

# **Impacts of Sludge Volume and Sludge Age on Disinfection By-Product Formation in a Full-Scale Water Treatment Facility**

William Hunter Carson

Thesis submitted to the faculty of Virginia Polytechnic Institute and State University in partial fulfillment of the requirements for the degree of

Master of Science

in

Environmental Engineering

Gregory D. Boardman, Chairman

Andrea M. Dietrich

Shawn H. Veltman

March 30, 2006

Blacksburg, Virginia

Keywords: sludge, disinfection byproducts, haloacetic acids, trihalomethanes

# **Impact of Sludge Volume and Water Quality on DBPs in a Full-Scale Water Works**

**William Hunter Carson**

## **(Abstract)**

The goal of this research was to determine the role of settled sludge on the formation of disinfection by-products in a full-scale water treatment plant. The occurrence of disinfection by-products in chlorinated drinking water has become a major concern to treatment facilities in their effort to comply with strict regulations set by the United States Environmental Protection Agency. Water samples were tested for trihalomethanes and haloacetic acids at both ends of the sedimentation process to evaluate formation over the length of the basin. Sludge volume and other important water quality parameters were also measured at the time of sample collection. Statistical analyses were used to analyze contributions from the sludge and to determine influential factors leading to disinfection by-product formation. The treatment plant incorporated chlorine dioxide into the treatment process seasonally, and effects were evaluated. Predictive models were developed from the data to be used under various treatment methods. The models created for trihalomethanes and haloacetic acids require measurements of chlorine dose, reaction time, total organic carbon, pH, water temperature, and sludge volume. The models performed well in predicting actual trihalomethane and haloacetic acid concentrations and could serve as a valuable tool in the control of disinfection by-products.

# **DBP Formation Potential of Settled Sludge in a Full-Scale Water Treatment Facility**

**William Hunter Carson**

## **(Abstract)**

It is still a common occurrence for water treatment facilities to store sludge in sedimentation basins for extended periods, rather than relying on mechanical collection equipment. The goal of this research was to characterize contributions from settled sludge to the formation of disinfection by-products (DBPs), and determine whether continuous removal is essential in the control of DBPs. Samples were taken from top and bottom sludge layers in the sedimentation basin and water was extracted either by draining or centrifugation. The water was analyzed for trihalomethanes and haloacetic acids and water quality measurements were recorded. Concentrations of both DBPs were very high in top-layer sludge; trihalomethanes ranged from 321.5  $\mu\text{g/L}$  to 568  $\mu\text{g/L}$  and haloacetic acids ranged from 74.6  $\mu\text{g/L}$  to 409.8  $\mu\text{g/L}$ . Evidence of biodegradation was observed in the bottom-layer sludge. The water samples were dosed with 4 mg/L chlorine, the United States Environmental Protection Agency's maximum residual disinfectant level, to determine if further DBP formation was possible. The extracted water from the bottom-layer sludge was shown to form high trihalomethane concentrations when chlorinated, and haloacetic acid concentrations were observed to increase when samples from the top-layer sludge were chlorinated.

# TABLE OF CONTENTS

CHAPTER 1: LITERATURE REVIEW .....	1
Disinfection by-product formation. ....	2
<i>Natural Organic Matter</i> .....	3
<i>Disinfectant Dose</i> .....	5
<i>Contact Time</i> .....	6
<i>pH</i> .....	7
<i>Water temperature</i> . ....	8
<i>Bromide concentration</i> .....	9
Chlorine dioxide and DBP formation. ....	10
Degradation of DBPs.....	12
Toxicity of HAAs and THMs. ....	13
TABLES .....	15
TABLE 1 THMs and HAAs .....	15
Chapter 2: Impact of Sludge Volume and Water Quality on DBPs in a Full-Scale Water Works.....	16
BACKGROUND .....	17
Formation and types of HAAs and THMs.....	17
Factors contributing to THM and HAA formation.....	18
Study Objectives. ....	19
EXPERIMENTAL APPROACH.....	20
Sampling Procedures. ....	20
Analytical Methods.....	22

RESULTS AND DISCUSSION.....	23
Models by Amy et al. and AWWARF for THMs and HAAs.....	24
Development of a predictive model.....	28
Influences of water quality parameters on DBP formation. ....	32
<i>Sludge Volume.</i> ....	32
<i>TOC.</i> .....	34
<i>Water Temperature.</i> ....	35
<i>Contact time.</i> .....	36
<i>Chlorine Dosage.</i> .....	37
Chlorine dioxide use and incorporation into predictive models. ....	38
Model Evaluations. ....	42
CONCLUSIONS.....	45
CHAPTER 2 TABLES.....	47
TABLE 1 Statistical summary of water quality parameters and DBP concentrations in sedimentation basins.....	47
TABLE 2 Summary of statistical output from R for HAA5 predictive model (Equation 3) .....	48
TABLE 3 Summary of statistical output from R for TTHM predictive model (Equation 4) .....	48
TABLE 4 R-Squared values for various models .....	49
CHAPTER 2 FIGURES.....	50
FIGURE 1 BCVPI TTHM data vs. Amy et al. model (1987) .....	50
FIGURE 2 BCVPI actual HAA data vs. AWWARF model (1991).....	50

FIGURE 3 BCVPI HAA5 data vs. predictive model data (Equation 3).....	51
FIGURE 4 BCVPI TTHM data vs. predictive model data (Equation 4).....	51
FIGURE 5 Basin 1 HAA5 concentration (sludge contact experiment).....	52
FIGURE 6 Basin 1 TTHM concentration (sludge contact experiment).....	52
FIGURE 7 DBP concentrations in Basin 1 during high ClO <sub>2</sub> addition.....	53
FIGURE 8 Predicted 2004 HAA5 concentrations in BCVPI plant.....	53
FIGURE 9 Predicted 2004 TTHM concentrations in BCVPI plant.....	54
FIGURE 10 Predicted HAA5 values using chlorine dioxide model.....	54
FIGURE 11 Predicted TTHM values using chlorine dioxide model.....	55
ACKNOWLEDGEMENT.....	56
CHAPTER 2 REFERENCES.....	57
CHAPTER 3: DBP Formation Potential of Settled Sludge in a Full-Scale Water	
Treatment Facility.....	59
BACKGROUND.....	60
Formation of THMs and HAAs.....	60
Types of THMs and HAAs.....	61
Degradation of THMs and HAAs.....	61
Study Objectives.....	62
EXPERIMENTAL APPROACH.....	63
Sampling techniques.....	63
Analytical methods.....	65
RESULTS AND DISCUSSION.....	67
Sludge age vs. TTHM and HAA5.....	68

TOC concentrations and release .....	71
Chlorination of sludge waters .....	71
CONCLUSIONS.....	73
CHAPTER 3 TABLES .....	75
TABLE 1 TTHM and HAA5 species .....	75
TABLE 2 Partition coefficients of DBPs and common volatile compounds .....	75
TABLE 3 Extracted water and sludge characteristics from top and bottom layers..	76
TABLE 4 HAA5 percentage distribution in top sludge layer.....	76
TABLE 5 HAA5 percentage distribution in bottom sludge layer .....	76
TABLE 6 HAA5 and TTHM concentrations following chlorination.....	77
CHAPTER 3 FIGURES.....	78
FIGURE 1 Schematic of sample collection and treatment .....	78
FIGURE 2 Sludge Age and TTHM concentrations in centrifuged.....	78
FIGURE 3 Sludge Age and HAA5 concentrations in centrifuged .....	79
FIGURE 4 TOC release from top and bottom sludge samples.....	79
FIGURE 5 TTHM concentration in top-centrifuged sludge sample .....	80
FIGURE 6 TTHM concentration in top-drained sludge sample.....	80
FIGURE 7 HAA5 concentration in top-centrifuged sludge sample .....	81
FIGURE 8 HAA5 concentration in top-drained sludge sample .....	81
ACKNOWLEDGEMENT .....	82
CHAPTER 3 REFERENCES .....	83
LITERATURE REVIEW REFERENCES .....	85
APPENDIX A: R code for TTHM predictive model (no ClO <sub>2</sub> ).....	88

APPENDIX FIGURE 1 TTHM Pairwise Plot.....	96
APPENDIX B: R code for HAA5 predictive model (no ClO <sub>2</sub> ).....	97
APPENDIX B FIGURE 1 HAA5 Pairwise Plot.....	106
APPENDIX C: R code for TTHM model with ClO <sub>2</sub> .....	107
APPENDIX D: R code for HAA5 model with ClO <sub>2</sub> .....	114
APPENDIX E: Supplemental figures.....	128
FIGURE 1 Predicted HAA5 values using chlorine dioxide model when ClO <sub>2</sub> is absent .....	128
FIGURE 2 Predicted TTHM values using chlorine dioxide model when ClO <sub>2</sub> is absent .....	128



## CHAPTER 1: LITERATURE REVIEW

The disinfection of water using chlorine has been a strategy widely used in drinking water treatment to protect consumers from waterborne diseases. However, when free chlorine reacts with natural organic matter (NOM) such as humic and fulvic acids, disinfection by-products (DBPs) are generated (Sérodès et al, 2003). Among the most prevalent DBPs are haloacetic acids (HAAs) and trihalomethanes (THMs). While pathogenic organisms provide the primary health risk associated with treated drinking water, DBPs have presented an unintended threat.

The formation and occurrence of disinfection by-products has been acknowledged for many years; however, only recently have they been the focus of particular attention. This is due to their potentially carcinogenic effects. Concerns of health risks have prompted the United States and other countries to establish maximum contaminant levels (MCLs) for HAA and THM concentrations in finished drinking water. Five of the nine chlorine/bromine based haloacetic acid compounds are considered a health threat and are regulated. These are referred to as “HAA5” and include mono-, di-, and trichloroacetic acid and mono- and dibromoacetic acid. Total THM (TTHM) represents the sum of four THMs-chloroform, bromoform, bromodichloromethane, and dibromochloromethane. Table 1 lists the DBPs of interest along with chemical structure and federal MCL values.

In January, 2002, the Stage 1 Disinfectants/Disinfection By-Products (D/DBP) Rule became effective, lowering the MCLs for HAA5 and TTHM to 60 µg/L and 80 µg/L, respectively. Stage 1 regulations are based on four-quarter running averages, which represent a system-wide average concentration over a one year period. This regulation has presented some water authorities with costly treatment updates (e.g.

alternative coagulants, disinfectants, and filtration methods) due to MCL violations. Furthermore, the Stage 2 D/DBP signed in January, 2006 will require that MCLs be based on locational running averages, meaning that each location within the distribution system will need to comply with the annual average (Richardson, 2003). This rule will diminish, if not eliminate the permissive MCL violations which may occur at some locations (particularly those located furthest from the treatment facility); thereby reducing the variability of human exposure throughout the distribution system.

### **Disinfection by-product formation.**

Haloacetic acid and trihalomethane formation is dependent upon water quality characteristics and their fluctuations due to environmental conditions and treatment plant operations. Natural organic matter levels, disinfectant dose, contact time, pH, water temperature, and bromide concentration are all factors which influence HAA and THM formation (AWWA, 1999). In the interest of the research being conducted, chlorine will be the disinfectant addressed. Chlorine is the most widely used disinfectant in water treatment today due to its effectiveness and low cost; however, it results in the highest total organic halide concentration (TOX) of any disinfectant, of which 25% are THMs and approximately 18-20% are HAAs (Dalvi et al, 2000).

Both THMs and HAAs are formed via hydrolysis reactions as shown in equations 1-4. An example of THM formation (especially at high pH) is expressed in equations 1 and 2 as propanone is oxidized by hypochlorous acid and forms trichloropropanone (Equation 1). Trichloropropanone is subsequently hydrolyzed and forms chloroform and other by-products (Equation 2) (Xie, 2004).



Trichloropropanone may be further oxidized at lower pH to form tetra-, penta-, and hexachloropropanone. The chloropropanone groups may then undergo a hydrolysis reaction and form mono-, di-, or trichloroacetic acids. Trichloropropanone is oxidized and forms pentachloropropanone (Equation 3) and further hydrolyzed to form both dichloroacetic acid and chloroform (Equation 4) (Xie, 2004).



### ***Natural Organic Matter.***

Natural organic matter serves as the principal precursor to DBPs, and many studies agree that NOM concentrations are directly related to DBP formation (Singer, 1993). An increase in NOM levels affects DBP formation primarily in two ways: (1) DBP precursors are increased, and (2) chlorine demand is increased in order to satisfy disinfection criteria and maintain a proper residual within the distribution system (Xie, 2004). Haloacetic acids, such as trichloroacetic acid can be formed by the following reaction with generalized organic matter,  $\text{CH}_3\text{-CO-R}$  (where R is an oxidizable group), and chlorine (Equations 5 and 6).



Aqueous NOM is composed of two fractional groups, a humic fraction and a transphilic fraction. The humic fraction is typically broken down further into humic acids and fulvic acids (Xie, 2004). Garcia-Villanova et al (1997) found aqueous humic matter to be composed of approximately 90% fulvic acid and 10% humic acid, in most waters. Although both the humic group (hydrophobic) and transphilic group (hydrophilic) display similar characteristics, it is the humic fraction that is most easily removed by conventional water treatment (Barret et al, 2000). However, it is this group which contributes more to the formation of DBPs. Garcia-Villanova et al (1997) found that the humic acid fraction contributes greatly to the formation of THMs due to its reactivity with chlorine. Both fractions react differently under chlorination conditions and do yield different DBP levels. Using five surface waters, Reckhow, Singer, and Malcolm (1990) found humic acids to consume higher amounts of chlorine than did fulvic acid. Additionally, DBP formation potentials for all waters were found to be higher for humic acids. Croué et al (2000) on the other hand, found that all humic matter, both hydrophobic and hydrophilic components, contribute to DBP formation. One water source studied, displayed dominant hydrophilic characteristics and resulted in higher THM production than another, more hydrophobically characterized source.

NOM is generally measured using surrogates such as total and dissolved organic carbon, TOC and DOC, respectively, and UV absorbance at 254 nanometers. Dalvi et al (2000) found that the formation potential of HAAs peaks when the ratio of TOC to

residual chlorine is between 1 and 2 (Dalvi et al, 2000). Under the Stage 1 D/DBP Rule, an emphasis was placed on the reduction of TOC via enhanced coagulation in order to minimize the precursor levels and to limit the formation of DBPs. This has been implemented at many water treatment facilities because a 40 percent reduction in TOC across conventional treatment has been found to reduce DBPs by 50 percent and higher (AWWA, 1999). Specific UV absorbance (SUVA), the ratio of  $UV_{254}$  to DOC is used as a good indicator of the humic content of a water. A strong correlation was found by Chin, Aiken, and O'Loughlin (1994) between SUVA and the aromatic-carbon contents of many fulvic acids. Therefore, SUVA can in some instances be representative of the aromatic-carbon content of NOM and can be used to identify the chemical characteristics of the DOC involved. Waters containing a low humic acid fraction, and therefore a typically low DOC concentration, will tend to have SUVA values less than 2 L/mg C/m. High humic acid waters on the other hand typically portray SUVA values between 3-5 L/mg C/m (AWWA, 1999). Edwald and Van Benschoten (1990) noted that in waters with SUVA values of less than 3 L/mg C/m, relatively low DOC removal rates (20-50%) are likely.

### ***Disinfectant Dose.***

Higher chlorine dosage and residual levels have portrayed linear relationships with increased DBP formation in most finished water studies (Garcia-Villanova et al, 1997). An increase in chlorine may not only increase DBP levels, but also determine the species of DBP formed. Yuefeng Xie (2004) found that some DBPs are intermediate products and others are end products of the chlorine reaction. This is true for THMs

where a higher disinfectant dose was found to yield higher chloroform concentrations, and for most other DBPs when mono- and dihalogenated acids are further chlorinated to trihalogenated acids. This however is not the case with mono- and dichloroacetic acid, both of which are end products of the chlorine reaction (Xie, 2004). Research has also suggested that higher chlorine doses and residuals may actually favor HAAs over THMs resulting in higher HAA formation rates and ultimately an increase in tri-halogenated HAAs (Singer, 1999).

The linear correlation between DBP formation and chlorine levels is possible only when both chlorine and organic precursor concentrations are available, a situation that is not always the case. During primary disinfection, low doses of chlorine (well below the long-term demand) are added in order to achieve the majority of microbial inactivation. This step generally takes place prior to sedimentation (in conventional surface water treatment) where levels of organic material are similar to that of the raw water source. Here, disinfection by-products become chlorine-limited as opposed to later on in the process when DBPs are precursor-limited due to coagulation and sedimentation processes (AWWA, 1999).

### ***Contact Time.***

Contact time is among the most important factors in HAA and THM formation as it reflects contact availability between a disinfectant and organic matter. As mentioned previously, THMs and HAAs are end products in a series of reactions involving chlorine and DBP precursors, and various intermediate reaction products. For this reason, increasing the reaction time will most likely increase THM and HAA formation (Xie,

2004). THM and HAA formation occurs rapidly at first and will continue at a slower rate as long as water contains a chlorine residual (Singer, 1993). Rossman et al (2001) found that levels at a consumers tap may be as much as two to three times higher than what they are leaving the treatment works depending on locality. Typically, this is the case but other studies have suggested that certain DBPs, including HAAs actually decay after extended periods within the distribution system (Adams et al., 2005). This is most likely the result of microbial degradation; THMs appear to be biodegradable only under anaerobic conditions (AWWA, 1999). This will be discussed further in the “Degradation of DBPs” section.

Many considerations must be taken into account when studying DBP levels over time within various distribution systems. Several factors may influence formation and degradation, including the condition of the pipe in which the water is in contact. Older pipes may exhibit DBP precursors in the form of organic material from scale or biofilm attached to the inside wall (Rossman et al, 2001). Chlorine residual is also a contributing factor.

### ***pH.***

The pH of water either during treatment or upon distribution plays a role in the formation of THMs and HAAs, primarily when chlorination is implemented. THM formation increases with an increase in pH, while HAAs increase in concentration with a decrease in pH. One exception to this case is dichloroacetic acid (DCAA) which has been observed to be independent of pH variation (Dalvi et al, 2000). THM formation is

very sensitive to pH fluctuations; values of up to three-fold per pH unit have been observed (Garcia-Villanova et al, 1997).

The lower the pH, the higher the non-ionized HOCl form of hypochlorous acid is found, resulting in faster reaction rates with humic matter. The chlorine species does contribute to DBP formation rates, but base-catalyzed hydrolysis mechanisms may play an even greater role in THM and HAA formation (AWWA, 1999). The acidic functional groups of humic matter are not ionized and result in the aggregation of molecules and ultimately the “folding” of humic molecules (Adin et al, 1991). This folding action leaves fewer sites available for chlorine to invade and consequently reduces THM production (Garcia-Villanova et al, 1997) at lower pH. On the contrary, other halogenated DBPs such as HAAs excel at lower pH but hydrolyze at pH values of approximately 8.0 and above (Singer, 1993).

***Water temperature.***

There is a pronounced seasonal effect on the rate of DBP formation where high levels are recorded in the summer months and the lowest levels in the winter months (Singer, 1993). This can be linked to: (1) an increase in primary production = higher NOM levels, (2) photodegradation of chlorine via sunlight (a higher chlorine concentration is demanded) and (3) accelerated DBP reaction rates. Collectively, these aspects make DBP control harder in the summer months and contribute to the majority of MCL violations.

Higher water temperatures may also accelerate DBP degradation in both the distribution system and especially in open systems (Garcia-Villanova et al, 1997).



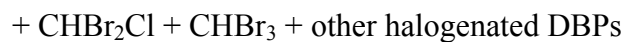
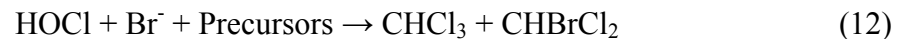
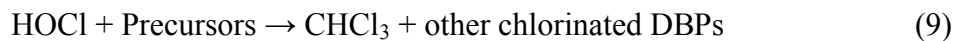
Studies conducted on the thermal effects of halogenated DBPs show that boiling water significantly decreases the concentrations of all THMs and removes >95% (Wu et al, 2001). While comparing the similarities of a boiled water sample to the temperature fluctuations in a distribution system may and be extreme, it does indicate the volatility of all THMs. Another study which monitored chloroform levels through a treatment facility and distribution system over the course of one year obtained results also demonstrating high volatility. In the treatment utility, which was an open system, chloroform levels rose until the water temperature reached 18.97 °C and then dramatically reduced. Similar occurrences were true in the distribution system as levels experienced a sharp decrease at 17.30 °C (Garcia-Villanova et al, 1997).

Chemical and biological degradation of HAAs has also been observed as a result of increased temperature (Adams et al, 2005). Reactive DBPs undergo abiotic reactions with free chlorine at a faster rate at higher temperatures, and may actually cause a decrease in the concentration (AWWA, 1999). Two exceptions have been observed when concentrations of DCAA and monochloroacetic acid (MCAA) increased in a heated tap water sample. Volatilization has been found to be of negligible importance to HAA levels (Wu et al, 2001).

### ***Bromide concentration.***

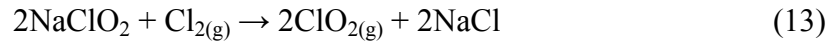
Bromide is a naturally occurring element in the groundwater of coastal areas due to the intrusion of seawater (Kampioti and Stephanou, 2002) and plays a significant, yet indirect impact on the formation of DBPs. Initially, chlorine reacts with water to form HOCl, OCl<sup>-</sup>, or Cl<sub>2</sub> (Equations 7 and 8), depending upon pH. When water containing

bromide is chlorinated, chlorine oxidizes the bromide to hypobromous acid (Equation 10) or the hypobromite ion,  $\text{OBr}^-$ , leading to formation of bromo-derivatives and/or bromo-chloro DBPs (Equations 11 and 12) (Dalvi et al, 2000). Equation 9 shows the reaction between chlorinated water and organic precursors. Waters containing bromide and low levels of NOM lead to highly brominated DBPs, whereas bromide containing waters with high NOM may have lower concentrations of brominated DBPs due to a high chlorine demand (Xie, 2004).



