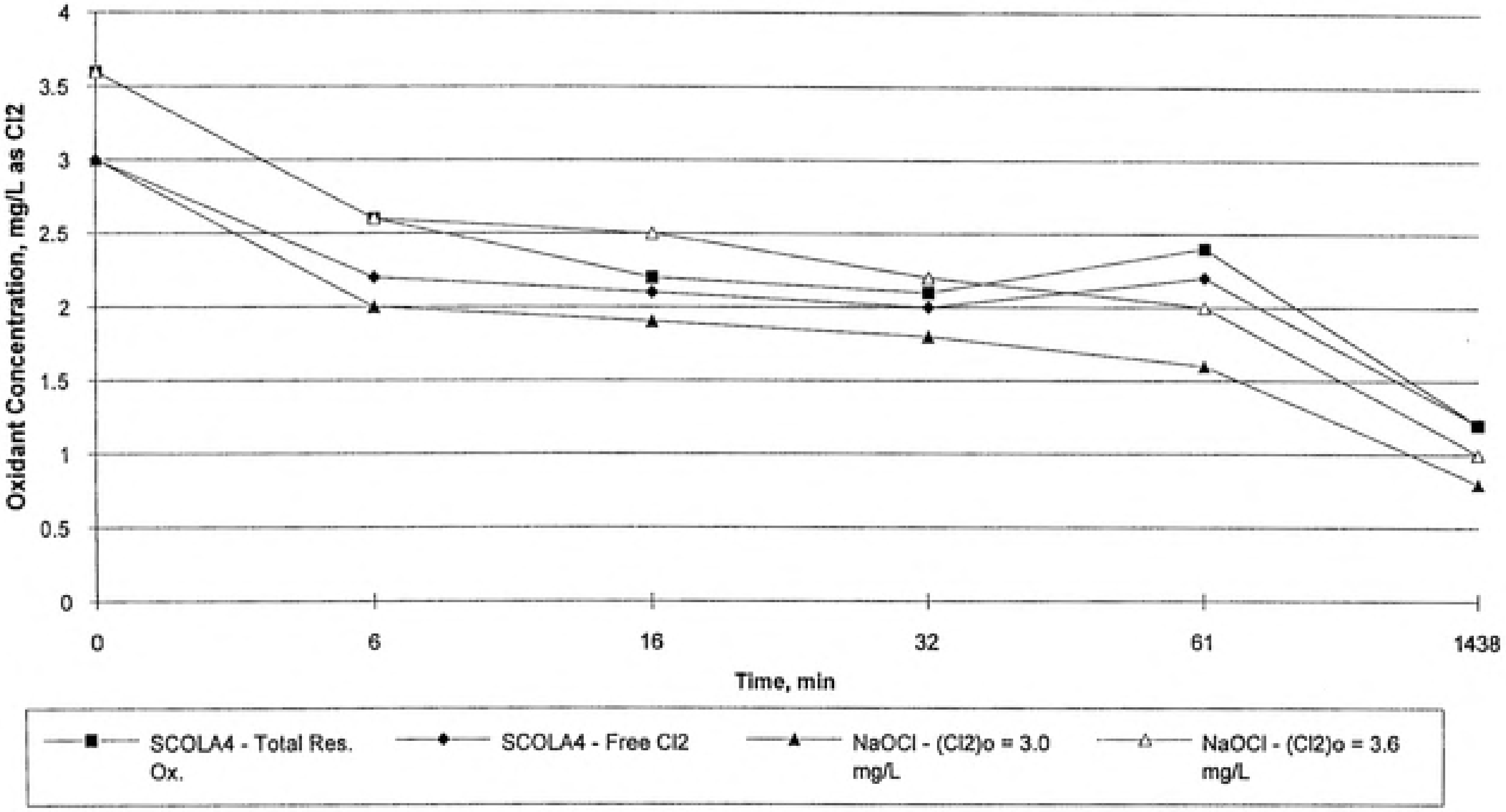

Figure 4-17 Short-Term Oxidant Consumption in Model Waters Treated with NaOCl and with SCOLA4

Although none of the known or proposed oxidant species present in SCOLA are capable of oxidizing Cl^- to Cl_2, it is possible that another oxidant species is formed that is capable of this oxidation when SCOLA reacts with NOM. If this were the case, however, one would expect to see faster initial rates of THM formation in SCOLA-treated waters than in NaOCl treated waters. Because this was not seen, it can be concluded that the oxidation of Cl^- to Cl_2 is not occurring.