### **Chlorine dioxide and DBP formation.**

Chlorine dioxide has been widely used in water treatment for taste and odor control, oxidation of soluble iron, manganese and organic material, and disinfection. It is generated by reacting a  $\text{NaClO}_2$  solution with an oxidizing agent; generally gaseous or aqueous chlorine alone, a mineral acid by itself or in addition to chlorine, or acid in combination with a hypochlorite salt solution (Gates, 1998). The basic equation for the generation of chlorine dioxide is as follows:



Upon initiation of the Stage 1 D/DBP Rule, chlorine dioxide has become popular in the control of HAAs and THMs. Chlorine dioxide serves to oxidize specific components of NOM which can change particle size and charge distribution of organic molecules. Therefore,  $\text{ClO}_2$  does not solely reduce TOC, but rather alter the composition of NOM in order to increase solubilization and aid in better coagulation and sedimentation (Gates, 1998). The most important characteristic of chlorine dioxide is the fact that  $\text{ClO}_2$  oxidizes organics without chlorinating (Newlove et al, 2004). Chlorine dioxide is a strong oxidant but will undergo addition/substitution reactions which result in the formation of halogenated by-products (Newlove et al, 2004). As mentioned earlier, chlorine dioxide may be used to oxidize manganese and iron species but Carlson et al (1986) found that  $\text{ClO}_2$  has an affinity for fulvic acids over Mn (II), resulting in rapid consumption in raw waters high in fulvic acid. Complete consumption was found to occur in less than two hours in a sample containing a  $\text{ClO}_2$  to TOC weight ratio of 0.5 or smaller (Werdehoff and Singer, 1987). Typical chlorine dioxide concentrations applied to raw waters are between 0.1 and 5.0 mg/L (Newlove et al, 2004) so as not to exceed chlorine dioxide MCLs in finished waters and to reduce the chance of producing chlorite, a chlorine dioxide by-product. According to Carlson et al (1986),  $\text{ClO}_2$  dosages less than 1.4 mg/L may lower THM and TOX precursor concentrations by more than 10% (in waters with TOC concentrations <4 mg/L).

## **Degradation of DBPs.**

DBP degradation may occur via one of four reactions including hydrolysis, oxidation, dehalogenation, and biodegradation. Degradation of some DBPs actually leads to the formation of others as is the case when trichloropropanone undergoes hydrolysis degradation to form chloroform (Xie, 2004). THMs and HAAs are biologically degraded, although as mentioned earlier, THMs have been found to biodegrade only under anaerobic conditions. Bacteria that are responsible for this degradation are commonly found in drinking water, especially where disinfectant residuals are low. These points which are likely at the outskirts of a distribution system have been observed to contain HAA concentrations near zero (AWWA, 1999). Due to molecular stability, biodegradation of THMs is slower than that of HAAs; therefore, one would expect to find high THM levels at these same points. However, Muller et al (1996) studied the environmental fate of TCAA in lake water and found concentrations to persist up to 230 days, suggesting a long degradation rate. This estimation was based on a mathematical model. A similar study done by Zhou and Xie (2002) investigated the degradation of DCAA and TCAA in waters containing no disinfectant residual. A complete reduction of DCAA with an original concentration of 88  $\mu\text{g/L}$  was found to occur in 256 hours. Over the same time period, TCAA was found to degrade only 30% of its original concentration (Zhou and Xie, 2002). At the same time, heterotrophic bacteria counts increased approximately 6000 times in both samples. Previous data showed that MCAA biodegrades faster than DCAA, suggesting that molecules containing more halogen atoms are more likely to have a longer life within a distribution system. Similar results were reported by Hashimoto et al (1998) while studying the fate of HAAs

in river and sea water, with the rate of degradation being greater for MCAA, followed by DCAA and then TCAA.

Ellis et al (2001) examined the fate of MCAA, DCAA, and TCAA in pond waters, and in laboratory microcosms using prepared sediments consisting of sand, loam, and 20% organic matter. The objective of the study was to show that HAA degradation occurs through a microbial process by comparing systems that allowed the growth of microbes to the sterilized microcosms. Persistence in the environment was found to follow the order TCAA>MCAA>DCAA, while no degradation was seen for any of the HAAs where sediment was absent from the laboratory microcosm (Ellis et al, 2001).

### **Toxicity of HAAs and THMs.**

In 1976 the U.S. National Cancer Institute published a report linking chloroform to cancer in laboratory animals; two years earlier J.J. Rook reported that this compound was present in chlorinated drinking water (cited from Garcia-Villanova et al, 1997). Since then, great emphasis has been placed on better understanding the mechanisms behind DBPs and upon limiting their formation.

A number of epidemiology and animal studies have been carried out to explore the effects of DBPs commonly found in chlorinated drinking waters, including chloroform, bromodichloromethane, bromoform, trichloroacetic acid and dichloroacetic acid. A study conducted by the National Cancer Institute, initially developed to investigate the correlation between bladder cancer and artificial sweeteners, discovered a link between chlorinated drinking water and cancer. Information on drinking water source and treatment over their lifetime was gathered for 1,244 cases and 2,550 controls.

Additional data on beverage and smoking intake was gathered. Researchers observed a two-fold increase in bladder cancer of those individuals consuming chlorinated drinking water for 60 years or more who never smoked (Singer, 1999).

Numerous lifetime studies conducted on rats have shown an increase in the number of tumors at various sites, most commonly on the liver and kidney (Fawell, 1999). There is no data, however, suggesting any activity within the bladder. Therefore, the correspondence with epidemiological data is limited. Historically, only chronic exposure has been linked to adverse health affects, however, recent epidemiological studies have also suggested that THMs may have negative acute reproductive effects, including spontaneous abortion, birth defects, and stillbirths (Waller et al, 1998). A study of over 57,000 births conducted in 1990 showed that exposure to high TTHM levels (80µg/L) in drinking water was associated with a 14% increase in a risk of low birth weight for gestational age (Wright and Dockery, 2003).

## TABLES

**TABLE 1** THMs and HAAs

Disinfection By-Product	Name	Formula	MCLG (mg/L)	MCL (mg/L)
Total Trihalomethane (TTHM)	Chloroform	CHCl <sub>3</sub>	0	0.080 (annual average)
	Bromodichloromethane	CHBrCl <sub>2</sub>	0	
	Chlorodibromomethane	CHBr <sub>2</sub> Cl	0.06	
	Bromoform	CHBr <sub>3</sub>	0	
Haloacetic Acids (HAA5)	Monochloroacetic acid	CH <sub>2</sub> ClCOOH	-	0.060 (annual average)
	Dichloroacetic acid	CHCl <sub>2</sub> COOH	0	
	Trichloroacetic acid	CCl <sub>3</sub> COOH	0.3	
	Monobromoacetic acid	CH <sub>2</sub> BrCOOH	-	
	Dibromoacetic acid	CHBr <sub>2</sub> COOH	-	
Other Haloacetic Acids	Bromochloroacetic acid	CHBrClCOOH	n/a	n/a
	Bromodichloroacetic acid	CBrCl <sub>2</sub> COOH		
	Tribromoacetic acid	CBr <sub>3</sub> COOH		
	Chlorodibromoacetic acid	CBr <sub>2</sub> ClCOOH		

Cited from *Federal Register* (1998); - no maximum contaminant level goal (MCLG) established

## **Chapter 2: Impact of Sludge Volume and Water Quality on DBPs in a Full-Scale Water Works**

In 1974, chloroform was found to be present in chlorinated drinking water. Two years later, a report was published by the National Cancer Institute linking this compound to cancer in laboratory animals (Garcia-Villanova et al, 1997). Concerns of health risks have prompted the United States and other countries to establish maximum contaminant levels (MCLs) for disinfection by-products (DBPs). The United States Environmental Protection Agency's (USEPA) 1998 Stage 1 Disinfectants/Disinfection By-Product Rule (D/DBPR) set MCLs for two of the most prevalent DBPs, haloacetic acids (HAAs) and trihalomethanes (THMs). The adoption of the D/DBP Rule limited HAA and THM formation to 60 µg/L and 80 µg/L, respectively, in finished drinking water. Since then, modifications to many treatment facilities and their operations have been mandatory to meet current rules and regulations. Additionally, a Stage 2 D/DBP Rule was signed in January, 2006 which will challenge water treatment authorities even further. Current Stage 1 regulations are based on four-quarter running averages, which represent a system-wide average concentration over a one year period. The Stage 2 D/DBPR however, will be based on locational running averages where each location within the distribution system must comply with the annual average (Richardson, 2003). This rule will diminish, if not eliminate the permissive MCL violations which may occur at some locations within the system (particularly those located furthest from the treatment facility).



The control of DBPs in the distribution system is critical to meeting MCLs, but it may be even more important to focus on a reduction at the source of DBP formation, the treatment plant itself. Following years of research, the management of DBPs remains a balancing act between complying with MCLs and providing sufficient microbial control. Treatment strategies include the oxidation of DBP precursors, physical removal or reduction of DBP precursors prior to treatment, alteration in chlorine feed points, and alternative disinfectants. This paper, while identifying the impacts of various water quality parameters on DBP formation, also investigates potential DBP contributions from settled sludge within a full-scale water treatment facility.

## **BACKGROUND**

### **Formation and types of HAAs and THMs.**

The use of chlorine for disinfection has been a strategy widely used in drinking water treatment; however, when chlorine reacts with natural organic matter (NOM) such as humic and fulvic acids, DBPs are generated (Sérodès et al, 2003). Both THMs and HAAs are formed via hydrolysis reactions. DBP precursors react with free chlorine to form intermediate products which are then hydrolyzed into their respective compound (Xie, 2004). Chlorinated, brominated, and mixed halogenated DBPs are formed in waters containing bromide. Five of nine chlorine/bromine based haloacetic acid compounds are considered a health threat and are regulated. These are referred to as “HAA5” and include monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA) and dibromoacetic acid (DBAA). Total

trihalomethane (TTHM) represents the sum of four THMs-chloroform, bromoform, bromodichloromethane, and dibromochloromethane.

### **Factors contributing to THM and HAA formation.**

THM and HAA formation is dependent upon water quality characteristics and their fluctuations due to environmental conditions and treatment plant operations. NOM levels, chlorine dose, contact time, pH, water temperature, and bromide concentration are all factors which influence THM and HAA formation (AWWA, 1999).

NOM serves as the principal precursor to DBPs, and many investigators agree that its concentrations are directly related to DBP formation (Singer, 1993). An increase in NOM levels affects DBP formation primarily in two ways: (1) DBP precursors are increased, and (2) chlorine demand is increased to satisfy disinfection criteria and maintain a proper residual within the distribution system (Xie, 2004). As mentioned earlier, THMs and HAAs are formed when chlorine reacts with NOM. Therefore, higher chlorine doses have portrayed linear relationships with increased DBP formation in many finished water studies (Garcia-Villanova et al, 1997). Contact time reflects the availability of chlorine to react with NOM and is therefore an important factor in DBP formation. THM and HAA formation occurs rapidly at first and will continue at a slower rate as long as the given water contains a chlorine residual, and NOM (Singer, 1993). Rossman et al (2001) found that DBP levels at a consumers tap may be as much as two to three times higher than what they are leaving the treatment works, depending on locality.

THM and HAA formation are inversely affected by pH; THMs are more prevalent in high pH waters while HAA are formed more readily in low pH waters. Fluctuation in

pH also changes the species of chlorine present in the water from HOCl at low pH to predominately OCl<sup>-</sup> at pH >7.6. Research has shown that faster reaction rates occur with humic matter when higher levels of the non-ionized HOCl form of hypochlorous acid is present (AWWA, 1999). Water temperature has been noted to control THM and HAA formation due to accelerated reaction rates at higher temperatures. Accelerated rates, in addition to increased primary production and photodegradation of chlorine during the summer months, make THMs and HAAs especially difficult to control (Singer, 1993). Bromide concentration also contributes to DBP formation, but occurs only in the groundwater of coastal areas due to the intrusion of seawater (Kampioti and Stephanou, 2002). Waters rich in bromide and treated with chlorine will contain concentrations of chlorinated, brominated, and mixed halogenated THMs and HAAs.

### **Study Objectives.**

This study provides a greater understanding of the role of settled sludge and water quality parameters in the formation of HAA5 and TTHM. The water samples prepared in this study were taken from the Blacksburg/Christiansburg/VPI (BCVPI) Water Treatment Plant in Radford, Virginia, a conventional plant which uses chlorine as its primary disinfectant. The plant exceeded the HAA5 MCL in the second and third quarters of 2004 and has since been evaluating alternative DBP control strategies. The sedimentation basins are not equipped with mechanical sludge collecting equipment; therefore, the basins are cleaned manually approximately three times per year. In order to evaluate the impacts of sludge and the effectiveness of basin cleaning on DBP formation control, research was conducted from April, 2005 through November, 2005 to study DBP

levels at various sludge depths and upon basin cleaning. The study was designed to determine whether installing sludge collecting equipment would provide the treatment plant with an additional DBP control technique needed to comply with new regulations.

## **EXPERIMENTAL APPROACH**

### **Sampling Procedures.**

Samples were collected from three of six sedimentation basins located at the BCVPI Water Treatment Plant. The three basins used in the experiment were chosen due to their high variations in sludge present at the start of the experiment. Samples for TTHM, HAA5, and total organic carbon (TOC) were taken from both ends of the sedimentation basins, referred to in this paper as the “head” (post-flocculation) and “rear” (pre-filtration) of the basin. Prior to collecting TTHM samples, 100  $\mu\text{L}$  of a 10% sodium thiosulfate solution was added to 40-mL amber glass vials with TFE-lined screw caps to eliminate residual chlorine and prevent additional THM formation. Similarly, 100 mg/L granular ammonium chloride was added to identical 40-mL vials to satisfy HAA preservation standards. The collection procedures for THMs and HAAs were in accordance with USEPA Methods 502.2 and 552.2, respectively (USEPA, 1995). TOC samples were also collected in 40-mL amber glass vials with TFE-lined screw caps and preserved by addition of 100  $\mu\text{L}$  of 85% phosphoric acid to pH 2 until analyses could be performed. TTHM and HAA5 samples were collected headspace free, and all samples were placed on ice until storage at 4°C in darkness. Measurements of total chlorine and  $\text{UV}_{254}$  were taken from both ends of the basins, and were carried out at the BCVPI Water Treatment Plant at the same time as collection of samples for DBPs and organic matter

surrogates. Water temperature data were collected approximately two feet below the water surface at the head of basin 1 and was assumed to be the same for each basin. Measurements for pH were taken from the head of each basin as well. Water temperature and pH data were collected at the same time as the samples.

Along the length of each sedimentation basin, nine measurements of sludge depth were recorded by taking core sludge samples using a rigid piece of 2 in. (50 mm) clear piping. A curve was created representative of the sludge level present in the basin, and area under the curve was calculated using Microsoft Excel. The area was then multiplied by each basin's respective width to obtain sludge volume.

The calculated sludge volume was used to determine approximate detention times for each of the basins on the days sampled. Daily flowrates through each basin were calculated based on plant inflow, and the size and design detention time of individual basins. Each of the three basins sampled in the experiment were different sizes. Basin 1 was the largest of the three with a design volume of 44,650 ft<sup>3</sup> (1,264 m<sup>3</sup>). Basin 2 was the smallest at 29,275 ft<sup>3</sup> (829 m<sup>3</sup>), and basin 3 was 43,160 ft<sup>3</sup> (1,222 m<sup>3</sup>). Basins 1 and 2 were both 31 m in length, while basin 3 was 37 m. Based on the generated flowrate of a basin, water volume was determined and the sludge volume was subtracted, yielding the actual water volume in each basin. For calculation purposes, it was assumed that water did not pass through the sludge and that water volume was decreased as settled sludge accumulated.

Another experiment was conducted in order to determine DBP formation in the absence of sludge. One-liter beakers were filled with water from the head (prior to sludge exposure) of the basins and exposed to identical environmental conditions as the

water flowing into the basins (overcast skies, -2 °C air temperature). Samples for TTHM and HAA5 were taken from the beakers after 1 h, 2 h, and at each basin's respective, design residence time. Other samples were taken as mentioned in the first experiment in order to compare samples having been exposed to sludge. All samples were preserved as defined earlier.

The second experiment was conducted during winter conditions, when water temperature was 6.1 °C. In an effort to increase TTHM and HAA5 levels, and identify water temperature effects, additional 1-L samples were taken from the head of the basins and quickly warmed in a water bath to 20 °C. Once the determined temperature had been reached, samples were taken at 1 h, 2 h, and at each basin's final residence time. Head and rear samples were also collected, warmed in the same manner, and preserved.

### **Analytical Methods.**

Samples for HAA5, TTHM, TOC and DOC were analyzed at the Virginia Tech Environmental Engineering Laboratory. HAA5 analyses were conducted in accordance with USEPA Method 552.2 (USEPA, 1995) using a Hewlett Packard 5890 gas chromatograph (GC) equipped with an electron capture detector and Hewlett Packard autosampler. The capillary column used was a Supelco SPB-1701 (30 m long x 0.25 mm ID, 0.25 µm film thickness) (Bellefonte, PA).

Total THM analyses were conducted according to USEPA Method 502.2 (USEPA, 1995) using a Tremeetrics 9001 GC (Austin, TX) with a Tracer 1000 Hall detector (Austin, TX), Tekmar 3000 Purge and Trap Concentrator (Cincinnati, OH), and Tekmar 2016 Purge and Trap autosampler. The capillary column was a J&W Scientific

DB-624 column (30 m long x 0.53 mm ID, 3 $\mu$ m film thickness) (Agilent Technologies, Wilmington, DE).

Prior to analyses, TOC samples were purged with oxygen to remove carbon dioxide. Samples were analyzed within 28 days of collection using a Seivers 800 Portable TOC Analyzer with an autosampler (Ionics, Boulder, CO).

Samples for total chlorine were carried out using a Hach Pocket Colorimeter in accordance with USEPA-approved Hach Method 8167 (Hach Company, Loveland, CO). Chlorine dioxide measurements were made with a Hach AutoCat 9000 Amperometric Titration System under the USEPA-approved, Hach Method 10126. UV<sub>254</sub> was analyzed with a Hach DR/4000U spectrophotometer. A Hach SensIon4 pHISE meter was used for both pH and water temperature measurements.

## **RESULTS AND DISCUSSION**

DBP concentrations in 83% of all samples (n = 42) taken in the first experiment were found to increase over the length of the sedimentation basin. A t-test (paired two-sample for means) conducted with Microsoft Excel at an alpha value ( $\alpha$ ) of 0.05 revealed that the data from head and rear samples were statistically different in all cases with the exception of basin 2 TTHM data. Among all three basins, mean TTHM and HAA5 levels increased by an average 32% and 33%, respectively (Table 1). The greatest mean value increases were seen in basins 1 and 3; TTHM mean concentrations increased by 50% in basin 3 and HAA5 mean concentrations increased by 39% in basin 1 (Table 1). Mean TTHM levels in basins 1 and 2 increased by 32% and 13%, respectively, while mean HAA5 levels in basins 2 and 3 each increased 30% (Table 1).

In an effort to understand and possibly predict the DBP formation measured in the BCVPI sedimentation basins, various empirical models were evaluated. Two published DBP models were assessed using the collected BCVPI data. Additionally, models were developed with the same data using statistical software, and evaluated for their predictive abilities. The models were created to be used by the BCVPI treatment facility and other conventional treatment plants.

### **Models by Amy et al. and AWWARF for THMs and HAAs.**

Many empirical equations have been developed to predict DBP formation in treatment facilities and in distribution systems. A large number of these models; however, are often developed via laboratory studies or are based on water quality conditions not typical of treated water. Therefore, it can be difficult to use them to accurately predict TTHM and HAA5 concentrations under certain conditions in a full-scale water treatment facility. Two models, by Amy et al (1987) and AWWARF (American Water Works Association Research Foundation), were evaluated using comparisons of actual data collected at the BCVPI treatment plant and theoretical values calculated with empirical formulas. Collectively, the two models are incorporated into the Water Treatment Plant Simulation computer program developed for the USEPA to evaluate cost effect of alternative MCLs for THMs and HAAs. The first model (Equation 1) was created by Amy et al (1987) and is one of the most widely cited references in THM modeling. It is based on a large database of raw water chlorination experiments from variable water supplies across the United States.



$$\begin{aligned} \text{TTHM } (\mu\text{mol/L}) = & 0.00309(\text{UVABS} \cdot \text{TOC})^{0.440} & (1) \\ & \cdot (\text{CLDOSE})^{0.409} \\ & \cdot (\text{RXNTM})^{0.265} \\ & \cdot (\text{TEMP})^{1.06} \\ & \cdot (\text{PH} - 2.6)^{0.715} (\text{BR} + 1)^{0.0358} \end{aligned}$$

Where:

UVABS = ultraviolet absorbance at 254 nm,  $\text{cm}^{-1}$

TOC = total organic carbon concentration, mg/L

CLDOSE = chlorine dose at the beginning of the reaction, mg/L

RXNTM = reaction time, hours

TEMP = water temperature,  $^{\circ}\text{C}$

PH = reaction pH

BR = bromide concentration, mg/L

Although the model was developed based on copious amounts of data, it does have its limitations when predicting TTHM formation in water treatment plants. The water quality data and chlorination doses do not reflect the characteristics of treated water and operations in real water utilities. The database used to develop the model included chlorine dosages in the range of 1.5 to 69 mg/L. Water temperatures ranged from 10 to 30  $^{\circ}\text{C}$ ; reaction time ranged from 0.1 to 168 hours; pH ranged from 4.6 to 9.8; bromide levels ranged from 0.010 to 1.245 mg/L; TOC ranged from 3.0 to 13.8 mg/L; and, UV absorbance ranged from 0.063 to 0.489  $\text{cm}^{-1}$ . Typical measurements recorded at the

BCVPI water treatment plant for chlorine dose, reaction time, pH, TOC, and  $UV_{254}$  were all either below the ranges used in the development of the Amy et al (1987) model, or at the low end of each range (Table 1). Additionally, this model does not consider the use of chlorine dioxide; an oxidant sometimes used to minimize DBPs.

Bromide concentrations were considered negligible in the water samples collected for this research and daily measurements were not taken. For use in the two models, a sample was collected from the raw water source and was found to contain about 0.004 mg/L  $Br^-$ . The concentration was below the instrument's detectable limit and had to be estimated from chromatograph peaks. Once inputted, actual data from the BCVPI water treatment plant were compared with model-calculated values and were found not to correlate well ( $R^2 = 0.0981$ ) (Figure 1).

The second model, developed by AWWARF (1991), predicts HAA concentrations for all five regulated HAAs; however, DCAA and TCAA were the only empirical formulas evaluated due to their dominance in the samples studied (Equations 2 and 3). The database used for equations 2 and 3 included chlorine dosages from 3.0 to 25.0 mg/L. The water temperature ranged from 13 to 20 °C; reaction time ranged from 0.1 to 105 hours; pH ranged from 5.6 to 9.0; bromide levels ranged from 0.005 to 0.430 mg/L; TOC ranged from 2.8 to 11 mg/L; and, UV absorbance ranged from 0.05 to 0.38  $cm^{-1}$ . Typical chlorine dosages, TOC values, and UV absorbance values observed at the BCVPI treatment plant all fell below the ranges used in the development of this model, leading to inaccurate DBP predictions. Again, these empirical formulas did not consider the use of chlorine dioxide and, like the model for TTHM, actual BCVPI plant

concentrations did not correlate well ( $R^2 = 0.0297$  for DCAA;  $R^2 = 0.0654$  for TCAA) (Figure 2).

$$\begin{aligned} \text{DCAA } (\mu\text{g/L}) = & 0.605(\text{TOC})^{0.291}(\text{UVABS})^{0.726} & (2) \\ & \cdot (\text{BR} + 0.01)^{-0.568}(\text{CLDOSE})^{0.480} \\ & \cdot (\text{RXNTM})^{0.239}(\text{TEMP})^{0.665} \end{aligned}$$

$$\begin{aligned} \text{TCAA } (\mu\text{g/L}) = & 87.182(\text{TOC})^{0.355}(\text{UVABS})^{0.901} & (3) \\ & \cdot (\text{BR} + 0.01)^{-0.679}(\text{PH})^{-1.732} \\ & \cdot (\text{CLDOSE})^{0.881}(\text{RXNTM})^{0.264} \end{aligned}$$

Where:

UVABS = ultraviolet absorbance at 254 nm,  $\text{cm}^{-1}$

TOC = total organic carbon concentration, mg/L

CLDOSE = chlorine dose at the beginning of the reaction, mg/L

RXNTM = reaction time, hours

TEMP = water temperature,  $^{\circ}\text{C}$

PH = reaction pH

BR = bromide concentration, mg/L

### **Development of a predictive model.**

A regression analysis with multiple predictors (DBP formation factors) was used to develop a model which selected a subset among the predictive variables to sufficiently describe HAA5 and TTHM formation. The statistical software used in the study was R, Version 2.2.1. Input variables included chlorine and TOC levels from the head of the basins, water temperature, pH, detention (reaction) time, and sludge volume. Two-way interactions (e.g., chlorine:detention time; TOC:sludge volume) were also incorporated to determine the relationships of variables and their combined impacts on DBP formation. Every possible two-way interaction was considered in the original dataset. TTHM and HAA5 data and water quality parameter datasets were compared using 'R' to evaluate statistical differences among all basins (R Development Core Team, 2004). Rear TTHM and HAA5 data were used in the model development to better understand DBP formation over the entire length of the sedimentation basin. Individual basin data were not found to be significant at a 5 % confidence level ( $p = 0.3176$  for HAA5 subset;  $p = 0.1689$  for TTHM subset) (Appendices A and B); therefore, all basin data were grouped together to investigate facility-wide trends in DBP formation. A best-fit model was chosen with 'R' by using both a forward and backward selection procedure designed to minimize the AIC (Akaike Information Criterion) (R Development Core Team, 2004). This procedure was completed for TTHM and HAA5 separately.

Some variables and two-way interactions were eliminated from the TTHM and HAA5 models, however, many remained as they proved to be significant at the 5 % confidence level. After the ideal model had been selected by 'R', another test was performed to evaluate the significance of the interactive terms against a model composed

of single variables only. The two-way interactive variables were found to be very important to the model in determining HAA5 and TTHM and returned probability values of 0.01038 and 0.008105, respectively. The following models (Equations 3 and 4) were developed for HAA5 and TTHM and produced adjusted R-squared values of 0.7297 and 0.6836, respectively. Adjusted R-squared values are lower than multiple R-squared values as a result of penalizing the model for increasing the number of variables included. Each of the predictive models developed in ‘R’ contained many variables, some of which resulted in p-values > 0.05 (Tables 2 and 3). An attempt was made to eliminate these “insignificant” variables from the models; however, this affected other significant single or interactive variables by raising their p-value to > 0.05. Therefore, the models were left as developed and consisted of many variables, but proved to be accurate in estimating DBP formation at the actual facility (Figures 3 and 4).

$$\begin{aligned}
 \text{HAA5 } (\mu\text{g/L}) = & -166.3 - 22.56(\text{CLDOSE}) & (3) \\
 & + 111.3(\text{TOC}) \\
 & + 1.873(\text{TEMP}) \\
 & + 28.87(\text{RXNTM}) \\
 & + 0.009303(\text{SLUDGEVOL}) \\
 & + 4.918(\text{CLDOSE}\cdot\text{RXNTM}) \\
 & + 0.0006193(\text{CLDOSE}\cdot\text{SLUDGEVOL}) \\
 & - 20.46(\text{TOC}\cdot\text{RXNTM}) \\
 & - 0.004849(\text{TOC}\cdot\text{SLUDGEVOL}) \\
 & - 0.0008717(\text{RXNTM}\cdot\text{SLUDGEVOL})
 \end{aligned}$$

Where:

TOC = total organic carbon concentration, mg/L

CLDOSE = chlorine dose at the beginning of the reaction, mg/L

RXNTM = reaction time, hours

TEMP = water temperature, °C

PH = reaction pH

SLUDGEVOL = volume of sludge in sedimentation basin, ft

$$\begin{aligned}
\text{TTHM } (\mu\text{g/L}) = & -180.3 + 14.56(\text{CLDOSE}) & (4) \\
& + 4.434(\text{CLDOSE})^2 \\
& - 19.25(\text{TOC}) \\
& + 11.58(\text{TEMP}) \\
& + 0.7207(\text{TEMP})^2 \\
& + 51.66(\text{PH}) \\
& - 1.078(\text{RXNTM}) \\
& - 0.01572(\text{SLUDGEVOL}) \\
& - 3.266(\text{CLDOSE} \cdot \text{TEMP}) \\
& + 10.04(\text{CLDOSE} \cdot \text{RXNTM}) \\
& - 2.571(\text{TOC} \cdot \text{TEMP}) \\
& + 0.005158(\text{TOC} \cdot \text{SLUDGEVOL}) \\
& - 3.46(\text{TEMP} \cdot \text{PH}) \\
& - 1.015(\text{TEMP} \cdot \text{RXNTM}) \\
& - 0.0001586(\text{TEMP} \cdot \text{SLUDGEVOL}) \\
& + 0.001293(\text{PH} \cdot \text{SLUDGEVOL}) \\
& + 0.0004943(\text{RXNTM} \cdot \text{SLUDGEVOL})
\end{aligned}$$

\*Parameters used in Equation 4 are the same as those defined in Equation 3.

## **Influences of water quality parameters on DBP formation.**

### ***Sludge Volume.***

Variation in sludge volume was observed to play a significant role in DBP formation, however, accumulated sludge was not shown to increase TTHM or HAA5 concentrations as expected. Using the empirical formulas created from the BCVPI data, and inputting high (340 m<sup>3</sup>) (12,000 ft<sup>3</sup>) and low (0 m<sup>3</sup>) sludge volumes, average DBP levels during the sampling period were found to be lower when large amounts of sediment were present in the basins. When no sediment was present in the basin, average calculated HAA5 values were 36.4 µg/L and TTHM values were 29.7 µg/L. Modeled concentrations were significantly lower for HAA5 when basins were full and an average value of 23.5 µg/L was calculated. TTHM was not affected as greatly, but levels were still lower at 27.1 µg/L.

Actual data collected from the sedimentation basins did not correlate exactly with predicted trends, but did show some similar effects. Sludge was removed from full sedimentation basins every four to five months. Over the course of this study, basin 1 was cleaned twice while basins 2 and 3 were each cleaned one time. Following the first cleaning of basin 1, rear samples of both DBPs decreased from concentrations found during the previous sampling event; however, water temperatures were low (12.7 °C) and incoming TOC and chlorine concentrations were also low, averaging 1.34 mg/L and 1.01 mg/L, respectively. In fact, TOC averages were lower than the previous sampling event. TTHM concentrations fell from 17.7 µg/L to 13.8 µg/L and HAA5 concentrations were reduced from 9.9 µg/L to 8.4 µg/L. Reductions were also noted following the second cleaning of basin 1. The samples analyzed prior to the second cleaning had very high



TTHM and HAA5 levels, 101 µg/L and 52.3 µg/L, respectively, which fell to 40 µg/L and 24.3 µg/L during the following sampling event. Unaware to the author, basin 1 had been “valved” off for three days prior to cleaning in order to eliminate residual chlorine. Therefore, the high DBP levels were most likely due to the 72-h contact time and elevated water temperatures during the time of sampling. These data were not considered in the multiple regression analysis and therefore did not influence the model produced in ‘R’. If values from the previous sampling date were considered for a comparison (when the basin was approximately two weeks from being cleaned), TTHM levels increased after cleaning, but HAA5 values fell 8.7 µg/L.

Increases in DBP levels were observed following the cleaning of basins 2 and 3, supporting the predictions of the model and suggesting influences of water temperature and detention time. The cleanings were made in early and late July when water temperatures were warm (23.5 – 24.5 °C) and TOC and chlorine levels were at their peak. TTHM levels in basin 2 increased 21.6 µg/L from the previous sampling event when the basin was full, and HAA5 concentrations increased dramatically by 32.5 µg/L from the previous date. An increase was noted in basin 3 following cleaning as TTHM levels increased 7.5 µg/L, but HAA5 levels decreased by 3 µg/L.

The second experiment conducted provided additional insight into the role of sludge on TTHM and HAA5 formation. The data supported the findings of the model and suggested that sludge contact did not directly influence DBP formation. Higher TTHM and HAA5 concentrations were observed in the water samples that were taken from the head of the basins and left to react in 1-L beakers. Only basins 1 and 2 were sampled for this experiment; basin 3 was being cleaned. Rear TTHM and HAA5 samples

were compared to the 1-L beaker samples at both 6.1 °C and 20 °C, and seven of the eight beaker samples contained higher DBP levels than the samples in contact with sludge.

The one exception occurred in basin 1 and is circled in Figure 8. Water temperature and contact time therefore appeared to be the most influential factors in DBP formation.

### ***TOC.***

TOC values remained relatively steady throughout the study period in all of the basins despite seasonal effects and changes in sludge volume. The greatest range in TOC concentration was recorded in basin 1 (1.04 to 2.38 mg/L, Table 1). Basin 1 also showed the highest mean TOC value, followed closely by basin 2 and then basin 3. The order of the values may be the result of their placement in the treatment plant. Basin 3 is located furthest from the plant intake and rapid mixing station. Therefore, the time for flocculation and adsorption processes is longer for basins 2 and 3. In all cases, mean TOC concentrations in the water were reduced from head to rear samples. Basins 1 and 2 exhibited average reductions of 7%, while concentrations in basin 3 dropped 10%, most likely due to its greater length. The reductions observed over the study period suggest that TOC release from sludge was not evident and therefore not a contributing factor to DBP formation.

Values from both ends of the TOC range observed in the BCVPI treatment plant (Table 1) were inputted to the predictive model to study the effects of various concentrations throughout the sampling period. Surprisingly, higher TTHM and HAA5 values were revealed at lower TOC concentrations. Average TTHM levels were 40 µg/L and 13.2 µg/L when TOC values of 0.97 mg/L and 2.38 mg/L were entered into the

model. Similar results were observed for HAA5. On the sampling date when TOC levels reached their maximum of 2.38 mg/L, TTHM and HAA5 levels did decrease dramatically; however, this was the same day that the treatment plant began using chlorine dioxide. On multiple occasions, TTHM and HAA5 predicted values were 0 µg/L due to negative interactive TOC variables. For this reason, further calibration is needed using additional data from the BCVPI plant or another water treatment facility.

### ***Water Temperature.***

Water temperature was shown to have a direct correlation with DBP formation and was significant in the development of both models (Tables 2 and 3). DBP levels in all three basins increased as water temperature increased over the sampling period, and the predictive models responded well, also. HAA5 levels increased on average by 31.9 µg/L when temperatures of 9.7 °C to 26.8 °C were entered. Average TTHM values decreased, however, when high temperature values were inputted, possibly the result of volatilization.

The highest TTHM and HAA5 concentrations recorded were in basin 1 at peak water temperature (26.8 °C). However, as noted before, this measurement occurred three days after the basin was valved off prior to cleaning on August 24, 2005. High temperatures and a long detention time most likely aided TTHM and HAA5 formation to concentrations of 101 µg/L and 52.3 µg/L, respectively. Although basins 2 and 3 followed similar patterns, both showing correlations with water temperature, neither produced record high DBP levels. In fact, DBP concentrations dropped significantly when water temperatures peaked at 26.8 °C. TTHM and HAA5 levels in basins 2 and 3

decreased from the previous sampling event on average by 11% and 48% in head samples, and 19% and 32% in rear samples. Garcia-Villanova et al (1997) studied an open-system treatment facility and found chloroform levels increased until water temperatures reached 18.97 °C and then declined dramatically. It was noted that this was probably due to a higher rate of DBP degradation (volatilization) due to increased water temperatures. It was, however, the HAA5 concentrations that underwent the greatest change and not TTHM species, suggesting that HAAs are also susceptible to degradation at higher water temperatures. Based on the data collected, TTHM formation was greatest when water temperature was 24.5 °C, and HAA5 formation the greatest at 23.5 °C.

Water temperature was also shown to have an effect on DBP levels in the second experiment conducted. TTHM and HAA5 concentrations increased in all of the samples that were warmed (Figures 5 and 6). Rear samples, having been exposed to sludge, showed an average increase in concentration among both basins of 69 % for HAA5, but only 4.2 % for TTHM, when warmed from 6.1 °C to 20 °C. The beaker samples, following their respective residence time, also experienced an increase in concentration when the temperature was increased. Averaged values from both basins showed a 55 % increase in HAA5 and 15 % increase for TTHM. This suggests that HAA formation is enabled at warm temperatures and supports the findings of high HAA5 levels during summer months.

#### ***Contact time.***

Based on the predictive models and the second experiment conducted, chlorine contact time was shown to possibly have the greatest influence on DBP formation. All

three basins showed some correlation between reaction time and DBP formation. Basin detention times ranged from 2.5 h to 6.5 h and averaged 3.8, 3.7, and 4.6 h for basins 1, 2, and 3, respectively (Table 1). This could explain the differences in mean DBP values observed over the length of the basins, especially for TTHM. Research has shown HAAs form faster than THMs (AWWA, 1999), implying that the majority of HAA5 formation may have taken place soon after initial chlorination, and during the beginning of the sedimentation process. Hence, the small deviation in percent increase from head to rear HAA5 samples (39 % in basin 1, and 30 % in basins 2 and 3). THMs, which are more time dependent, were found to correlate well with their respective basin's detention time. TTHM percent increases were smallest in basin 2 (13 %) while basin 3, with an average detention time of 4.6 h, was observed to increase by an average of 50%.

Contact time showed an obvious correlation with TTHM and HAA5 levels during the second experiment. DBP levels in both basins were shown to increase over time and TTHM results were similar to the percent increases seen throughout the main experiment. TTHM levels increased 25 % in basin 1 (Figure 5) and 12 % in basin 2. TTHM percent increases were less than what was seen on average over the length of the basin. This may have been because the experiment was based on design detention times which were found to be shorter than actual residence time. HAA5 levels increased in both basins as well, however, more profoundly in basin 1.

### ***Chlorine Dosage.***

As expected, chlorine levels dropped between the head and rear of the sedimentation process due to chlorination of organic matter, while at the same time DBP

levels increased. Chlorine levels were found to decrease on average by 19%, 28%, and 44% (Table 1) for basins 1, 2 and 3, respectively. Basins 2 and 3 typically received more chlorine than basin 1 due to a chlorine feed positioned in the flocculator which is in close proximity to both basin's headwalls. Similar to TOC reduction, the high chlorine reduction in basin 3 may also have resulted from the longer residence time.

Chlorine dosage did not reveal any linear relationships with DBP formation over the course of the experiment, but it was determined to be significant in HAA5 formation (Table 2). When high and low concentrations were entered into the predictive model, results suggested that high chlorine concentrations yield much higher DBP levels for HAA5 and TTHM. When a concentration of 5.3 mg/L was used in the formula, HAA5 values rose on average by 13.9 µg/L from those concentrations observed when using 0.49 mg/L (the minimum level recorded at BCVPI). TTHM values increased significantly, as well. Although actual data were not seen to peak on the day when the maximum chlorine level was recorded, HAA5 and TTHM did peak in basin 3 when chlorine levels were measured at 4.2 mg/L, the second highest measurement recorded.

### **Chlorine dioxide use and incorporation into predictive models.**

The BCVPI Water Treatment Plant applies chlorine dioxide (ClO<sub>2</sub>) seasonally at its raw water intake and did so from early June to late October. Problems with the system resulted in fluctuations of ClO<sub>2</sub> concentrations being applied, and the equipment being shutdown completely on several occasions. The plant typically applied 0.7 mg/L ClO<sub>2</sub>. A powerful oxidant, chlorine dioxide alters the composition of NOM particles in order to increase solubilization and aid in better coagulation and sedimentation of organic

molecules (Gates, 1998). Chlorine dioxide does not specifically reduce TOC, but rather aid in its removal. Raw water TOC was periodically measured during summer months and was found to average 2.24 mg/L. During those same days, and when ClO<sub>2</sub> was being applied, TOC averages were reduced to 1.66 mg/L across the three basins at the beginning of the sedimentation process.

Chlorine dioxide levels were not measured in the sedimentation basins during the two sampling events following the start-up of ClO<sub>2</sub> addition (June 9, 2005 and June 27, 2005). However, daily plant logs were inspected and levels in the finished water were 0.5 mg/L and 0.2 mg/L for the two days. ClO<sub>2</sub> concentrations were taken at the head of each basin for the remainder of the sampling dates, but each measurement was 0 mg/L ClO<sub>2</sub>. The BCVPI plant intended to add 0.7 mg/L ClO<sub>2</sub> and measured levels were 0 mg/L (in the basin), suggesting that concentrations in the raw water were much higher (than 0.7 mg/L) during the two days previously recorded (June 9, 2005 and June 27, 2005). The DBP values correlated very well. All three basins showed similar trends (Figure 7) where a decrease in both TTHM and HAA5 levels occurred on the specified dates. The ClO<sub>2</sub> system was turned off on June 12, 2005, the following sampling event, and DBP levels spiked in all basins. Basin 2 reached its highest HAA concentration of the entire sampling event on that day. Once the ClO<sub>2</sub> system was turned on again, it was left running until water temperatures receded in October; however, no direct correlation was observed.

Using 'R', chlorine dioxide was incorporated into the data set as an indicator variable and models were developed for prediction of DBPs during days with and without the application of chlorine dioxide. Indicator variables had to be used since actual

chlorine dioxide concentrations (mg/L) were not known. This process simply kept ClO<sub>2</sub> in the model by substituting a (1) into the equation for days when ClO<sub>2</sub> was applied, or eliminated the term by substituting a (0) for days when the system was not in use.

Actual data (2005) collected from the basins was again compared to model-predicted concentrations and R-squared values were obtained (Table 4). Since two large models (one for TTHM and one for HAA5) were created to integrate ClO<sub>2</sub>, R-developed R-squared values could only be created for the models which included ClO<sub>2</sub>, and not for the ones where ClO<sub>2</sub> was eliminated. For this reason, R-squared values for Equations 5 and 6, minus the ClO<sub>2</sub> term, had to be determined using Excel (Table 4).

$$\begin{aligned}
 \text{HAA } (\mu\text{g/L}) = & -33.72 + 82.3(\text{ClO}_2) & (5) \\
 & - 58.38(\text{CLDOSE}) \\
 & - 29.59(\text{TOC}) \\
 & + 3.6(\text{TEMP}) \\
 & + 1.267(\text{RXNTM}) \\
 & + 0.003403(\text{SLUDGEVOL}) \\
 & - 22.73(\text{ClO}_2 \cdot \text{CLDOSE}) \\
 & - 10.8(\text{ClO}_2 \cdot \text{RXNTM}) \\
 & + 1.713(\text{CLDOSE} \cdot \text{TEMP}) \\
 & + 7.604(\text{CLDOSE} \cdot \text{RXNTM}) \\
 & + 0.001224(\text{CLDOSE} \cdot \text{SLUDGEVOL}) \\
 & - 2.338(\text{TOC} \cdot \text{TEMP}) \\
 & - 0.000137(\text{TEMP} \cdot \text{SLUDGEVOL})
 \end{aligned}$$



$$- 0.000749(\text{RXNTM} \cdot \text{SLUDGEVOL})$$

Where:

$\text{ClO}_2$  = chlorine dioxide in use = 1; chlorine dioxide not in use = 0

TOC = total organic carbon concentration, mg/L

CLDOSE = chlorine dose at the beginning of the reaction, mg/L

RXNTM = reaction time, hours

TEMP = water temperature, °C

PH = reaction pH

SLUDGEVOL = volume of sludge in sedimentation basin,

$$\begin{aligned}
\text{TTHM } (\mu\text{g/L}) = & -1531 - 677(\text{ClO}_2) & (6) \\
& - 228.5(\text{CLDOSE}) \\
& + 565.9(\text{TOC}) \\
& + 75.87(\text{TEMP}) + 237(\text{PH}) - 11.54(\text{RXNTM}) \\
& + 0.008414(\text{SLUDGEVOL}) + 8.907(\text{CLDOSE}^2) \\
& + 0.7949(\text{TEMP}^2) + 18.36(\text{ClO}_2 \cdot \text{CLDOSE}) \\
& - 67.18(\text{ClO}_2 \cdot \text{TOC}) - 6.361(\text{ClO}_2 \cdot \text{TEMP}) \\
& + 118.9(\text{ClO}_2 \cdot \text{PH}) + 13.15(\text{ClO}_2 \cdot \text{RXNTM}) \\
& - 0.003849(\text{ClO}_2 \cdot \text{SLUDGEVOL}) - 5(\text{CLDOSE} \cdot \text{TEMP}) \\
& + 37.4(\text{CLDOSE} \cdot \text{PH}) + 3.191(\text{CLDOSE} \cdot \text{RXNTM}) \\
& + 0.0004768(\text{CLDOSE} \cdot \text{SLUDGEVOL}) \\
& + 8.969(\text{TOC} \cdot \text{TEMP}) - 96.46(\text{TOC} \cdot \text{PH}) \\
& - 0.004402(\text{TOC} \cdot \text{SLUDGEVOL}) - 14.23(\text{TEMP} \cdot \text{PH}) \\
& - 2.223(\text{TEMP} \cdot \text{RXNTM}) \\
& + 0.0003216(\text{TEMP} \cdot \text{SLUDGEVOL}) + 7.77(\text{PH} \cdot \text{RXNTM}) \\
& - 0.001374(\text{RXNTM} \cdot \text{SLUDGEVOL})
\end{aligned}$$

\*Parameters used in Equation 6 are the same as those defined in Equation 5

### **Model Evaluations.**

The BCVPI treatment plant was issued notices of violation for HAA5 after the 2<sup>nd</sup> and 3<sup>rd</sup> quarters of 2004. Documents from the Virginia Department of Health noted that quarterly average concentrations were 77  $\mu\text{g/L}$  and 73  $\mu\text{g/L}$ , respectively (Notice of

Violation, 2004). Daily treatment logs were acquired for those quarters and the water quality data was used to predict DBP concentrations formed within the treatment plant. Water temperature, chlorine dosage, pH, and flowrate were available for use in the model; other parameter values had to be assumed. Daily TOC concentrations were estimated based on data collected from 2005 for the research conducted. Since sludge volume was not measured, extreme values were incorporated into the model to approximate DBP formation under various conditions. Clean basins were represented by using 0 m<sup>3</sup> of sludge and full basins with 340 m<sup>3</sup> (12,000 ft<sup>3</sup>) of sludge. Based on sludge volume and the provided plant flowrates, a daily reaction time was calculated in the same way as before; however, since the predictive model groups the basin data together, an overall average reaction time had to be used. Reaction times were calculated for all three basins and then averaged. The 2004 database and theoretical values used with the empirical formula had a chlorine dosage ranging from 1.03 to 4.33 mg/L. Water temperature ranged from 9.7 to 26.9 °C; pH ranged from 6.54 to 7.44; TOC values ranged from 1.25 to 2.13 mg/L; reaction times when no sludge was present ranged from 3.7 to 7.0 h, and 2.5 to 4.5 h when 340 m<sup>3</sup> of sludge was considered.