A final theory that has yet to be proposed is that the short-lived oxidant species may be altering the NOM in some way as to make it more amenable to THM formation by free chlorine. This does not imply that more sites are made available for chlorine substitution because that would be accompanied by an increase in chlorine demand. Rather, what is proposed is that the NOM is being altered in such a way as to increase the yield of THMs per site. Higher TTHM:Cl_2 ratios (ug TTHM/mg Cl_2) for SCOLA-treated real waters (38:1) than those of NaOCl-treated real waters (22:1) seem to support this theory. However, this is only speculation. The reason why SCOLA produces the same amount of THMs as NaOCl from less chlorine cannot be determined from the results of this project.

Chapter 5 Conclusions and Recommendations

5.1 Conclusions

The MIOX system produced a mixed oxidant solution (SCOLA) that is composed of free chlorine and other, as of yet unknown, oxidant species. The percentage of free chlorine in the mixed oxidant solution was approximately 75%, and this percentage was unaffected by variations in flow rate between 2 and 7 gph/side. Preliminary investigations of the composition of SCOLA indicated only trace amounts of ozone and no detectable chlorine dioxide. The non-chlorine oxidants were stable at pH 2 and pH 8 in the absence of NOM, yet very short-lived in its presence (about 5 minutes).

As a result of the presence of the non-chlorine oxidant species, the chlorine demands of SCOLA-treated waters were consistently less than those of solutions treated with equivalent amounts of NaOCl. However, the level of THM formation in SCOLA- treated waters was essentially the same as that of NaOCl-treated waters. This was the case in both model waters containing commercial grade humic acid as well as in all of the real waters tested. THM formation in SCOLA-treated waters increased with increasing TOC concentration and pH which is consistent with the behavior exhibited by free chlorine. In the model water studies, the THMs formed by SCOLA were essentially all $CHCl_3$, with little Br^- incorporation into the THMs. In the real water studies, the level of Br- incorporation into the THMs was the same in the SCOLA-treated waters as in those treated with equivalent amounts of NaOCl. Initial investigations into the rate of THM formation in SCOLA-treated waters showed no difference from NaOCl-treated waters.

THM formation in the real waters treated with SCOLA correlated well with both the chlorine demand ($r^2 = 0.88$) and the total oxidant demand ($r^2 = 0.79$). The relationship between THM formation and total oxidant demand for SCOLA treatment was similar to that between THM formation and chlorine demand for NaOCl-treated waters. This suggests that the short-lived oxidants are behaving like free chlorine in their ability to form THMs. Determination of the actual mechanisms involved will have to be preceded by a determination of the identity of the non-chlorine oxidants present in SCOLA.

5.2 Implications of Results to Water Treatment Practice

The results of this study show that MIOX does not offer any advantage in terms of THM reduction when compared to free chlorination. On the other hand, MIOX does not enhance the formation of THMs. At the present time, the biggest advantages that MIOX offers are that it appears to be a superior disinfectant than free chlorine (based on reports from the literature), and it is a safer system to operate than one using chlorine gas. If current and future investigations validate the superior disinfecting capabilities of MIOX, then THM reductions may be realized due to lower required CT values when using SCOLA compared to free chlorine. The availability of a source of salt and the costs associated with installing and maintaining salt-handling equipment will also have to be considered by any treatment plant that is considering MIOX as an alternative.

MIOX is already a feasible alternative for use in small communities, both in developing and developed countries, and in disaster areas. However, more research must be done before it can be considered a viable alternative for treatment plants on a larger scale.