Predicted DBP concentrations from the 2004 data were found to be very similar to those observed in the treatment plant during sampling events in 2005. Additionally, a significant difference was noted when sludge volume was changed in the model. HAA5 concentrations for quarters two and three were 32.2 µg/L and 46.3 µg/L, respectively, following a simulated cleaning (0 m<sup>3</sup> of sludge). When 340 m<sup>3</sup> of sludge was inputted to the model, concentrations were 27.4 µg/L and 30.6 µg/L for the two quarters (Figure 8). Results for TTHM were very similar to HAA5 for both quarters. When no sludge was

present, quarterly averages were 43.3 µg/L and 32.5 µg/L; and, when 340 m<sup>3</sup> was used in the model, averages were 29.3 µg/L and 29 µg/L (Figure 9). By making the assumption that water volume is diminished with accumulating sediment and detention times are shortened, it can be implied that reaction time is a major contributor to HAA5 formation. It should also be noted that concentrations such as the ones predicted could easily contribute to MCL violations, especially when given long detention times within the distribution system. HAA5 data for 2004 were acquired from the BCVPI Water Authority for the distribution system entry point and were also found to correlate well with predicted values (Figure 8). Since each sedimentation basin was cleaned at different times throughout the year, it can be assumed that actual HAA5 levels formed in the basin would fall between the “no sludge” and “340 m<sup>3</sup>” data (Figure 8). The actual 2004 data were higher than predicted values, possibly due to storage time in the clearwell and/or additional chlorine being added.

The chlorine dioxide models were analyzed in the same manner as before, by entering 2004 BCVPI water quality data from the 2<sup>nd</sup> and 3<sup>rd</sup> quarters, and high and low sludge volumes. Results were interesting as they differed completely from those observed using the “overall model”. Mentioned earlier (Figures 8 and 9), TTHM and HAA5 levels were predicted to be higher when sludge was removed from the sedimentation basins. Based on the assumption that the sludge was impermeable to the flow of water, and that lower sludge volumes resulted in longer detention times, it could easily be inferred that higher DBP levels were occurring due to longer chlorine contact times. However, when chlorine dioxide was introduced into the model, the role of sludge was reversed (Figures 10 and 11). In both cases, the model predicted that lower sludge

levels would result in lower DBP concentrations when chlorine dioxide was in use. Assuming that there was always some sludge present in the basins, it may again be presumed that actual formation in the basins would fall between the two data sets. With this being true, actual 2004 distribution system entry point data correlated well in both models; however, the TTHM model may be slightly conservative. The difference observed could have resulted from volatilization during transport from the sedimentation basins to the clearwell, given the warm water temperatures. In both cases, the models suggest that if chlorine dioxide is being used during summer months and basins are not kept clean, a treatment facility could easily exceed TTHM and HAA5 MCLs.

## **CONCLUSIONS**

The role of settled sludge on DBP formation was investigated by analyzing water samples from the sedimentation basin before and after sediment contact. TTHM and HAA5 samples were found to increase in most cases over the length of the basins, and statistical software was used to help determine influential factors. The first set of models grouped the entire dataset and did not incorporate ClO<sub>2</sub> addition. The adjusted R-squared values for HAA5 and TTHM were 0.7297 and 0.6836, respectively, which were shown to predict values similar to actual data recorded in 2004 from the distribution system entry point. Either of the two models (Equations 3 and 4) would be acceptable for use in water treatment facilities which do not use ClO<sub>2</sub> throughout the year. Both models indicated that settled sludge does not contribute to DBP formation, and actually helps reduce formation by speeding up flowrates through the sedimentation basin. Therefore, as long

as chlorine contact time (CT) requirements are met and disinfection is adequate, sludge should not be removed.

Predictive models were also developed to be used in summer months when chlorine dioxide is applied. Equations 5 and 6 predict HAA5 and TTHM concentrations and have adjusted R-squared values of 0.7827 and 0.7464, respectively. Both models, when analyzed by using 2004 data, were found to predict concentrations similar to those observed prior to distribution. The models are also capable of estimating values when ClO<sub>2</sub> is not in use; however, predicted concentrations did not correlate well with actual data despite R-squared values of 0.7131 and 0.6351. When ClO<sub>2</sub> was factored into the models, influences from sludge became great, suggesting that sludge should be removed during summer months when applying chlorine dioxide.

This research was conducted over the course of 8 months, consisting of 14 sampling events for each of three sedimentation basins. Due to the small size of the database used for model development, future analyses should be conducted at the BCVPI facility and other conventional treatment plants for calibration of the proposed models.

## CHAPTER 2 TABLES

**TABLE 1 Statistical summary of water quality parameters and DBP concentrations in sedimentation basins**

Water Quality Parameters and DBPs	n	Basin 1						n	Basin 2					
		Front			Rear				Front			Rear		
		Mean	Median	Range	Mean	Median	Range		Mean	Median	Range	Mean	Median	Range
TOC (mg/L)	14	1.52	1.46	1.04-2.38	1.42	1.40	0.93-2.16	14	1.46	1.51	0.97-1.79	1.36	1.33	0.92-1.70
pH	14	6.84	6.96	6.23-7.23	---	---	---	14	6.83	6.92	6.23-7.23	---	---	---
Water Temperature (°C)	14	19.3	20.6	9.7-26.8	---	---	---	14	19.3	20.6	9.7-26.8	---	---	---
Cl <sub>2</sub> Dose (mg/L)	14	1.29	1.25	0.49-2.74	1.04	1.14	0.33-1.69	14	1.88	1.75	0.55-5.3	1.36	1.38	0.61-2.11
Detention Time (hrs)	14	3.8	3.5	2.7-5.4	---	---	---	14	3.7	3.4	2.5-6.2	---	---	---
UV <sub>254</sub> (cm <sup>-1</sup> )	14	0.02	0.018	0.014-0.026	0.02	0.02	0.014-0.030	14	0.02	0.022	0.011-0.035	0.02	0.021	0.008-0.048
HAA5 (µg/L)	14	15.1	9.7	2.8-37.3	21.0	20.6	7.3-48.1	14	18.3	13.5	2.8-51.6	23.7	23.1	4.9-52.6
TTHM (µg/L)	14	19	17.4	2.2-38.3	25.1	23.2	6.8-40.0	14	23.7	20.9	9.9-40.2	26.7	23.8	6.7-50.8
Water Quality Parameters and DBPs	n	Basin 3												
		Front			Rear									
		Mean	Median	Range	Mean	Median	Range							
TOC (mg/L)	14	1.42	1.35	1.16-2.03	1.28	1.33	0.90-1.83							
pH	14	6.83	6.89	6.23-7.22	---	---	---							
Water Temperature (°C)	14	19.3	20.6	9.7-26.8	---	---	---							
Cl <sub>2</sub> Dose (mg/L)	14	1.8	1.62	0.49-4.2	1.0	0.84	0.45-1.82							
UV <sub>254</sub> (cm <sup>-1</sup> )	14	0.02	0.023	0.011-0.032	0.02	0.02	0.008-0.032							
Detention Time (hrs)	14	4.6	4.5	3.3-6.5	---	---	---							
HAA5 (µg/L)	14	22.5	19.2	3-51.5	29.3	31.6	8.1-54.6							
TTHM (µg/L)	14	20.8	20.7	4.9-40.1	31.2	26.1	12.8-53.2							

**TABLE 2 Summary of statistical output from R for HAA5 predictive model (Equation 3)**

	Coefficient Estimate	Std. Error	t value	Pr (> t )
(Intercept)	-1.663E+02	7.391E+01	-2.250	0.03196 *
CLDOSE	-2.256E+01	9.647E+00	-2.339	0.02621 *
TOC	1.113E+02	5.060E+01	2.199	0.03570 *
TEMP	1.873E+00	3.730E-01	5.015	2.23e-05 ***
RXNTM	2.887E+01	1.190E+01	2.425	0.02153 *
SLUDGEVOL	9.303E-03	4.487E-03	2.073	0.04681 *
CLDOSE:RXNTM	4.918E+00	2.479E+00	1.984	0.05651 .
CLDOSE:SLUDGEVOL	6.193E-04	3.349E-04	1.849	0.07433 .
TOC:RXNTM	-2.046E+01	9.515E+00	-2.151	0.03969 *
TOC:SLUDGEVOL	-4.849E-03	2.663E-03	-1.821	0.07858 .
RXNTM:SLUDGEVOL	-8.717E-04	3.111E-04	-2.802	0.00881 **

Multiple R-Squared: 0.7972, Adjusted R-Squared: 0.7297, p-value: 6.717e-08

Signif. Codes: 0 '\*\*\*' 0.001 '\*\*' 0.01 '\*' 0.05 '.' 0.1 ' ' 1

**TABLE 3 Summary of statistical output from R for TTHM predictive model (Equation 4)**

	Coefficient Estimate	Std. Error	t value	Pr (> t )
(Intercept)	-1.803E+02	1.671E+02	-1.079	0.291695
CLDOSE	1.456E+01	1.311E+01	1.110	0.278302
I(CLDOSE^2)	4.434E+00	2.487E+00	1.783	0.087767 .
TOC	-1.925E+01	3.281E+01	-0.587	0.563095
TEMP	1.158E+01	6.373E+00	1.817	0.082329 .
I(TEMP^2)	7.271E-01	1.333E-01	5.408	0.0000171 ***
PH	5.166E+01	2.265E+01	2.280	0.032188 *
RXNTM	-1.078E+00	1.091E+01	-0.099	0.922176
SLUDGEVOL	-1.572E-02	8.670E-03	-1.813	0.082951 .
CLDOSE:TEMP	-3.266E+00	1.025E+00	-3.185	0.004125 **
CLDOSE:RXNTM	1.004E+01	2.329+00	4.311	0.000259 ***
TOC:TEMP	-2.571E+00	1.317E+00	-1.952	0.063155 .
TOC:SLUDGEVOL	5.158E-03	2.643E-03	1.951	0.063297 .
TEMP:PH	-3.460E+00	9.866E-01	-3.507	0.001893 **
TEMP:RXNTM	-1.015E+00	4.682E-01	-2.167	0.040800 *
TEMP:SLUDGEVOL	-1.586E-04	7.389-05	-2.147	0.042585 *
PH:SLUDGEVOL	1.293E-03	1.098E-03	1.177	0.251366
RXNTM:SLUDGEVOL	4.943E-04	3.727E-04	1.326	0.197776

Multiple R-Squared: 0.818, Adjusted R-Squared: 0.6836, p-value: 4.983e-05

Signif. Codes: 0 '\*\*\*' 0.001 '\*\*' 0.01 '\*' 0.05 '.' 0.1 ' ' 1

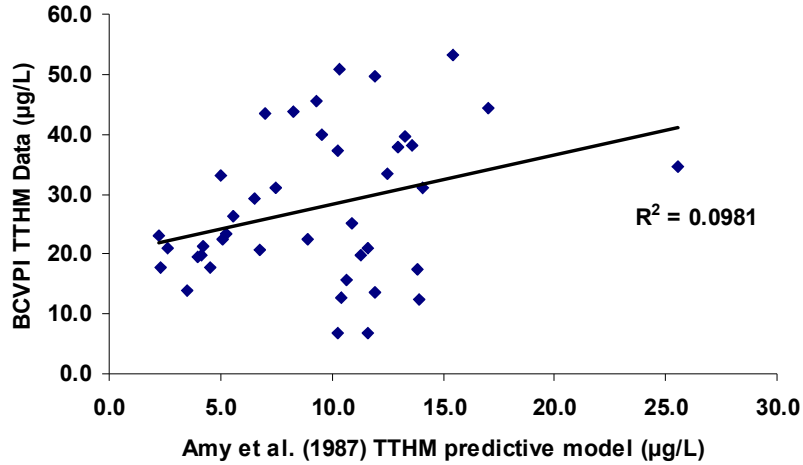


**TABLE 4 R-Squared values for various models**

	<b>R<sup>2</sup> Type</b>	<b>HAA5 R<sup>2</sup></b>	<b>TTHM R<sup>2</sup></b>
Overall Model	Excel	0.7984	0.8193
	R Multiple	0.7972	0.818
	R Adjusted	0.7297	0.6836
Model with ClO <sub>2</sub>	Excel	0.6945	0.8431
	R Multiple	0.8351	0.9294
	R Adjusted	0.7464	0.7827
Model without ClO <sub>2</sub>	Excel	0.7131	0.6351

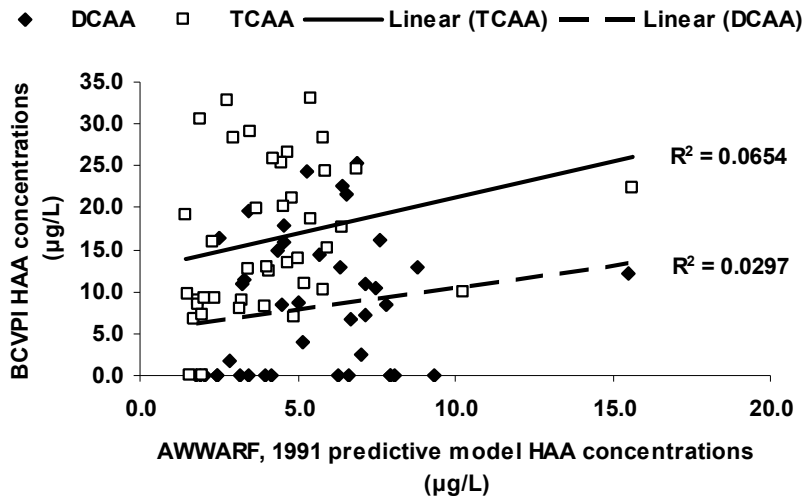
## CHAPTER 2 FIGURES

**FIGURE 1** BCVPI TTHM data vs. Amy et al. model (1987)

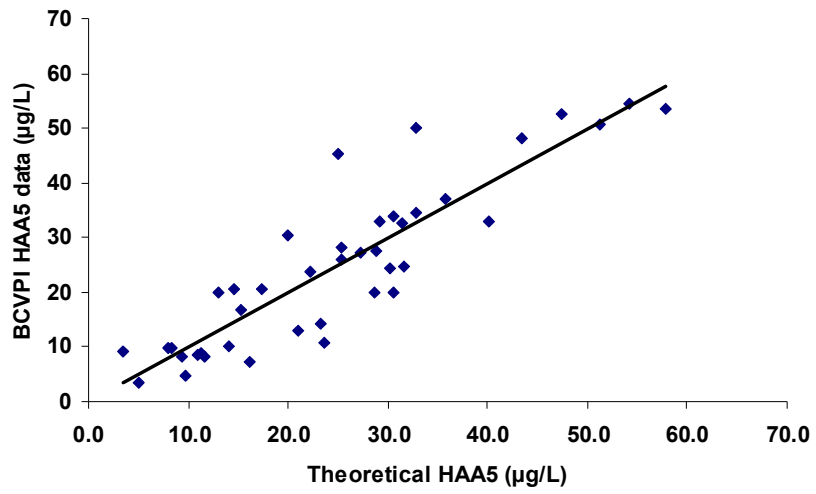


Amy et al (1987) model values converted from µmol/L to µg/L

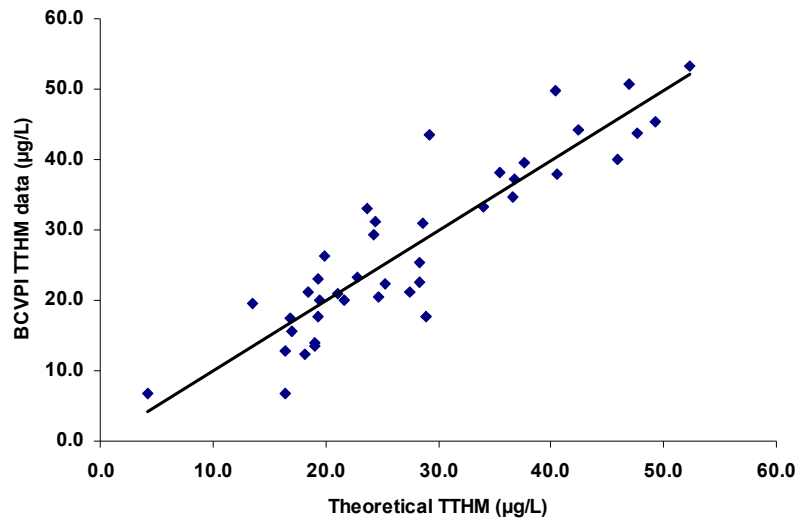
**FIGURE 2** BCVPI actual HAA data vs. AWWARF model (1991)



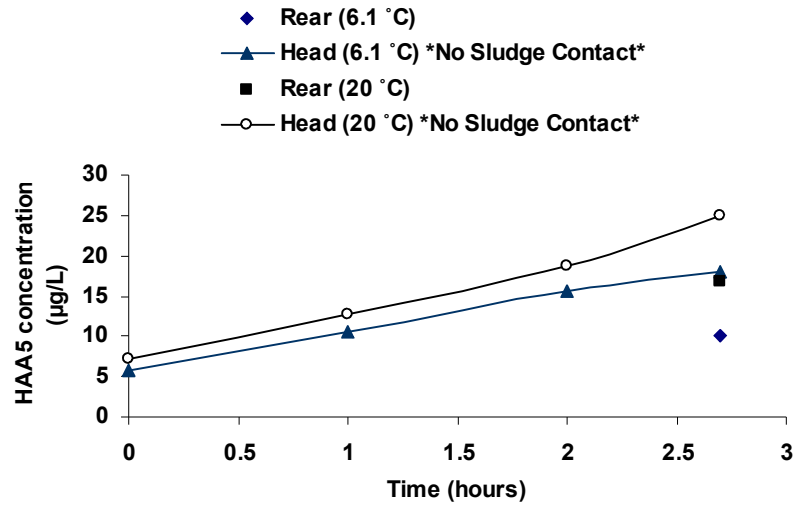
**FIGURE 3** BCVPI HAA5 data vs. predictive model data (Equation 3)



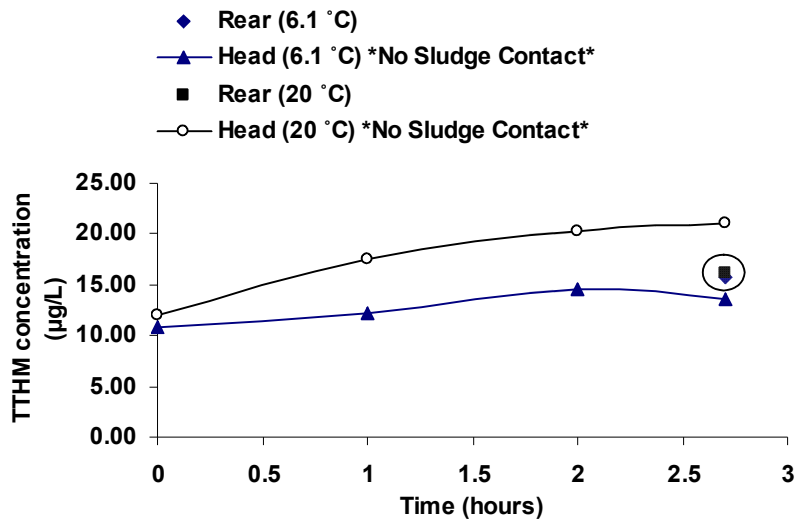
**FIGURE 4** BCVPI TTHM data vs. predictive model data (Equation 4)



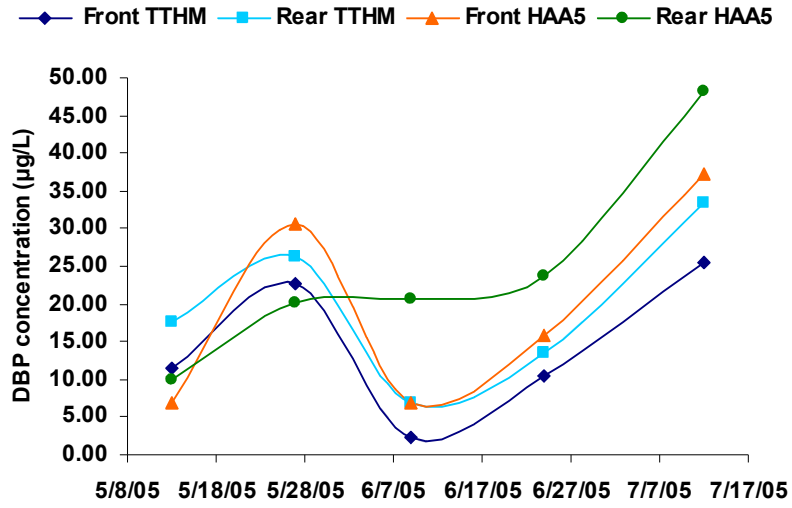
**FIGURE 5** Basin 1 HAA5 concentration (sludge contact experiment)



**FIGURE 6** Basin 1 TTHM concentration (sludge contact experiment)

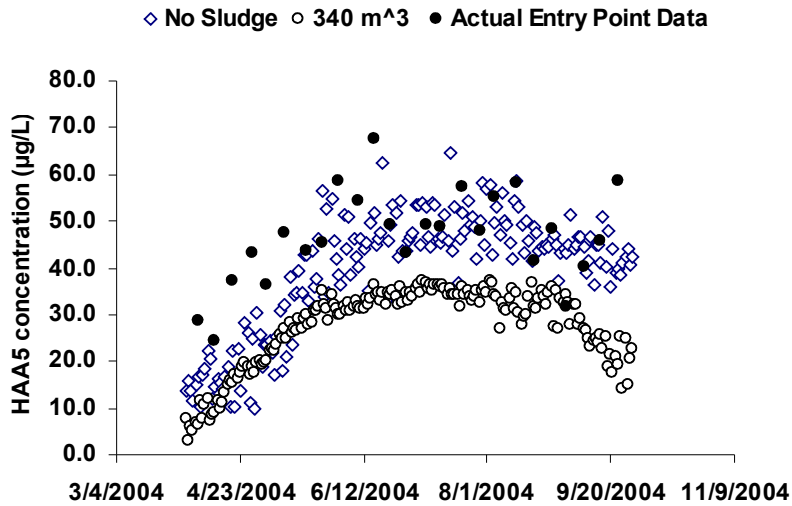


**FIGURE 7** DBP concentrations in Basin 1 during high ClO<sub>2</sub> addition

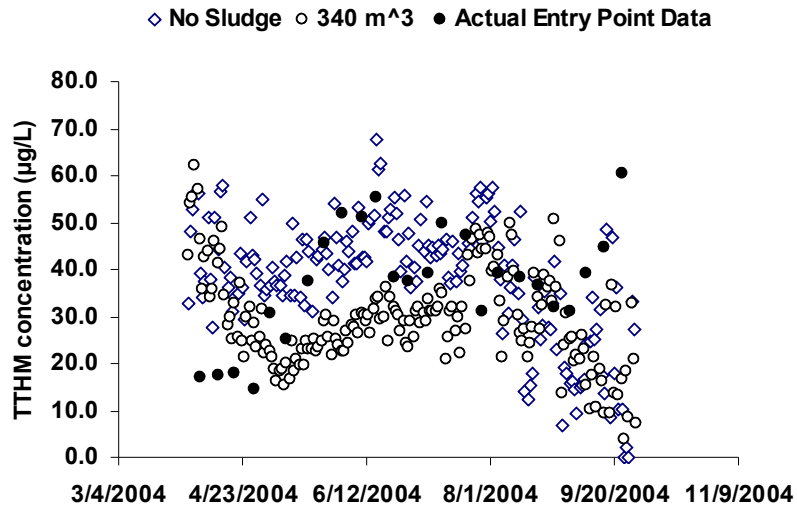


ClO<sub>2</sub> addition began 6/9/05 and concentrations were found high on 6/9/05 and 6/27/05. Levels of 0.5 mg/L and 0.2 mg/L, respectively, were measured in finished water.

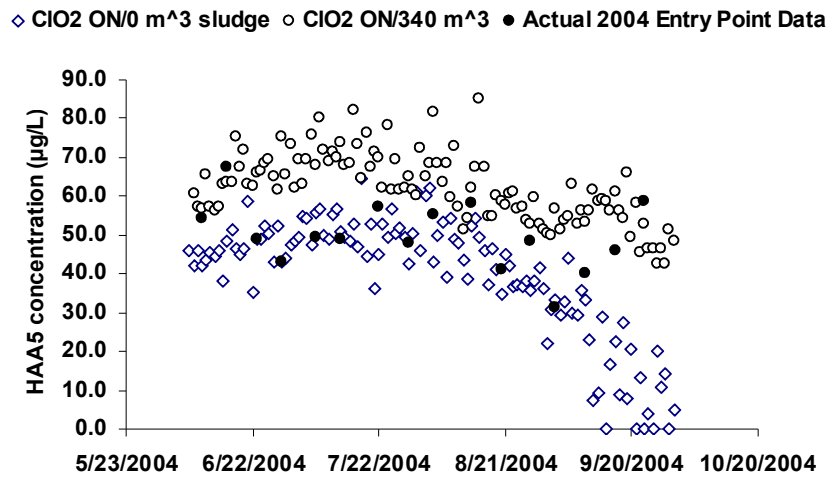
**FIGURE 8** Predicted 2004 HAA5 concentrations in BCVPI plant



**FIGURE 9** Predicted 2004 TTHM concentrations in BCVPI plant

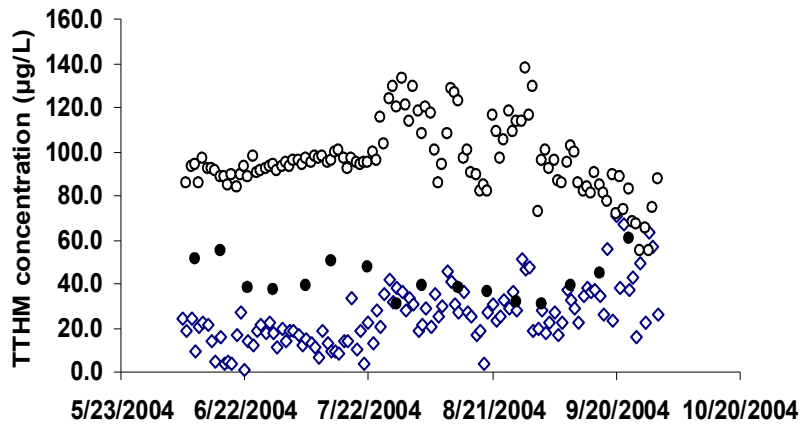


**FIGURE 10** Predicted HAA5 values using chlorine dioxide model



**FIGURE 11** Predicted TTHM values using chlorine dioxide model

◇ ClO<sub>2</sub>/No Sludge ○ ClO<sub>2</sub>/340 m<sup>3</sup> ● Actual 2004 Entry Point Data (ClO<sub>2</sub>)



## **ACKNOWLEDGEMENT**

The authors wish to thank the Blacksburg/Christiansburg/VPI Water Authority for their financial support and friendship, and also wish to thank the Edna Bailey Sussman Fund for their generous funding.



## CHAPTER 2 REFERENCES

- AWWA (American Water Works Association), 1999. *Water Quality & Treatment: A Handbook of Community Water Supplies*. (R.D. Letterman, editor). McGraw-Hill, Inc. New York, New York.
- Amy, G.L.; Chadik, P.A.; & Chowdhury, Z.K., 1987. Developing Models for Predicting Trihalomethane Formation Potential and Kinetics. *Jour. AWWA*, 79:7:89.
- AWWARF (American Water Works Association Research Foundation), 1991. *Disinfection By-Products Database and Model Project*. American Water Works Association Research Foundation, Denver, Colorado.
- Garcia-Villanova, R.J. et al, 1997. Formation, Evolution and Modeling of Trihalomethanes in the Drinking Water of a Town: I. At the Municipal Treatment Utilities. *Water Research*, 31:6:1299.
- Gates, D., 1998. *The Chlorine Dioxide Handbook: Water Disinfection Series*. (B. Cobban, editor). American Water Works Association, Denver, Colorado.
- Kampioti, A.A. and Stephanou, E.G., 2002. The Impact of Bromide on the Formation of Neutral and Acidic Disinfection By-Products (DBPs) in Mediterranean Chlorinated Drinking Water. *Water Research*, 36:2596.
- Notice of Violation. 2004. Department of Health, Office of Drinking Water, Commonwealth of Virginia. PWSID No.: 1121052. Issued on August 12, 2004 and October 28, 2004.
- R Development Core Team, 2004. *R: A Language and Environment for Statistical Computing*. R Foundation for Statistical Computing, Vienna, Austria. ISBN 3-900051-07-0, URL <http://www.R-project.org>.
- Richardson, S.D., 2003. Disinfection By-Products and Other Emerging Contaminants in Drinking Water. *Trends in Analytical Chemistry*, 22:10:666.
- Rossmann, L.A. et al, 2001. DBP Formation Kinetics in a Simulated Distribution System. *Water Research*, 35:14:3483.
- Sérodes J.B. et al, 2003. Occurrence of THMs and HAAs in Experimental Chlorinated Waters of the Quebec City Area (Canada). *Chemosphere*, 51:253.
- Singer P.C., 1993. Basin Concepts of Disinfection By-Product Formation and Control. AWWA D/DBP Rule Teleconference: Presentation 1, 1-20.

USEPA (United States Environmental Protection Agency), 1995. Methods for the Determination of Organic Compounds in Drinking Water, Supplement III. EPA 600-R-95-131. PB 95-261616.

Xie, Y.F., 2004. Disinfection Byproducts in Drinking Water: Formation, Analysis and Control. CRC Press Inc., Boca Raton, Fl.

## **Chapter 3: DBP Formation Potential of Settled Sludge in a Full-Scale Water Treatment Facility**

Disinfection by-products (DBPs) were first discovered in 1974 when J.J. Rook reported the presence of chloroform in chlorinated drinking water. Since then, many other DBPs have been discovered and scientists have revealed their potentially harmful effects. The two most studied groups of DBPs are trihalomethanes (THMs) and haloacetic acids (HAAs). Many reports have been released identifying THMs and HAAs as carcinogens, and recent studies have also linked THMs with negative acute reproductive effects, including spontaneous abortion, birth defects, and stillbirths (Waller et al., 1998). Increased health risks due to the consumption of chlorinated drinking water has led the United States Environmental Protection Agency (USEPA) to regulate THM and HAA production in the nation's water treatment facilities and distribution systems. Current USEPA legislation sets maximum contaminant levels (MCLs) for THMs and HAAs at 80 µg/L and 60 µg/L, respectively, in finished drinking water. The 1998 Stage 1 Disinfectants/Disinfection By-Product Rule (D/DBPR), which lowered the MCLs to their current standards, was released by the USEPA to regulate DBPs within the distribution system. The Stage 1 Rule is based on four-quarter running averages, which represent a system-wide average concentration over one year. A Stage 2 D/DBPR, signed in January, 2006 will be based on locational running averages where each location within the distribution system must comply with the annual average (Richardson, 2003).

The Stage 1 Rule introduced many surface water-treating utilities with problematic issues of complying with new standards. The next Stage will add to those

complications and force treatment plants to find alternative or innovative ways to purify and disinfect drinking water. Many steps have been taken through research to identify chemical additives and treatment processes to reduce the formation of DBPs in both the treatment plant and distribution system. This paper serves as an informative device for conventional treatment plants trying to better understand DBP formation within the treatment facility, and emphasizes the potential role of sedimentation basin sludge on this process.

## **BACKGROUND**

### **Formation of THMs and HAAs.**

Chlorinated DBPs are formed when chlorine reacts with the humic fraction of aqueous natural organic matter (NOM). This fraction is broken down further into humic and fulvic acids, of which humic acid composes approximately 10% and fulvic acid approximately 90% (Garcia-Villanova et al. 1997). Although both humic and fulvic acids contribute to DBP formation, it is the small humic percentage that consumes the greatest amount of chlorine, leading to the highest concentrations of THMs and HAAs.

High NOM levels have been directly related to increased DBP levels (Singer, 1993), but other water quality parameters affect THM and HAA concentrations, as well. A high chlorine dose in a treatment facility or distribution system will provide for optimal DBP formation conditions assuming the water is not NOM-limiting. The longer this reaction is allowed to take place, with sufficient NOM levels and a chlorine residual, the higher the THM and HAA levels will be (Xie, 2004). Similar studies conducted in distribution systems have found THM and HAA levels to increase with residence time,

and Rossman et al. (2001) found DBP levels to be two to three times higher at a consumer's tap than those leaving the treatment facility. Water temperature also influences THM and HAA concentrations by speeding up or slowing down reactions between NOM and chlorine (Singer, 1993). Summer months prove to be the hardest in controlling DBP formation for this reason, and due to the increase in primary production (higher NOM levels). Lower pH levels cater to HAA formation while THMs form more quickly under high pH conditions. Additionally, bromide containing waters, commonly found in coastal areas contribute to DBP formation by forming brominated and/or mixed halogenated DBPs (Kampioti & Stephanou, 2002).

### **Types of THMs and HAAs.**

Five of the nine chlorine/bromine based HAAs are regulated by the USEPA and are referred to as "HAA5". Total trihalomethane (TTHM) represents the sum of four THMs (Table 1).

### **Degradation of THMs and HAAs.**

Degradation of DBPs can occur either biologically or physiochemically (Xie, 2004). The common pathway taken by THMs and HAAs is biodegradation; however, THMs have been found to biodegrade only under anaerobic conditions (AWWA, 1999). Fram et al. (2003) noted that this process under anaerobic conditions is typically observed only among the brominated TTHM compounds. Hydrolysis is a common degradation reaction for other trihalogenated DBPs (e.g. trichloropropanone), and THMs have been

observed to be the end products. One HAA follows this example however.

Tribromoacetic acid undergoes a hydrolysis reaction to form bromoform (Xie, 2004).

Due to the molecular stability of THMs under aerobic conditions, it is common to find high THM levels at the extremes of a distribution system, at the same points where HAA concentrations may have fallen. Bacteria are the cause of these declines and are found commonly within distribution systems (AWWA, 1999). In an attempt to demonstrate that microbial processes are behind the fate of HAAs, Ellis et al. (2001) measured HAA degradation in pond waters, in laboratory microcosms containing organic sediments, and in sterilized microcosms. Degradation was observed in the pond water and sediment-containing microcosm to follow the order: dichloroacetic acid (DCAA) < monochloroacetic acid (MCAA) < trichloroacetic acid (TCAA). No degradation was observed in the sterilized microcosm. Zhou and Xie (2002) compared degradation rates of TCAA and DCAA to heterotrophic bacteria counts in a water containing no disinfectant residual. One sample contained an original DCAA concentration of 88 µg/L and was observed to completely biodegrade after 256 hours. Following the same time period, TCAA concentrations were noted to have decreased only 30% while heterotrophic bacteria counts increased 6000 times in both samples. Both of the experiments illustrated the persistence of TCAA and suggested that molecules containing more halogen atoms have a longer life in the distribution system.

### **Study Objectives.**

This research provides a better understanding of settled sludge and its potential for further DBP formation within a water treatment facility. The study was conducted at

the Blacksburg/Christiansburg/VPI (BCVPI) Water Treatment Plant in Radford, VA.

The BCVPI Water Treatment Plant is a conventional surface water plant which employs chlorine as a primary disinfectant. Currently, the plant does not have mechanical sludge collecting equipment, and sedimentation basins are cleaned manually approximately three times per year. The goals of the study were to characterize the contributions of the accumulated sludge to TTHM and HAA5 formation and to evaluate the potential benefits of installing sludge collecting equipment.

## **EXPERIMENTAL APPROACH**

### **Sampling techniques.**

The BCVPI plant has six sedimentation basins, two of which were used throughout this experiment. The basin holding the greatest amount of sludge during the day of sampling was the one chosen.

Two 1-L Nalgene® containers were each filled with sedimentation sludge from both top and bottom layers (Figure 1). Top layers were carefully collected with a 1-L dipping bucket in order to collect a representative sample of the sludge. Top-layer sediments were extremely “fluffy” and difficult, unless collected slowly, to withdraw from the water with an open-top bucket. Bottom-layer samples were collected using a rigid piece of 2 in. (50 mm) clear piping in order to obtain a core sample of sludge. The pipe was approximately 4.4 meters long so that bottom sediments could be reached from the side of the basin. The pipe was filled with sludge from the entire depth of the basin; however, only the bottom 0.9 meters of the sample was placed in the 1-L container. This process was repeated as necessary to fill the container, and the samples were then capped,

headspace free. The samples were placed on ice until returned to the Virginia Tech Environmental Engineering Laboratory and stored at 4 °C in darkness.

Additional 1-L Nalgene® containers were filled using the same methods with top- and bottom-layer sludge. These two samples were collected to measure HAA5 and TTHM concentrations and were therefore treated with a 10% sodium thiosulfate solution in order to eliminate residual chlorine. Both samples were capped headspace free and stored at 4 °C until analyzing. Water temperature and dissolved oxygen (DO) within the sedimentation basin were also recorded at the time of sampling.

At the Virginia Tech Environmental Engineering Laboratory, the 1-L containers were gently shaken to homogenize the solutions, and samples were withdrawn for total solids (TS), total volatile solids (TVS), and chemical oxygen demand (COD) measurements. Samples for COD were preserved with concentrated sulfuric acid to pH <2 and kept refrigerated until analysis. In order to characterize sludge properties further, and to determine whether additional precursor material could be released from the sludge, half of the samples were centrifuged and the others slowly drained (Figure 1). Centrifuged samples of both top and bottom layers were spun for 15 minutes at 4400 rpm and the supernatant was collected. Centrifugation resulted in sludge that was approximately 7% solids. The other samples were drained using standard cheesecloth, and the decanted water was collected in a large glass beaker. Prior to draining, the cheesecloth was thoroughly rinsed with Nanopure® water to reduce any organic contaminants. The decanted water was placed in a temperature controlled room at 4 °C and any remaining particles were allowed to settle further. Clear water was then pipetted from the top of the sample. Centrifuged and drained samples were placed in clean plastic



bottles and measurements for pH and total organic carbon (TOC) were performed immediately.

The water samples were poured into 40-ml glass amber vials with TFE-lined screwcaps and capped headspace free. The collected samples consisted of top-centrifuged, top-drained, bottom-centrifuged, and bottom-drained sludge waters. The samples were then dosed with 4 mg/L chlorine, the USEPA's maximum residual disinfectant level, using a chlorine solution made up of bleach (6% NaOCl). Water samples from each group were left in contact with the chlorine residual at 20 °C for 15 minutes, 30 minutes, and 1 hour until being quenched with approximately 100 µL of a 10% sodium thiosulfate solution. All samples maintained a free chlorine residual of at least 0.5 mg/L at the end of the reaction time. The samples, along with those collected for pre-chlorination measurements were then analyzed for TTHM and HAA5 concentrations.

Two 1-L containers were filled with top and bottom sludge samples to evaluate TOC release from the sediments over time. Each sample was homogenized and distributed equally among three smaller bottles and placed in a 20 °C controlled room. Three, 10 mL samples were withdrawn from each of the bottles so as not to cause significant changes in TOC concentration. The study was conducted over a three week period.

### **Analytical methods.**

Analyses for all sludge and water parameters were conducted at the Virginia Tech Environmental Engineering Laboratory. Prior to analyses, centrifuged samples were

spun in a Forma Scientific, Inc. 5678 centrifuge, with four 250-mL IEC 3224 swinging buckets. HAA5 analyses were conducted in accordance with USEPA Method 552.2 (USEPA, 1995) using a Hewlett Packard 5890 gas chromatograph (GC) equipped with an electron capture detector and Hewlett Packard autosampler. The capillary column used was a Supelco (Bellefonte, PA) SPB-1701 (30 m long x 0.25 mm ID, 0.25  $\mu\text{m}$  film thickness).

Total THM were analyzed according to USEPA Method 502.2 (USEPA, 1995) using a Tometrics 9001 GC (Austin, TX) with a Tracer 1000 Hall detector (Austin, TX), Tekmar 3000 Purge and Trap Concentrator, and Tekmar 2016 Purge and Trap autosampler (Cincinnati, OH). The capillary column was a J&W Scientific DB-624 column (30 m long x 0.53 mm ID, 3 $\mu\text{m}$  film thickness) (Agilent Technologies, Wilmington, DE).

All TOC samples were purged with oxygen ( $\text{O}_2$ ) prior to analysis to remove carbon dioxide and were analyzed using a Seivers 800 Portable TOC Analyzer with an autosampler (Ionics, Boulder, CO). The COD measurements were conducted in accordance to USEPA-approved APHA Method 5220D (*Standard Methods*) using a closed reflux, colorimetric method and read spectrophotometrically with a Hach DR/2400 (Hach Company, Loveland, CO). The pH was measured in the lab using a Fisher Scientific Accumet pH meter 25 (Atlanta, GA). The DO and water temperature measurements were taken in the field with a YSI 550 DO meter (Yellow Springs, OH).

## RESULTS AND DISCUSSION

Samples tested for TTHM and HAA5 concentrations suggest that sedimentation basin sludge is actually a “sink” for DBPs; however, degradation does occur. According to Fram et al. (2003), sorption of hydrophobic organic compounds such as THMs has been observed on sedimentary materials. Adsorption of organic chemicals from water to sediment is described by the  $K_{oc}$ , the organic carbon/water partition coefficient. Karickhoff et al. (1979) determined a relationship between the  $K_{oc}$  and the  $K_{ow}$ , the octanol/water partition coefficient, to be  $K_{oc} = 0.63K_{ow}$ . Walton et al. (1992) discovered that the extent of sorption is based on a bulk partition coefficient,  $K_p$ , which is dependent on a sediment’s organic content and the  $K_{oc}$  of the organic compound (Equation 1).

$$K_p = K_{oc} \times f_{oc} \quad (1)$$

Where:

$K_p$  is the linear bulk sediment-water partition coefficient

$K_{oc}$  is the organic carbon/water partition coefficient, and

$f_{oc}$  is the fraction of organic carbon in sediment

Organic carbon/water partition coefficients for TTHM and DCAA and TCAA are all smaller, with the exception of bromoform, than the common volatile organic compounds listed in Table 2. Therefore, DBPs would not be adsorbed as easily to sedimentary material as these organics; however, the organic carbon content of the sludge is apparently high enough for THMs and HAAs to adsorb and cause a noticeable affect on DBP concentrations in the extracted water. Sludge samples from the BCVPI

treatment plant were found to contain 38 % organic content in top layers and 32 % in bottom layers on average (Table 3 – averages based on TVS:TS data). Fram et al. (2003) noted that sedimentary organic material consists of approximately 60 % (by mass) organic carbon, which may help explain the high TTHM and HAA5 values recorded.

Sludge waters that were extracted from top sediment layers, even those not subjected to additional chlorine, were found to contain very high TTHM and HAA5 levels. The study was conducted over a 4-month period, from 8/05 to 11/05, and consisted of four sampling events. Four-month mean HAA5 levels from top sludge layers (no additional chlorine added) were 298 µg/L and 330 µg/L, in centrifuged and drained samples, respectively. The same averages taken from the top layer contained TTHM concentrations of 417 µg/L and 415 µg/L, in centrifuged and drained samples. Significant degradation was observed in the bottom sludge, primarily in HAA5 samples; mean HAA5 values were 72 µg/L and 73 µg/L for centrifuged and drained samples, respectively. These values would have been much lower (close to 0 µg/L) had it not been for one sampling date in particular when HAA5 levels were still 287 µg/L and 212 µg/L. TTHM mean values from bottom sludge waters were 292 µg/L and 282 µg/L for centrifuged and drained samples. The mean value data suggested that there were no correlations between centrifuged or drained samples and DBP levels, in the samples that were not further chlorinated.

#### **Sludge age vs. TTHM and HAA5.**

Daily water treatment logs were examined to verify dates when both sedimentation basins were cleaned. From this data, the age of the bottom sludge layer

could be determined exactly. Samples collected on 8/8/05 and 8/25/05 were from one basin, and samples from 10/14/05 and 11/12/05 were from another. Based on data, the bottom-layer sludge age followed the order 10/14/05 (105 days), 8/8/05 (125 days), 11/12/05 (133 days), and 8/25/05 (142 days). The order correlated with degradation processes well for both TTHM and HAA5 samples. Basin sludge was tested for DO and was found to be anoxic approximately two feet beneath the sludge surface. Levels within the top, flocculated region of sludge were typically around 1.00 mg/L dissolved oxygen. The assumption that THM degradation takes place under anaerobic conditions was seen in this study (Figure 2). The results also suggested that biodegradation did not occur until approximately 100 days of storage within the basin (Figure 2). This could not be explained but one possibility may have been a delayed biodegradation reaction. The study was limited by the small dataset (four sampling events) and introduces the question of TTHM degradation rate between days 105 and 125. Additional research would help to fill voids in the data where the majority of degradation occurred, thereby providing valuable information into the fate of THMs.

The dominant TTHM species found was chloroform, both in top and bottom sludge layers. Chloroform represented 96.8 % of the TTHM species on average across the four sampling events in the top sludge layers, and 98.4 % in the bottom layer. Trace amounts of bromodichloromethane and dibromochloromethane were measured in bottom sludge samples during the 8/8/05 sampling event. This said, the higher chloroform percentage in bottom samples may indicate biodegradation of the three brominated THMs. This is in agreement with Fram et al. (2003), but the results also suggest that chloroform is biodegradable (Figure 2).