5.3 Recommendations for Future Research

The results of this study strongly indicate a need to determine the chemical composition of SCOLA. This is imperative if the results of this study and of corresponding disinfection studies are to be explained. Secondly, a clear understanding of SCOLA composition will help in identifying other potential uses for MIOX. Once the composition of SCOLA has been ascertained, the applicability of MIOX to other water treatment problems currently treated by other oxidants should be investigated. These applications include the following:

- iron and manganese removal
- control of taste and odor
- color removal
- destruction of synthetic organic chemicals (SOCs)

Additionally, the effect of SCOLA on other DBPs, such as the haloacetic acids (HAAs), and on total organic halide (TOX) formation should be evaluated.

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Appendix 1

Results of 6 volt BPS and 12 volt SBS Experiments

Using the procedures outlined in Section 3.3.2, the formation of THMs by two other MIOX units was investigated. The two units used were a 6-volt brine pump system (BPS), and a 12-volt, high-capacity, automated, SAL-I BPS. The results of these studies are shown in Tables A-1 and A-2. The 6-volt experiments were done early in the project, before the addition of the amperometric titration procedure to the experimental program. The NaOCl data presented in both tables is taken from Table 4-4. The 12-volt experiments were conducted by the author at the University of New Mexico in Albuquerque, NM. Figure A-1 shows that SCOLA produced less THMs than NaOCl in the 4 mg/L humic acid (as HA) solution and comparable amounts in the 8 mg/L humic acid solution. The SCOLA produced by the 12-volt SAL-I system produced essentially the same amount of THMs as did an equivalent amount of NaOCl for the 2 and 4 mg/L humic acid solutions, yet a significant reduction was seen for the 8 mg/L data. Because these experiments were only done once, it is uncertain whether or not the reductions in THM formation that were seen in the SCOLA-treated solutions are anomalies.

Table A-1 Results of 6-volt Miox Unit Experiments

conditions: 30 g/L NaCl, Q = 2.6 gph/side, [total oxidants] = 440 mg/L as Cl_2

		NaOCl				SCOLA			
TOC mg/L humic acid (as HA)	pH	Applied Oxidant Dose* mg/L as Cl_2	24 hour Residual Free Cl_2** mg/L	$CHCl_3$ ug/L	TTHM ug/L	Applied Oxidant Dose* mg/L as Cl	24 hour Residual Free Cl_2** mg/L	$CHCl_3$ ug/L	TTHM ug/L
4	8	3.5	0.8			2	0.1		
		4.0	1.3	89		3	0.9	60	64
		4.5	1.7			4	1.5		
8	8	6.5	0.8			4	0.1		
		7.0	1.4	190		6	1.5	170	183
		7.5	1.7	198		8	2.7		

* determined by thiosulfate titration
**determined by DPD titration

Table A-2 Results of 12-volt SAL-I Experiments

conditions: 7.8 g/L NaCl, Qanode = 17 gph, Qcathode = 15 gph
[Cl_2] = 210 mg/L, current = 27 amps

		NaOCl			SCOLA		
TOC mg/L humic acid (as HA)	pH	Applied Oxidant Dose** mg/L	24 hour Residual Free Cl_2* mg/L	$CHCl_3$ ug/L	Applied Free Cl_2 Dose* mg/L	24 hour Residual Free Cl_2* mg/L	$CHCl_3$ ug/L
2	8	2.0	0.5		2.0	1.0	39
		2.5	1.0	44	2.5	1.3	
		3.0	1.4	44	3.0	1.7	
					3.5	2.8	
4	8	3.5	0.8		3.0	0.4	
		4.0	1.3	89	4.0	1.6	91
		4.5	1.7		5.0	2.5	
					6.0	2.9	
8	8	6.5	0.8		5.0	0.6	147
		7.0	1.4	190	7.0	2.7	
		7.5	1.7	198	9.0	4.5	
					11.0	6.4	

* determined by amperometric titration
** determined by thiosulfate titration