Biodegradation was also evident for HAA5 species between top and bottom sludge layers. During two sampling events (8/8/05 and 8/25/05), HAA5 levels were 0 µg/L in both centrifuged and drained bottom-layer samples. Concentrations were also extremely low in bottom samples from 11/12/05; HAA5 averaged 4 µg/L in centrifuged and drained samples. Similar to the results observed for TTHM, bottom-layer HAA5 values were highest in the younger, 105 day-old sludge, but plummeted following approximately 100 days of residence time (Figure 3). Again, the results could not be explained but were perhaps the consequence of increasing bacterial counts within the sediment or a delayed biodegradation reaction. While collecting samples, the appearance of top and bottom samples was observed. Top layers were light brown and very fluffy, while bottom layers were condensed and very dark brown with dark green algal streaks. The bottom layers appeared nutrient-rich and able to host a large bacterial population; however, bacterial counts were not determined.

The dominating HAA5 species in three of the four top-layer samples was DCAA, while TCAA represented 90 % and 95 % of the HAA5s in centrifuged and drained samples from 8/25/05 (Table 4). The implication that TCAA biodegrades most slowly was found to be true in the 11/12/05 bottom-layer sample; 100 % of the HAA5 concentration was TCAA, but levels were merely 1.9 µg/L and 6 µg/L in centrifuged and drained samples, respectively. This was not the case for the 10/14/05 bottom samples, as HAA5 concentrations were comprised of 72-73 % DCAA and 24-25 % TCAA following 105 days of retention (Table 5).

### **TOC concentrations and release.**

Supernatant and decanted water was taken from top- and bottom-layer sludge samples and tested for TOC concentrations. The TOC of top-layer samples ranged from 2.88 – 3.96 mg/L and averaged 3.39 mg/L over the four sampling dates. The TOC of bottom sludge waters ranged from 7.0 – 12.75 mg/L and averaged 9.93 mg/L (Table 3). As mentioned earlier, the bottom sludge appeared very rich and dense, and evidently had a large impact on TOC levels. The variation in TOC levels observed corresponds to the organic content found in the sludge. As the higher organic-containing top layers aged and were covered with new sludge, organic matter was apparently released to the water, resulting in a lower organic content in the bottom sludge (Table 3). This is important to understand since TOC release may contribute to DBP formation in the overlying, chlorinated waters. Therefore, sludge samples were taken to determine whether organic carbon was readily released from the sediment. The TOC concentrations maintained steady levels, similar to the averages recorded in the sludge waters, and no significant release was observed over the 3 week study period (Figure 4). This suggests that major TOC release did not occur in sludge that was less than 3 weeks old and implied that TOC release takes place gradually over the course of one to four months.

### **Chlorination of sludge waters.**

Centrifuged and drained samples were chlorinated with 4 mg/L, the USEPA's maximum residual disinfection level, to determine whether further chlorination could contribute to DBP formation in accumulated sludge. Results varied as some samples increased in TTHM and HAA5 levels, some remained similar to pre-chlorination levels,

and others actually decreased slightly in post-chlorination studies (Table 6). Pre-chlorinated samples and samples dosed for 60 minutes were evaluated to study the influence of additional chlorine; and, the percent change between the two was calculated. Only slight increases were observed for TTHM concentrations in the top-layer sludge; 0.3 % in centrifuged samples and 10.2 % in drained samples (Figures 5 and 6). This suggests that the NOM, which had already reacted with chlorine, was not susceptible to increased THM formation upon further chlorination. The additional chlorine caused a greater impact on bottom samples, as centrifuged TTHM values increased 18 % and drained sample concentrations rose 28.7 %. The values could have resulted from NOM release and higher TOC concentrations in the bottom-layer extracted waters, as mentioned above.

The HAA5 results observed following chlorination were opposite of those recorded for TTHM. Top-layer samples were greatly influenced by the additional chlorine and showed increases of 23.6 % in centrifuged samples and 55.3 % in drained samples (Figures 7 and 8). The most significant changes to HAA5 concentrations were observed between 0 – 30 minutes, when a greater chlorine concentration was present. Nikolaou et al. (2004) noted that THMs undergo a rapid formation during the first 30 – 100 minutes, followed by a slower rate of increase. Research has shown HAA formation to occur more quickly than THMs (AWWA, 1999). Although the top sludge layer was not shown to favor TTHM formation with the addition of extra chlorine, it was observed that the previously “reacted” NOM could still produce HAA5. This could be problematic for treatment plants such as BCVPI which store sludge in basins for extended periods. Bottom-layer sludge samples were almost totally dependent on one sampling date,



10/14/05. A significant reduction of 48.7 % was observed in the centrifuged sample, while an increase of 29.4 % was noted in the drained sample. Increases in TTHM and HAA5 were measured more frequently in drained samples than centrifuged samples with the addition of extra chlorine. This may suggest that particulate organic matter concentrations were actually higher in some drained samples, the opposite of what was expected following centrifugation.

## CONCLUSIONS

The conclusions derived from this study are as follows:

- Settled sludge may serve as a deposit for THMs and HAAs depending on the organic carbon content of the sedimentary material. Equation 1, developed by Karickhoff et al. (1979), indicates that higher organic carbon levels will increase the sorption of organic compounds such as THMs and HAAs.
- Although not observed in the laboratory experiment, TOC is released from sludge over time. Organic content in top-layer sludge was higher than that observed in bottom layers, and much higher TOC concentrations were recorded in extracted water samples from bottom layers.
- Following chlorination with 4 mg/L chlorine, further TTHM formation occurred in bottom-layer samples and additional HAA5 formation was observed in top-layer water samples. Initial chlorine doses in treatment plants are typically lower than 4 mg/L; however, this study suggests that additional DBPs may be formed when highly chlorinated water is in contact with settled sludge. Additional research conducted by the authors (submitted for publication) suggested that

sludge does not play a large role in DBP formation. That research took place under normal operating conditions, where typical chlorine doses were 1-2 mg/L. Therefore, the results suggest that basin cleaning may only be necessary when a facility is treating with high chlorine doses, close to 4 mg/L.

## CHAPTER 3 TABLES

**TABLE 1 TTHM and HAA5 species**

Disinfection By-Product	Name	Formula	MCLG (mg/L)	MCL (mg/L)
Total Trihalomethane (TTHM)	Chloroform	CHCl <sub>3</sub>	0	0.080 (annual average)
	Bromodichloromethane	CHBrCl <sub>2</sub>	0	
	Chlorodibromomethane	CHBr <sub>2</sub> Cl	0.06	
	Bromoform	CHBr <sub>3</sub>	0	
Haloacetic Acids (HAA5)	Monochloroacetic acid	CH <sub>2</sub> ClCOOH	-	0.060 (annual average)
	Dichloroacetic acid	CHCl <sub>2</sub> COOH	0	
	Trichloroacetic acid	CCl <sub>3</sub> COOH	0.3	
	Monobromoacetic acid	CH <sub>2</sub> BrCOOH	-	
	Dibromoacetic acid	CHBr <sub>2</sub> COOH	-	
Other Haloacetic Acids	Bromochloroacetic acid	CHBrClCOOH	n/a	n/a
	Bromodichloroacetic acid	CBrCl <sub>2</sub> COOH		
	Tribromoacetic acid	CBr <sub>3</sub> COOH		
	Chlorodibromoacetic acid	CBr <sub>2</sub> ClCOOH		

Cited from *Federal Register* (1998); - no maximum contaminant level goal (MCLG) established

**TABLE 2 Partition coefficients of DBPs and common volatile compounds**

	Chemical	K <sub>ow</sub>	K <sub>oc</sub> *
DBPs	Chloroform*	93	59
	Bromodichloromethane*	76	48
	Dibromochloromethane*	123	77
	Bromoform*	240	151
	Dichloroacetic acid*	8	5.2
	Trichloroacetic acid*	50	32
Common Volatile Compounds	Benzene <sup>†</sup>	135	85
	Toluene <sup>‡</sup>	513	323
	Ethylbenzene <sup>‡</sup>	1413	890
	p-Xylene <sup>†</sup>	1413	890
	Carbon tetrachloride <sup>‡</sup>	437	275

All K<sub>oc</sub> values calculated based on Karickhoff et al. (1979)

\* cited from Karickhoff et al. (1979)

<sup>†</sup> cited from Chiou et al. (1983)

<sup>‡</sup> cited from Walton et al. (1992)

**TABLE 3 Extracted water and sludge characteristics from top and bottom layers**

Sludge Layer	Parameter	8/8/2005	8/25/2005	10/14/2005	11/12/2005
Top	pH	6.64	6.87	6.79	6.73
	TS (mg/L)	1850	1823	2593	2130
	TVS (mg/L)	-	670	827	937
	TOC (mg/L)	3.58	3.25	2.88	3.96
	Soluble COD (mg/L)	-	-	326	432
	Water Temperature (°C)	24.8	26.8	17.8	15
Bottom	pH	6.84	6.82	6.99	6.71
	TS (mg/L)	23520	25220	19847	28050
	TVS (mg/L)	-	7990	6390	9223
	TOC (mg/L)	7	9.72	12.75	9.57
	Soluble COD (mg/L)	-	-	2245	3145
	Water Temperature (°C)	24.8	26.8	17.8	15

**TABLE 4 HAA5 percentage distribution in top sludge layer**

Sampling Date	HAA5 Top Sludge				
	centrifuged / drained				
	MCAA	DCAA	TCAA	MBAA	DBAA
8/8/2005	16% / 0	59% / 74%	25% / 26%	nd	nd
8/25/2005	nd	10% / 5%	90% / 95%	nd	nd
10/14/2005	1% / 2%	74% / 72%	25% / 26%	nd	nd
11/12/2005	nd	73% / 75%	27% / 25%	nd	nd

nd – non-detectable

**TABLE 5 HAA5 percentage distribution in bottom sludge layer**

Sludge Age (days)	Sampling Date	HAA5 Bottom Sludge				
		centrifuged / drained				
		MCAA	DCAA	TCAA	MBAA	DBAA
125	8/8/2005	nd	nd	nd	nd	nd
142	8/25/2005	nd	nd	nd	nd	nd
105	10/14/2005	3% / 4%	72% / 73%	25% / 24%	nd	nd
133	11/12/2005	nd	nd	100% / 100%	nd	nd

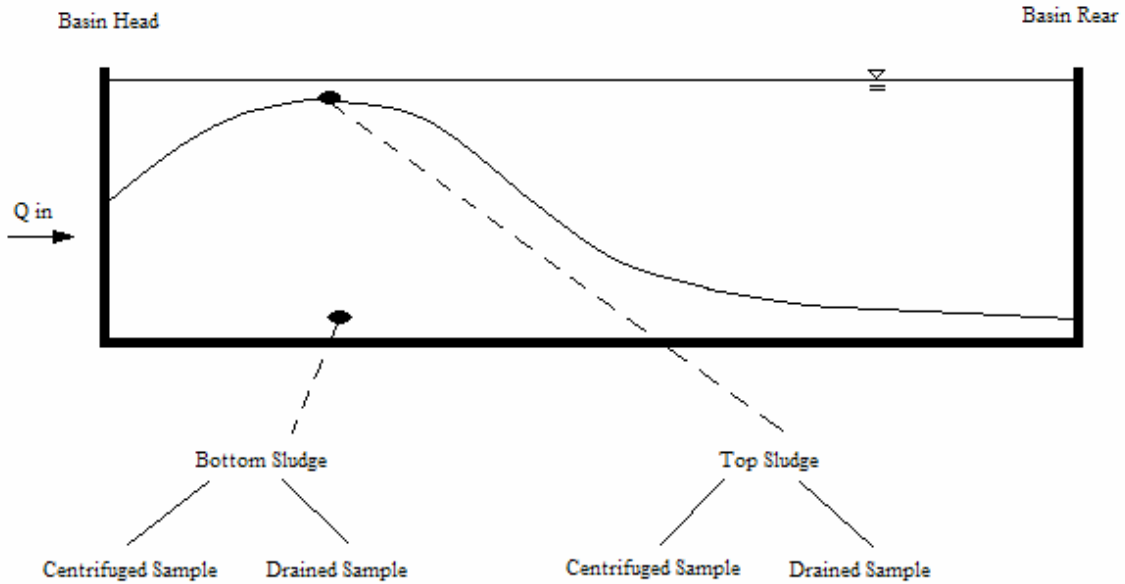
nd – non-detectable

**TABLE 6 HAA5 and TTHM concentrations following chlorination**

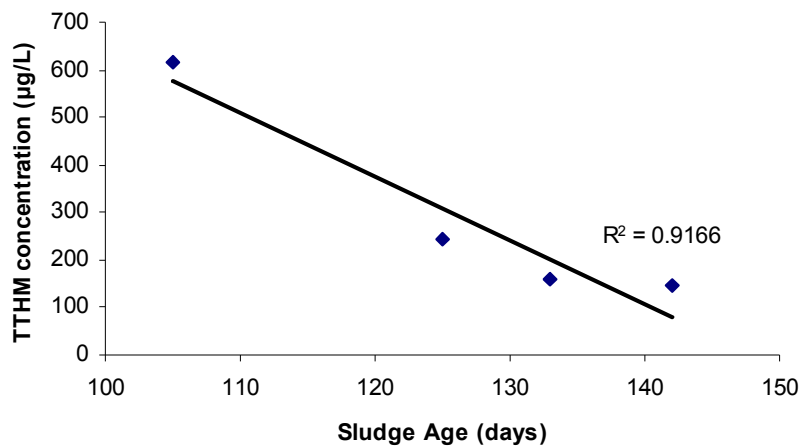
Sampling Date	Chlorine Contact (min)	HAA5 (µg/L)				TTHM (µg/L)			
		Top		Bottom		Top		Bottom	
		Centrifuged	Drained	Centrifuged	Drained	Centrifuged	Drained	Centrifuged	Drained
8/8/2005	0	409.8	268.8	0	0	321.5	283.4	243	381.1
	60	412.2	404.6	0	9.5	332.1	380	420.5	362.7
8/25/2005	0	74.6	66.4	0	0	401.6	406	148.4	231.4
	60	321.9	265.3	0	0	399	460.3	116	160.7
10/14/2005	0	401.4	413.2	286.5	212.1	586	598.7	616.9	452.8
	60	385	392.7	127.6	318.3	504.4	554.4	197.6	836.1
11/12/2005	0	306.7	168.1	1.9	6.0	377.5	370.6	160.6	128
	60	354.9	361.1	20.5	48.5	437.7	432.3	224.1	175.6

## CHAPTER 3 FIGURES

**FIGURE 1** Schematic of sample collection and treatment



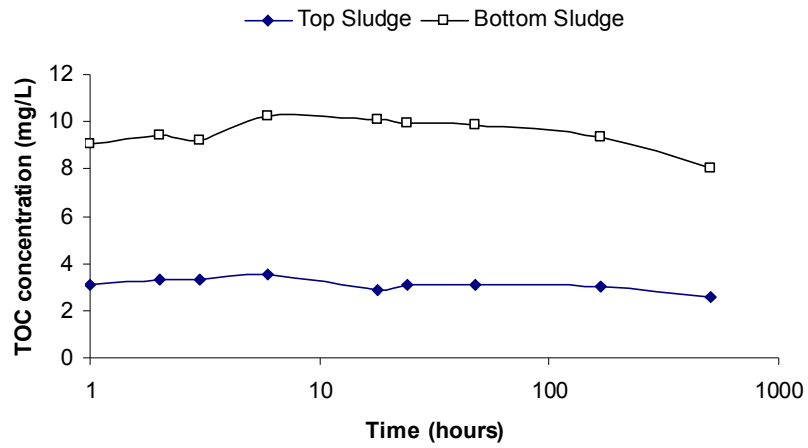
**FIGURE 2** Sludge Age and TTHM concentrations in centrifuged bottom samples



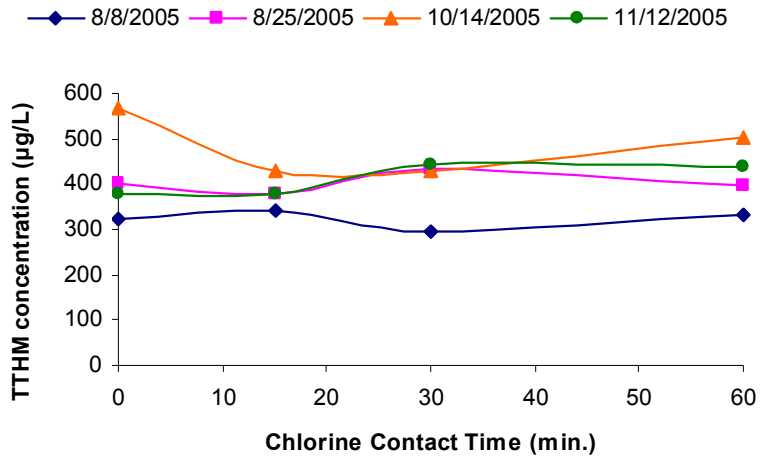
**FIGURE 3** Sludge Age and HAA5 concentrations in centrifuged bottom samples



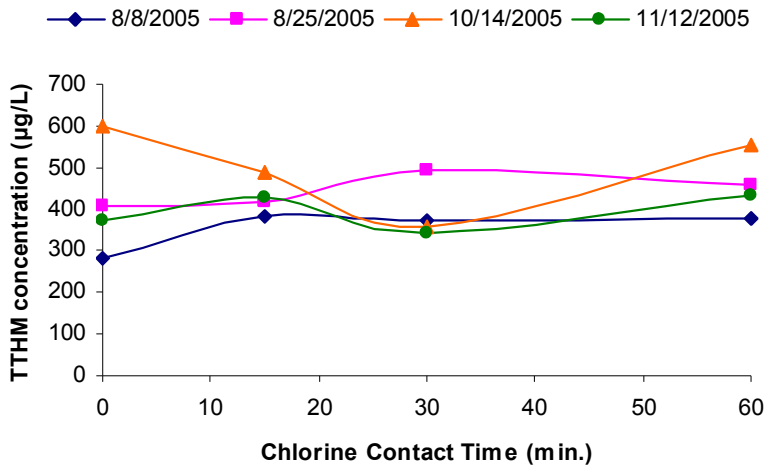
**FIGURE 4** TOC release from top and bottom sludge samples



**FIGURE 5** TTHM concentration in top-centrifuged sludge sample

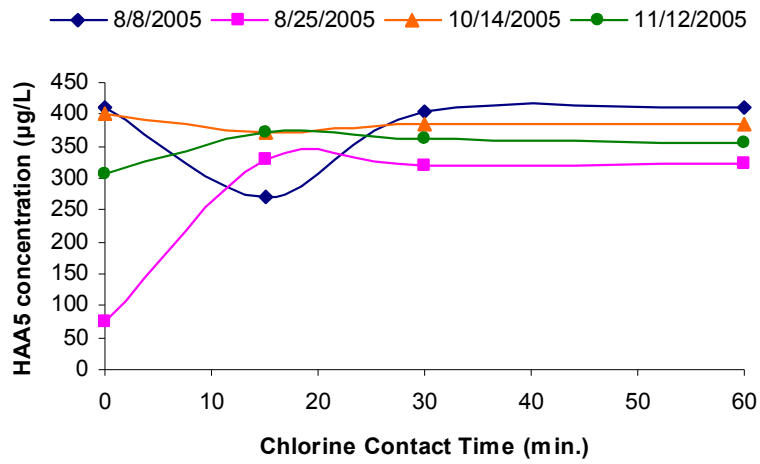


**FIGURE 6** TTHM concentration in top-drained sludge sample

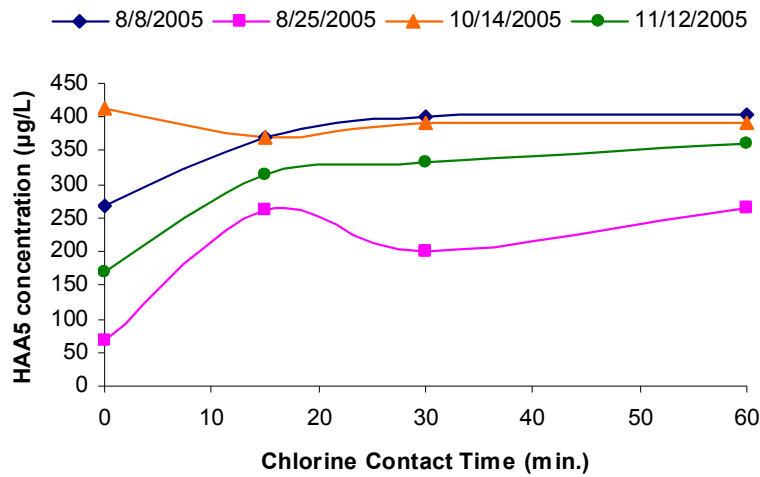




**FIGURE 7** HAA5 concentration in top-centrifuged sludge sample



**FIGURE 8** HAA5 concentration in top-drained sludge sample



## **ACKNOWLEDGEMENT**

The authors wish to thank the Blacksburg/Christiansburg/VPI Water Authority for their financial support and friendship, and also wish to thank the Edna Bailey Sussman Fund for their generous funding.

## CHAPTER 3 REFERENCES

- AWWA (American Water Works Association), 1999. Water Quality & Treatment-A Handbook of Community Water Supplies. 5<sup>th</sup> Edition. R.D. Letterman, editor. McGraw-Hill, Inc
- Chiou, C.T.; Porter, P.E.; & Schmedding, D.W., 1983. Partition Equilibria of Nonionic Organic Compounds Between Soil Organic Matter and Water. *Envir. Science and Technol.*, 17:4:227.
- Ellis, D.A. et al, 2001. The Fate and Persistence of Trifluoroacetic and Chloroacetic Acids in Pond Waters. *Chemosphere*, 42:309.
- Federal Register*. 1998. National Primary Drinking Water Regulations: Disinfectants and Disinfection Byproducts; Final Rule. 40 CFR Parts 9, 141 and 142, 63:241:69389.
- Fram, M.S. et al, 2003. Processes Affecting the Trihalomethane Concentrations Associated with the Third Injection, Storage, and Recovery Test at Lancaster, Antelope Valley, California, March 1998 through April 1999. United States Geological Survey. Water Resources Investigations Report 03-4062.
- Garcia-Villanova, R.J. et al, 1997. Formation, Evolution and Modeling of Trihalomethanes in the Drinking Water of a Town: I. At the Municipal Treatment Utilities. *Water Research*, 31:6:1299.
- Kampioti A.A. & Stephanou E.G., 2002. The Impact of Bromide on the Formation of Neutral and Acidic Disinfection By-Products (DBPs) in Mediterranean Chlorinated Drinking Water. *Water Research*, 36:2596.
- Karickhoff, S.W.; Brock, R.D.; & Scott, T.A., 1979. Sorption of Hydrophobic Pollutants on Natural Sediments. *Water Research*, 13:241.
- Nikolaou, A.D.; Lekkas, T.D.; & Golfinopoulos, S.K., 2004. Kinetics of the Formation and Decomposition of Chlorination By-Products in Surface Waters. *Chemical Engineering Journal*, 100:139.
- Richardson, S.D., 2003. Disinfection By-Products and Other Emerging Contaminants in Drinking Water. *Trends in Analytical Chemistry*, 22:10:666.
- Rossmann, L.A. et al, 2001. DBP Formation Kinetics in a Simulated Distribution System. *Water Research*, 35:14:3483.
- Singer P.C., 1993. Basin Concepts of Disinfection By-Product Formation and Control. AWWA D/DBP Rule Teleconference: Presentation 1, 1-20.

*Standard Methods for the Examination of Water and Wastewater*, 1998 (20<sup>th</sup> ed.). APHA, AWWA, and WEF, Washington.

United States Environmental Protection Agency (USEPA), 1995. Methods for the Determination of Organic Compounds in Drinking Water, Supplement III. EPA 600-R-95-131. PB 95-261616.

Waller, K. et al, 1998. Trihalomethanes in Drinking Water and Spontaneous Abortion. *Epidemiology*, 9:2:134.

Walton, B.T. et al, 1992. Soil Sorption of Volatile and Semivolatile Organic Compounds in a Mixture. *Jour. of Environmental Quality*, 21:4:552.

Xhou, H. & Xie, Y.F., 2002. Biologically Active Carbon for HAA Removal: Part I, Batch Study. *Jour. AWWA*, 94:4:194.

Xie, Y.F., 2004. Disinfection Byproducts in Drinking Water: Formation, Analysis and Control. CRC Press Inc., Boca Raton, Fla.

## LITERATURE REVIEW REFERENCES

- Adams, C. et al, 2005. Trihalomethane and Haloacetic acid disinfection by-products in full-scale drinking water systems. *Jour. of Environmental Engineering*, 131:4:526.
- Adin, A. et al, 1991. Trihalomethane formation in chlorinated drinking water: A kinetic model. *Water Research*, 25:7:797.
- AWWA (American Water Works Association), 1999. Water Quality & Treatment-A Handbook of Community Water Supplies. 5<sup>th</sup> Edition. (R.D. Letterman, editor). McGraw-Hill, Inc.
- Barrett, S.E.; Krasner, S.W.; & Amy, G.L., 2000. Natural Organic Matter and Disinfection By-Products: Characterization and Control in Drinking Water-An Overview. In: Natural Organic Matter and Disinfection By-Products: Characterization and Control in Drinking Water. Chapter 1. (S.E. Barrett, S.W. Krasner, G.L. Amy, editors). American Chemical Society, Washington, D.C.
- Carlson M.A. et al, 1986. Experiences with the use of chlorine dioxide and potassium permanganate as preoxidants for trihalomethane and manganese control. Annual Conference Proceedings, American Water Works Association; Water -- Key to Life. Denver, CO.
- Chin, Y.; Aiken, G.; & O'Loughlin, E., 1994. Molecular Weight, Polydispersity, and Spectroscopic Properties of Aquatic Humic Substances. *Environmental Science and Technology*, 28:1853.
- Croué, J.; Violleau, D.; & Labouyrie, L., 2000. Disinfection By-Product Formation Potentials of Hydrophobic and Hydrophilic Natural Organic Matter Fractions: A Comparison Between Low- and a High-Humic Water. American Chemical Society Symposium Series 761. In: Natural Organic Matter and Disinfection By-Products: Characterization and Control in Drinking Water. Chapter 10. (S.E. Barrett, S.W. Krasner, G.L. Amy, editors). American Chemical Society, Washington, D.C.
- Dalvi, A.G.I.; Al-Rasheed, R.; Javeed, M.A., 2000. Haloacetic Acids (HAAs) Formation in Desalination Processes from Disinfectants. *Desalination*, 129:261.
- Edzwald, J.K. & Van Benschoten, J.E., 1990. Aluminum Coagulation of Natural Organic Material. *Chemical Water and Wastewater Treatment*. (H.H. Hahn and R. Klute, editors). Berlin: Springer-Verlag.
- Ellis D.A. et al, 2001. The Fate and Persistence of Trifluoroacetic and Chloroacetic Acids in Pond Waters. *Chemosphere*, 42:309.

- Fawell, J.K., 1999. The risk of DBPs in Perspective. In: Disinfection by-products in drinking water-Current issues. (M. Fielding & M. Farrimond, editors). The Royal Society of Chemistry, UK.
- Federal Register*. 1998. National Primary Drinking Water Regulations: Disinfectants and Disinfection Byproducts; Final Rule. 40 CFR Parts 9, 141 and 142, 63:241:69389.
- Garcia-Villanova R.J. et al, 1997. Formation, Evolution and Modeling of Trihalomethanes in the Drinking Water of a Town: I. At the Municipal Treatment Utilities. *Water Research*, 31:6:1299.
- Garcia-Villanova R.J. et al, 1997. Formation, Evolution and Modeling of Trihalomethanes in the Drinking Water of a Town: II. In the Distribution System. *Water Research*, 31:6:1405.
- Hashimoto, S.; Azuma, T.; & Otsuki, A., 1998. Distribution, Sources, and Stability of Haloacetic Acids in Tokyo Bay. *Japanese Environ. Science Technol.*, 17:798.
- Kampioti, A.A. & Stephanou, E.G., 2002. The Impact of Bromide on the Formation of Neutral and Acidic Disinfection By-Products (DBPs) in Mediterranean Chlorinated Drinking Water. *Water Research*, 36:2596.
- Muller, S.R. et al, 1996. Occurance, Sources, and Fate of Trichloroacetic Acid in Swiss Waters. *Environ. Toxicol. and Chemistry*, 15:9:1470.
- Reckhow, D.A.; Singer, P.C.; & Malcolm, R.L., 1990. Chlorination of Humic Materials: Byproduct Formation and Chemical Interpretations. *Environ. Sci. & Technol.*, 24:1655.
- Richardson, S.D., 2003. Disinfection By-Products and Other Emerging Contaminants in Drinking Water. *Trends in Analytical Chemistry*, 22:10:666.
- Rossmann, L.A. et al, 2001. DBP Formation Kinetics in a Simulated Distribution System. *Water Research*, 35:14:3483.
- Sérodes Jean-B. et al, 2003. Occurrence of THMs and HAAs in Experimental Chlorinated Waters of the Quebec City Area (Canada). *Chemosphere*, 51:253.
- Singer, P.C., 1993. Basin Concepts of Disinfection By-Product Formation and Control. AWWA D/DBP Rule Teleconference: Presentation 1.
- Singer, P.C., 1999. Formation and Control of Disinfection By-Products in Drinking Water. (P.C. Singer, editor). American Water Works Association, CO.
- Van Dijk-Looijaard, A.M. & Genderen, J.V., 2000. Levels of Exposure from Drinking Water. *Food and Chemical Toxicology*, 38:S37.

- Waller, K. et al, 1998. Trihalomethanes in Drinking Water and Spontaneous Abortion. *Epidemiology*, 9:2:134.
- Werdehoff, K.S. & Singer, P.C., 1987. Chlorine Dioxide Effects on THMFP, TOXFP, and the Formation of Inorganic By-Products. *Jour. AWWA*, 79:7:107.
- Wright J.M.; Schwartz, J.; & Dockery, D.W., 2003. Effect of Trihalomethane Exposure on Fetal Development. *Occupational and Environmental Medicine*, 60:3:173.
- Wu, W.W.; Benjamin, M.M.; & Korshin, G.V., 2001. Effects of Thermal Treatment on Halogenated Disinfection By-Products in Drinking Water. *Water Research*, 35:15:3545.
- Xhou, H. & Xie, Y.F., 2002. Biologically Active Carbon for HAA Removal: Part I, Batch Study. *Jour. AWWA*, 94:4:194.
- Xie, Y.F., 2004. Disinfection Byproducts in Drinking Water: Formation, Analysis and Control. CRC Press, Inc., Boca Raton, Fla.

## APPENDIX A: R code for TTHM predictive model (no ClO<sub>2</sub>)

```
#R Code for TTHM model without ClO2
> d <- read.csv("hunter2.csv")
> attach(d)
> t1 <-
data.frame(basin=rep(1,14),HAA=R1HAA,THM=R1THM,Cl=F1Cl,TOC=
F1TOC,Temp=Temp,PH=P1H,DET=D1ET,SLUDGE=S1ludge,time=1:14)
> t2 <-
data.frame(basin=rep(2,14),HAA=R2HAA,THM=R2THM,Cl=F2Cl,TOC=
F2TOC,Temp=Temp,PH=P2H,DET=D2ET,SLUDGE=S2ludge,time=1:14)
> t3 <-
data.frame(basin=rep(3,14),HAA=R3HAA,THM=R3THM,Cl=F3Cl,TOC=
F3TOC,Temp=Temp,PH=P3H,DET=D3ET,SLUDGE=S3ludge,time=1:14)
> detach(d)
> d1 <- rbind(t1,t2,t3)
> rownames(d1) <- 1:NROW(d1)
> d1$basin <- as.factor(d1$basin)
>
> # Plots
> pairs(d1[,-c(1,2,10)])
>
> # demonstrate basin is not significant
> m0 <- lm(THM ~ basin + Cl + TOC + Temp + PH + DET +
SLUDGE, data=d1)
> m1 <- lm(THM ~ Cl + TOC + Temp + PH + DET + SLUDGE,
data=d1)
> anova(m0,m1)
Analysis of Variance Table

Model 1: THM ~ basin + Cl + TOC + Temp + PH + DET + SLUDGE
Model 2: THM ~ Cl + TOC + Temp + PH + DET + SLUDGE
  Res.Df    RSS Df Sum of Sq    F Pr(>F)
1      32 3171.7
2      34 3544.6 -2    -372.9 1.8811 0.1689
>
> # Big model with all variables and 2-way interactions
> m2 <-
lm(THM~Cl+I(Cl^2)+TOC+Temp+I(Temp^2)+PH+DET+SLUDGE+Cl:TOC+C
l:Temp+Cl:PH+Cl:DET+Cl:SLUDGE+TOC:Temp
+
+TOC:PH+TOC:DET+TOC:SLUDGE+Temp:PH+Temp:DET+Temp:SLUDGE+PH:
DET+PH:SLUDGE+DET:SLUDGE, data=d1)
>
> m3 <- step(m2,direction="both")
Start: AIC= 180.97
```



THM ~ Cl + I(Cl^2) + TOC + Temp + I(Temp^2) + PH + DET + SLUDGE + Cl:TOC + Cl:Temp + Cl:PH + Cl:DET + Cl:SLUDGE + TOC:Temp + TOC:PH + TOC:DET + TOC:SLUDGE + Temp:PH + Temp:DET + Temp:SLUDGE + PH:DET + PH:SLUDGE + DET:SLUDGE

	Df	Sum of Sq	RSS	AIC
- Cl:TOC	1	0.52	1050.61	178.99
- PH:DET	1	0.94	1051.03	179.00
- Cl:SLUDGE	1	3.37	1053.45	179.10
- TOC:DET	1	4.79	1054.87	179.15
- Temp:PH	1	18.50	1068.58	179.68
- Cl:PH	1	23.42	1073.50	179.87
- TOC:Temp	1	32.45	1082.54	180.21
- DET:SLUDGE	1	41.58	1091.67	180.56
- TOC:PH	1	48.53	1098.62	180.82
<none>			1050.09	180.97
- PH:SLUDGE	1	60.35	1110.44	181.26
- I(Cl^2)	1	67.41	1117.49	181.52
- Temp:DET	1	81.83	1131.92	182.04
- Temp:SLUDGE	1	91.74	1141.82	182.40
- TOC:SLUDGE	1	124.75	1174.84	183.57
- Cl:Temp	1	175.62	1225.71	185.31
- Cl:DET	1	332.54	1382.62	190.24
- I(Temp^2)	1	561.10	1611.19	196.52

Step: AIC= 178.99

THM ~ Cl + I(Cl^2) + TOC + Temp + I(Temp^2) + PH + DET + SLUDGE + Cl:Temp + Cl:PH + Cl:DET + Cl:SLUDGE + TOC:Temp + TOC:PH + TOC:DET + TOC:SLUDGE + Temp:PH + Temp:DET + Temp:SLUDGE + PH:DET + PH:SLUDGE + DET:SLUDGE

	Df	Sum of Sq	RSS	AIC
- PH:DET	1	1.10	1051.71	177.03
- Cl:SLUDGE	1	4.43	1055.04	177.16
- TOC:DET	1	6.19	1056.80	177.23
- Temp:PH	1	19.41	1070.02	177.74
- Cl:PH	1	23.25	1073.86	177.88
- TOC:Temp	1	32.87	1083.48	178.25
- DET:SLUDGE	1	42.33	1092.94	178.61
- TOC:PH	1	48.72	1099.33	178.84
<none>			1050.61	178.99
- PH:SLUDGE	1	71.91	1122.52	179.70
- I(Cl^2)	1	78.73	1129.34	179.95
- Temp:DET	1	83.00	1133.61	180.10
+ Cl:TOC	1	0.52	1050.09	180.97
- Temp:SLUDGE	1	122.78	1173.39	181.52
- TOC:SLUDGE	1	144.59	1195.20	182.27

```

- Cl:Temp      1      181.05 1231.66  183.50
- Cl:DET       1      353.55 1404.16  188.88
- I(Temp^2)    1      568.68 1619.29  194.72

```

Step: AIC= 177.03

THM ~ Cl + I(Cl^2) + TOC + Temp + I(Temp^2) + PH + DET +  
 SLUDGE + Cl:Temp + Cl:PH + Cl:DET + Cl:SLUDGE + TOC:Temp +  
 TOC:PH + TOC:DET + TOC:SLUDGE + Temp:PH + Temp:DET +  
 Temp:SLUDGE + PH:SLUDGE + DET:SLUDGE

	Df	Sum of Sq	RSS	AIC
- Cl:SLUDGE	1	5.07	1056.78	175.23
- TOC:DET	1	5.70	1057.41	175.25
- Cl:PH	1	23.07	1074.78	175.92
- TOC:Temp	1	34.29	1086.00	176.34
- Temp:PH	1	36.91	1088.62	176.44
- DET:SLUDGE	1	44.46	1096.17	176.73
- TOC:PH	1	48.72	1100.43	176.89
<none>			1051.71	177.03
- I(Cl^2)	1	91.61	1143.32	178.45
+ PH:DET	1	1.10	1050.61	178.99
- PH:SLUDGE	1	106.66	1158.37	178.99
+ Cl:TOC	1	0.69	1051.03	179.00
- Temp:SLUDGE	1	134.27	1185.99	179.96
- TOC:SLUDGE	1	143.49	1195.20	180.27
- Temp:DET	1	178.62	1230.33	181.46
- Cl:Temp	1	231.04	1282.76	183.17
- Cl:DET	1	468.06	1519.78	190.12
- I(Temp^2)	1	834.01	1885.72	198.97

Step: AIC= 175.23

THM ~ Cl + I(Cl^2) + TOC + Temp + I(Temp^2) + PH + DET +  
 SLUDGE + Cl:Temp + Cl:PH + Cl:DET + TOC:Temp + TOC:PH +  
 TOC:DET + TOC:SLUDGE + Temp:PH + Temp:DET + Temp:SLUDGE +  
 PH:SLUDGE + DET:SLUDGE

	Df	Sum of Sq	RSS	AIC
- TOC:DET	1	2.45	1059.24	173.32
- Cl:PH	1	18.40	1075.19	173.93
- TOC:PH	1	43.85	1100.64	174.89
<none>			1056.78	175.23
- DET:SLUDGE	1	54.62	1111.40	175.29
- TOC:Temp	1	58.39	1115.17	175.43
- Temp:PH	1	70.86	1127.64	175.89
- I(Cl^2)	1	97.48	1154.27	176.84
+ Cl:SLUDGE	1	5.07	1051.71	177.03
+ PH:DET	1	1.75	1055.04	177.16

+ Cl:TOC	1	1.72	1055.07	177.16
- PH:SLUDGE	1	107.81	1164.59	177.21
- TOC:SLUDGE	1	138.96	1195.74	178.29
- Temp:DET	1	173.58	1230.36	179.46
- Temp:SLUDGE	1	263.90	1320.68	182.37
- Cl:Temp	1	275.99	1332.77	182.74
- Cl:DET	1	575.50	1632.29	191.05
- I(Temp^2)	1	1068.05	2124.84	201.86

Step: AIC= 173.32

THM ~ Cl + I(Cl^2) + TOC + Temp + I(Temp^2) + PH + DET + SLUDGE + Cl:Temp + Cl:PH + Cl:DET + TOC:Temp + TOC:PH + TOC:SLUDGE + Temp:PH + Temp:DET + Temp:SLUDGE + PH:SLUDGE + DET:SLUDGE

	Df	Sum of Sq	RSS	AIC
- Cl:PH	1	26.50	1085.74	172.33
- TOC:PH	1	45.43	1104.67	173.04
<none>			1059.24	173.32
- DET:SLUDGE	1	57.33	1116.57	173.48
- TOC:Temp	1	57.43	1116.67	173.49
- Temp:PH	1	68.62	1127.86	173.89
- I(Cl^2)	1	98.06	1157.30	174.95
+ TOC:DET	1	2.45	1056.78	175.23
+ Cl:SLUDGE	1	1.82	1057.41	175.25
+ PH:DET	1	1.04	1058.19	175.28
+ Cl:TOC	1	0.13	1059.11	175.32
- PH:SLUDGE	1	113.81	1173.04	175.51
- TOC:SLUDGE	1	189.47	1248.70	178.07
- Temp:DET	1	196.17	1255.41	178.29
- Temp:SLUDGE	1	263.78	1323.01	180.44
- Cl:Temp	1	286.61	1345.84	181.14
- Cl:DET	1	647.71	1706.94	190.88
- I(Temp^2)	1	1083.71	2142.94	200.21

Step: AIC= 172.33

THM ~ Cl + I(Cl^2) + TOC + Temp + I(Temp^2) + PH + DET + SLUDGE + Cl:Temp + Cl:DET + TOC:Temp + TOC:PH + TOC:SLUDGE + Temp:PH + Temp:DET + Temp:SLUDGE + PH:SLUDGE + DET:SLUDGE

	Df	Sum of Sq	RSS	AIC
- TOC:PH	1	33.27	1119.01	171.57
<none>			1085.74	172.33
- DET:SLUDGE	1	59.65	1145.39	172.53
- TOC:Temp	1	66.71	1152.45	172.78
+ Cl:PH	1	26.50	1059.24	173.32
- PH:SLUDGE	1	88.14	1173.88	173.53

+ TOC:DET	1	10.55	1075.19	173.93
+ PH:DET	1	3.10	1082.64	174.22
+ Cl:TOC	1	2.65	1083.09	174.23
+ Cl:SLUDGE	1	1.31	1084.43	174.28
- I(Cl^2)	1	175.11	1260.85	176.46
- TOC:SLUDGE	1	192.74	1278.48	177.03
- Temp:SLUDGE	1	239.11	1324.85	178.49
- Temp:DET	1	244.78	1330.52	178.67
- Cl:Temp	1	520.54	1606.28	186.39
- Temp:PH	1	599.09	1684.83	188.35
- Cl:DET	1	901.81	1987.55	195.12
- I(Temp^2)	1	1451.58	2537.32	205.14

Step: AIC= 171.57

THM ~ Cl + I(Cl^2) + TOC + Temp + I(Temp^2) + PH + DET +  
 SLUDGE + Cl:Temp + Cl:DET + TOC:Temp + TOC:SLUDGE + Temp:PH  
 + Temp:DET + Temp:SLUDGE + PH:SLUDGE + DET:SLUDGE

	Df	Sum of Sq	RSS	AIC
<none>			1119.01	171.57
- PH:SLUDGE	1	67.36	1186.38	171.97
+ TOC:PH	1	33.27	1085.74	172.33
- DET:SLUDGE	1	85.58	1204.59	172.59
+ Cl:PH	1	14.35	1104.67	173.04
+ PH:DET	1	7.54	1111.47	173.29
+ Cl:SLUDGE	1	2.29	1116.72	173.49
+ Cl:TOC	1	0.19	1118.82	173.56
+ TOC:DET	1	0.11	1118.91	173.57
- I(Cl^2)	1	154.70	1273.71	174.88
- TOC:SLUDGE	1	185.26	1304.28	175.85
- TOC:Temp	1	185.48	1304.49	175.86
- Temp:SLUDGE	1	224.23	1343.24	177.06
- Temp:DET	1	228.56	1347.58	177.19
- Cl:Temp	1	493.50	1612.51	184.55
- Temp:PH	1	598.55	1717.56	187.14
- Cl:DET	1	904.28	2023.29	193.86
- I(Temp^2)	1	1422.74	2541.75	203.21

>

> # Demonstrate why the interaction model is better than  
 the non-interaction model

```
> m4 <- lm(THM~Cl+I(Cl^2)+TOC+Temp+I(Temp^2)+PH+DET+SLUDGE,
data=d1)
```

```
> m5 <- step(m4,direction="both")
```

Start: AIC= 191.65

THM ~ Cl + I(Cl^2) + TOC + Temp + I(Temp^2) + PH + DET +  
 SLUDGE

	Df	Sum of Sq	RSS	AIC
- PH	1	8.7	2841.4	189.8
- DET	1	26.0	2858.7	190.0
- TOC	1	130.8	2963.5	191.5
<none>			2832.7	191.7
- SLUDGE	1	236.7	3069.4	192.9
- I(Cl^2)	1	325.1	3157.8	194.1
- Cl	1	404.6	3237.3	195.1
- Temp	1	533.4	3366.0	196.7
- I(Temp^2)	1	667.1	3499.8	198.3

Step: AIC= 189.78

THM ~ Cl + I(Cl^2) + TOC + Temp + I(Temp^2) + DET + SLUDGE

	Df	Sum of Sq	RSS	AIC
- DET	1	22.6	2864.0	188.1
<none>			2841.4	189.8
- TOC	1	145.1	2986.5	189.8
- SLUDGE	1	228.7	3070.1	191.0
+ PH	1	8.7	2832.7	191.7
- I(Cl^2)	1	317.5	3158.9	192.1
- Cl	1	399.0	3240.4	193.2
- Temp	1	599.6	3441.0	195.6
- I(Temp^2)	1	724.8	3566.2	197.1

Step: AIC= 188.1

THM ~ Cl + I(Cl^2) + TOC + Temp + I(Temp^2) + SLUDGE

	Df	Sum of Sq	RSS	AIC
<none>			2864.0	188.1
- TOC	1	194.0	3058.0	188.8
+ DET	1	22.6	2841.4	189.8
+ PH	1	5.3	2858.7	190.0
- I(Cl^2)	1	308.6	3172.6	190.3
- SLUDGE	1	379.3	3243.3	191.2
- Cl	1	387.7	3251.7	191.3
- Temp	1	582.4	3446.4	193.7
- I(Temp^2)	1	712.7	3576.7	195.2

> anova(m3,m5)

Analysis of Variance Table

Model 1: THM ~ Cl + I(Cl^2) + TOC + Temp + I(Temp^2) + PH +  
DET + SLUDGE + Cl:Temp + Cl:DET + TOC:Temp + TOC:SLUDGE +  
Temp:PH + Temp:DET + Temp:SLUDGE + PH:SLUDGE + DET:SLUDGE

Model 2: THM ~ Cl + I(Cl^2) + TOC + Temp + I(Temp^2) +  
SLUDGE

Res.Df	RSS	Df	Sum of Sq	F	Pr(>F)
--------	-----	----	-----------	---	--------

```

1      23  1119.0
2      34  2864.0 -11    -1745.0 3.2605 0.008105 **
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
>
> # Decided to stay with the more complicated model
> # Now remove interactions that definintely weren't
significant
> #m6 <- lm(THM ~ Cl + I(Cl^2) + TOC + Temp + I(Temp^2) +
PH +
> #      DET + SLUDGE + Cl:Temp + Cl:DET + TOC:Temp +
TOC:SLUDGE +
> #      Temp:PH + Temp:DET + Temp:SLUDGE, data=d1)
>
> # Summarize the best model
> summary(m3)

Call:
lm(formula = THM ~ Cl + I(Cl^2) + TOC + Temp + I(Temp^2) +
PH + DET + SLUDGE + Cl:Temp + Cl:DET + TOC:Temp +
TOC:SLUDGE + Temp:PH + Temp:DET + Temp:SLUDGE + PH:SLUDGE +
DET:SLUDGE, data = d1)

Residuals:
      Min       1Q   Median       3Q      Max
-11.20743  -3.68534  -0.08908   2.75356  14.77958

Coefficients:
            Estimate Std. Error t value Pr(>|t|)
(Intercept) -1.803e+02  1.671e+02  -1.079  0.291695
Cl           1.456e+01  1.311e+01   1.110  0.278302
I(Cl^2)      4.434e+00  2.487e+00   1.783  0.087767 .
TOC          -1.925e+01  3.281e+01  -0.587  0.563095
Temp         1.158e+01  6.373e+00   1.817  0.082329 .
I(Temp^2)    7.207e-01  1.333e-01   5.408  1.71e-05 ***
PH           5.166e+01  2.265e+01   2.280  0.032188 *
DET          -1.078e+00  1.091e+01  -0.099  0.922176
SLUDGE       -1.572e-02  8.670e-03  -1.813  0.082951 .
Cl:Temp      -3.266e+00  1.025e+00  -3.185  0.004125 **
Cl:DET        1.004e+01  2.329e+00   4.311  0.000259 ***
TOC:Temp     -2.571e+00  1.317e+00  -1.952  0.063155 .
TOC:SLUDGE   5.158e-03  2.643e-03   1.951  0.063297 .
Temp:PH      -3.460e+00  9.866e-01  -3.507  0.001893 **
Temp:DET     -1.015e+00  4.682e-01  -2.167  0.040800 *
Temp:SLUDGE  -1.586e-04  7.389e-05  -2.147  0.042585 *
PH:SLUDGE    1.293e-03  1.098e-03   1.177  0.251366

```

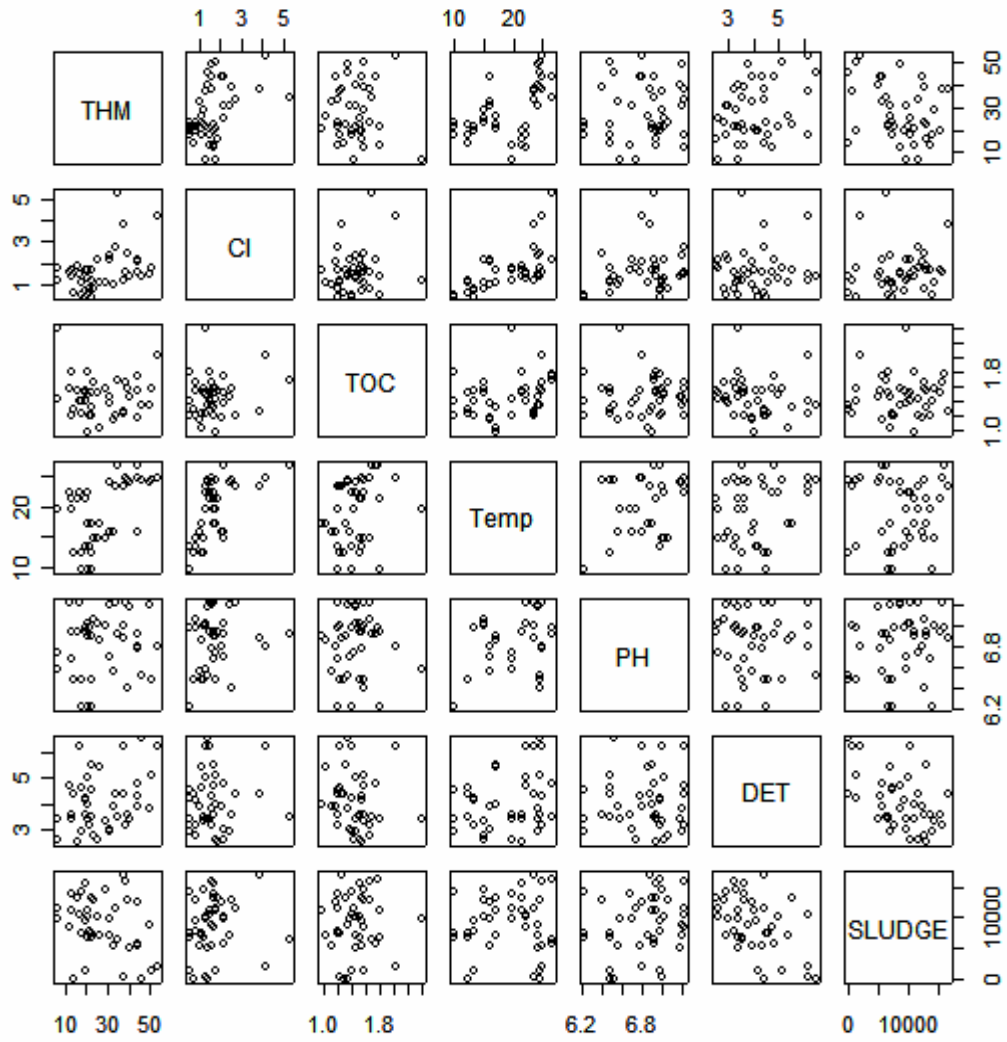
DET:SLUDGE 4.943e-04 3.727e-04 1.326 0.197776

---

Signif. codes: 0 '\*\*\*' 0.001 '\*\*' 0.01 '\*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 6.975 on 23 degrees of freedom  
Multiple R-Squared: 0.818, Adjusted R-squared: 0.6836  
F-statistic: 6.082 on 17 and 23 DF, p-value: 4.983e-05

APPENDIX FIGURE 1 TTHM Pairwise Plot





## APPENDIX B: R code for HAA5 predictive model (no ClO<sub>2</sub>)

```
#R Code for HAA5 model without ClO2
> d <- read.csv("hunter2.csv")
> attach(d)
> t1 <-
data.frame(basin=rep(1,14),HAA=R1HAA,THM=R1THM,Cl=F1Cl,TOC=
F1TOC,Temp=Temp,PH=P1H,DET=D1ET,SLUDGE=S1ludge,time=1:14)
> t2 <-
data.frame(basin=rep(2,14),HAA=R2HAA,THM=R2THM,Cl=F2Cl,TOC=
F2TOC,Temp=Temp,PH=P2H,DET=D2ET,SLUDGE=S2ludge,time=1:14)
> t3 <-
data.frame(basin=rep(3,14),HAA=R3HAA,THM=R3THM,Cl=F3Cl,TOC=
F3TOC,Temp=Temp,PH=P3H,DET=D3ET,SLUDGE=S3ludge,time=1:14)
> detach(d)
> d1 <- rbind(t1,t2,t3)
> rownames(d1) <- 1:NROW(d1)
> d1$basin <- as.factor(d1$basin)
>
> #> names(d1)
> # [1] "basin" "HAA" "THM" "Cl" "TOC" "Temp"
"PH" "DET"
> # [9] "SLUDGE" "time"
>
> pairs(d1[,-c(1,3,10)])
>
> # Demonstrate that basin is not significant
> m0 <-
lm(HAA~basin+Cl+TOC+Temp+PH+DET+SLUDGE+Cl:TOC+Cl:Temp+Cl:PH
+Cl:DET+Cl:SLUDGE+TOC:Temp+TOC:PH+TOC:DET+TOC:SLUDGE+
Temp:PH+Temp:DET+Temp:SLUDGE+PH:DET+PH:SLUDGE+DET:SLUDGE,
data=d1)
> m1 <-
lm(HAA~Cl+TOC+Temp+PH+DET+SLUDGE+Cl:TOC+Cl:Temp+Cl:PH+Cl:DE
T+Cl:SLUDGE+TOC:Temp+TOC:PH+TOC:DET+TOC:SLUDGE+Temp:PH
+Temp:DET+Temp:SLUDGE+PH:DET+PH:SLUDGE+DET:SLUDGE, data=d1)
> anova(m0,m1)
Analysis of Variance Table

Model 1: HAA ~ basin + Cl + TOC + Temp + PH + DET + SLUDGE
+ Cl:TOC + Cl:Temp + Cl:PH + Cl:DET + Cl:SLUDGE + TOC:Temp
+ TOC:PH + TOC:DET + TOC:SLUDGE + Temp:PH + Temp:DET +
Temp:SLUDGE + PH:DET + PH:SLUDGE + DET:SLUDGE
Model 2: HAA ~ Cl + TOC + Temp + PH + DET + SLUDGE + Cl:TOC
+ Cl:Temp + Cl:PH + Cl:DET + Cl:SLUDGE + TOC:Temp + TOC:PH
+ TOC:DET + TOC:SLUDGE + Temp:PH + Temp:DET + Temp:SLUDGE +
PH:DET + PH:SLUDGE + DET:SLUDGE
```

```

      Res.Df      RSS Df Sum of Sq      F Pr(>F)
1         17 1316.82
2         19 1507.03 -2   -190.21 1.2278 0.3176
>
> # Big model with all terms and all 2-way interactions
> m2 <-
lm(HAA~Cl+TOC+Temp+PH+DET+SLUDGE+Cl:TOC+Cl:Temp+Cl:PH+Cl:DE
T+Cl:SLUDGE+TOC:Temp+TOC:PH+TOC:DET+TOC:SLUDGE+Temp:PH
+Temp:DET+Temp:SLUDGE+PH:DET+PH:SLUDGE+DET:SLUDGE, data=d1)
>
> # AIC selected model for full model with all 2-way
interactions
> m3 <- step(m2,direction="both")

```

```

Start:  AIC= 191.78
  HAA ~ Cl + TOC + Temp + PH + DET + SLUDGE + Cl:TOC +
Cl:Temp + Cl:PH + Cl:DET + Cl:SLUDGE + TOC:Temp + TOC:PH +
TOC:DET + TOC:SLUDGE + Temp:PH + Temp:DET + Temp:SLUDGE +
PH:DET + PH:SLUDGE + DET:SLUDGE

```

	Df	Sum of Sq	RSS	AIC
- Temp:SLUDGE	1	0.14	1507.17	189.78
- PH:DET	1	0.17	1507.20	189.78
- Cl:TOC	1	0.41	1507.44	189.79
- TOC:PH	1	6.13	1513.16	189.94
- TOC:Temp	1	9.05	1516.07	190.02
- TOC:DET	1	15.09	1522.11	190.19
- PH:SLUDGE	1	18.32	1525.35	190.27
- TOC:SLUDGE	1	18.46	1525.49	190.28
- Cl:Temp	1	23.24	1530.26	190.40
- Cl:SLUDGE	1	24.13	1531.16	190.43
- Temp:PH	1	56.58	1563.61	191.29
- Temp:DET	1	59.02	1566.05	191.35
<none>			1507.03	191.78
- Cl:PH	1	163.03	1670.06	193.99
- Cl:DET	1	212.71	1719.73	195.19
- DET:SLUDGE	1	245.27	1752.30	195.96

```

Step:  AIC= 189.78
  HAA ~ Cl + TOC + Temp + PH + DET + SLUDGE + Cl:TOC +
Cl:Temp + Cl:PH + Cl:DET + Cl:SLUDGE + TOC:Temp + TOC:PH +
TOC:DET + TOC:SLUDGE + Temp:PH + Temp:DET + PH:DET +
PH:SLUDGE + DET:SLUDGE

```

	Df	Sum of Sq	RSS	AIC
- PH:DET	1	0.08	1507.25	187.78
- Cl:TOC	1	0.27	1507.44	187.79
- TOC:PH	1	6.48	1513.65	187.96

- TOC:Temp	1	9.04	1516.20	188.03
- TOC:DET	1	16.93	1524.10	188.24
- TOC:SLUDGE	1	19.00	1526.17	188.29
- Cl:Temp	1	23.15	1530.32	188.41
- PH:SLUDGE	1	41.34	1548.51	188.89
- Temp:PH	1	60.88	1568.05	189.40
- Cl:SLUDGE	1	68.19	1575.35	189.60
<none>			1507.17	189.78
- Temp:DET	1	79.92	1587.09	189.90
+ Temp:SLUDGE	1	0.14	1507.03	191.78
- Cl:PH	1	166.88	1674.05	192.09
- Cl:DET	1	216.02	1723.19	193.27
- DET:SLUDGE	1	245.22	1752.38	193.96

Step: AIC= 187.78

HAA ~ Cl + TOC + Temp + PH + DET + SLUDGE + Cl:TOC + Cl:Temp + Cl:PH + Cl:DET + Cl:SLUDGE + TOC:Temp + TOC:PH + TOC:DET + TOC:SLUDGE + Temp:PH + Temp:DET + PH:SLUDGE + DET:SLUDGE

	Df	Sum of Sq	RSS	AIC
- Cl:TOC	1	0.31	1507.56	185.79
- TOC:PH	1	8.79	1516.04	186.02
- TOC:Temp	1	9.16	1516.41	186.03
- TOC:DET	1	17.21	1524.45	186.25
- TOC:SLUDGE	1	19.59	1526.84	186.31
- Cl:Temp	1	23.11	1530.35	186.41
- PH:SLUDGE	1	56.38	1563.62	187.29
- Cl:SLUDGE	1	68.77	1576.02	187.61
- Temp:PH	1	71.41	1578.66	187.68
<none>			1507.25	187.78
- Temp:DET	1	93.58	1600.83	188.25
+ PH:DET	1	0.08	1507.17	189.78
+ Temp:SLUDGE	1	0.05	1507.20	189.78
- Cl:PH	1	174.35	1681.60	190.27
- Cl:DET	1	225.82	1733.07	191.51
- DET:SLUDGE	1	282.18	1789.43	192.82

Step: AIC= 185.79

HAA ~ Cl + TOC + Temp + PH + DET + SLUDGE + Cl:Temp + Cl:PH + Cl:DET + Cl:SLUDGE + TOC:Temp + TOC:PH + TOC:DET + TOC:SLUDGE + Temp:PH + Temp:DET + PH:SLUDGE + DET:SLUDGE

	Df	Sum of Sq	RSS	AIC
- TOC:PH	1	8.75	1516.31	184.03
- TOC:Temp	1	9.19	1516.75	184.04
- TOC:DET	1	18.68	1526.24	184.30

- TOC:SLUDGE	1	21.92	1529.48	184.38
- Cl:Temp	1	26.26	1533.82	184.50
- PH:SLUDGE	1	59.71	1567.26	185.38
- Temp:PH	1	71.71	1579.27	185.70
<none>			1507.56	185.79
- Temp:DET	1	112.62	1620.18	186.75
- Cl:SLUDGE	1	147.72	1655.28	187.62
+ Cl:TOC	1	0.31	1507.25	187.78
+ PH:DET	1	0.12	1507.44	187.79
+ Temp:SLUDGE	1	0.01	1507.54	187.79
- Cl:PH	1	182.98	1690.54	188.49
- Cl:DET	1	233.26	1740.82	189.69
- DET:SLUDGE	1	310.61	1818.16	191.47

Step: AIC= 184.03

HAA ~ Cl + TOC + Temp + PH + DET + SLUDGE + Cl:Temp +  
Cl:PH + Cl:DET + Cl:SLUDGE + TOC:Temp + TOC:DET +  
TOC:SLUDGE + Temp:PH + Temp:DET + PH:SLUDGE + DET:SLUDGE

	Df	Sum of Sq	RSS	AIC
- TOC:Temp	1	20.64	1536.95	182.58
- TOC:SLUDGE	1	29.22	1545.53	182.81
- Cl:Temp	1	32.22	1548.53	182.89
- TOC:DET	1	37.69	1553.99	183.04
- PH:SLUDGE	1	72.28	1588.59	183.94
<none>			1516.31	184.03
- Temp:PH	1	82.52	1598.83	184.20
- Temp:DET	1	108.86	1625.16	184.87
- Cl:SLUDGE	1	144.59	1660.89	185.76
+ TOC:PH	1	8.75	1507.56	185.79
+ PH:DET	1	2.53	1513.78	185.96
+ Temp:SLUDGE	1	2.31	1513.99	185.97
+ Cl:TOC	1	0.27	1516.04	186.02
- Cl:PH	1	189.93	1706.24	186.87
- Cl:DET	1	310.22	1826.53	189.66
- DET:SLUDGE	1	311.87	1828.18	189.70

Step: AIC= 182.58

HAA ~ Cl + TOC + Temp + PH + DET + SLUDGE + Cl:Temp +  
Cl:PH + Cl:DET + Cl:SLUDGE + TOC:DET + TOC:SLUDGE + Temp:PH  
+ Temp:DET + PH:SLUDGE + DET:SLUDGE

	Df	Sum of Sq	RSS	AIC
- Cl:Temp	1	28.93	1565.88	181.35
- PH:SLUDGE	1	59.58	1596.53	182.14
- TOC:SLUDGE	1	61.85	1598.80	182.20
- Temp:PH	1	69.71	1606.66	182.40

<none>			1536.95	182.58
- Temp:DET	1	89.10	1626.05	182.89
- TOC:DET	1	92.27	1629.22	182.97
+ TOC:Temp	1	20.64	1516.31	184.03
+ TOC:PH	1	20.20	1516.75	184.04
+ PH:DET	1	5.98	1530.97	184.42
+ Temp:SLUDGE	1	2.73	1534.22	184.51
+ Cl:TOC	1	1.74	1535.21	184.54
- Cl:PH	1	175.03	1711.98	185.01
- Cl:SLUDGE	1	215.75	1752.70	185.97
- Cl:DET	1	300.84	1837.79	187.91
- DET:SLUDGE	1	317.06	1854.01	188.27

Step: AIC= 181.35

HAA ~ Cl + TOC + Temp + PH + DET + SLUDGE + Cl:PH + Cl:DET  
+ Cl:SLUDGE + TOC:DET + TOC:SLUDGE + Temp:PH + Temp:DET +  
PH:SLUDGE + DET:SLUDGE

	Df	Sum of Sq	RSS	AIC
- PH:SLUDGE	1	44.35	1610.23	180.49
- Temp:PH	1	68.66	1634.54	181.11
- Temp:DET	1	74.27	1640.15	181.25
<none>			1565.88	181.35
- TOC:SLUDGE	1	88.85	1654.73	181.61
- TOC:DET	1	108.68	1674.55	182.10
+ Cl:Temp	1	28.93	1536.95	182.58
+ TOC:PH	1	26.25	1539.63	182.65
+ TOC:Temp	1	17.35	1548.53	182.89
+ Cl:TOC	1	11.85	1554.03	183.04
- Cl:PH	1	149.50	1715.37	183.09
+ PH:DET	1	5.54	1560.34	183.20
+ Temp:SLUDGE	1	0.66	1565.21	183.33
- Cl:SLUDGE	1	221.69	1787.57	184.78
- Cl:DET	1	284.84	1850.72	186.20
- DET:SLUDGE	1	329.65	1895.53	187.18

Step: AIC= 180.49

HAA ~ Cl + TOC + Temp + PH + DET + SLUDGE + Cl:PH + Cl:DET  
+ Cl:SLUDGE + TOC:DET + TOC:SLUDGE + Temp:PH + Temp:DET +  
DET:SLUDGE

	Df	Sum of Sq	RSS	AIC
- Temp:PH	1	41.94	1652.16	179.55
- Temp:DET	1	53.30	1663.53	179.83
<none>			1610.23	180.49
- TOC:SLUDGE	1	108.83	1719.06	181.17
- Cl:PH	1	109.94	1720.17	181.20

+ PH:SLUDGE	1	44.35	1565.88	181.35
+ TOC:PH	1	32.06	1578.16	181.67
+ PH:DET	1	29.76	1580.46	181.73
+ Cl:Temp	1	13.70	1596.53	182.14
- TOC:DET	1	149.94	1760.17	182.14
+ TOC:Temp	1	7.55	1602.68	182.30
+ Temp:SLUDGE	1	3.32	1606.90	182.41
+ Cl:TOC	1	1.31	1608.92	182.46
- Cl:SLUDGE	1	188.63	1798.85	183.03
- Cl:DET	1	289.86	1900.09	185.28
- DET:SLUDGE	1	301.01	1911.24	185.52

Step: AIC= 179.55

HAA ~ Cl + TOC + Temp + PH + DET + SLUDGE + Cl:PH + Cl:DET  
+ Cl:SLUDGE + TOC:DET + TOC:SLUDGE + Temp:DET + DET:SLUDGE

	Df	Sum of Sq	RSS	AIC
- Temp:DET	1	43.37	1695.53	178.61
<none>			1652.16	179.55
- Cl:PH	1	89.65	1741.81	179.71
+ Temp:PH	1	41.94	1610.23	180.49
+ TOC:PH	1	35.94	1616.23	180.65
- TOC:SLUDGE	1	135.40	1787.57	180.78
+ PH:SLUDGE	1	17.63	1634.54	181.11
+ Cl:Temp	1	17.01	1635.15	181.12
+ Temp:SLUDGE	1	8.74	1643.42	181.33
+ Cl:TOC	1	4.94	1647.22	181.42
+ TOC:Temp	1	3.34	1648.83	181.46
+ PH:DET	1	2.90	1649.26	181.47
- TOC:DET	1	184.38	1836.54	181.88
- Cl:SLUDGE	1	207.47	1859.63	182.40
- Cl:DET	1	261.91	1914.07	183.58
- DET:SLUDGE	1	356.92	2009.08	185.57

Step: AIC= 178.61

HAA ~ Cl + TOC + Temp + PH + DET + SLUDGE + Cl:PH + Cl:DET  
+ Cl:SLUDGE + TOC:DET + TOC:SLUDGE + DET:SLUDGE

	Df	Sum of Sq	RSS	AIC
- Cl:PH	1	83.4	1779.0	178.6
<none>			1695.5	178.6
- TOC:SLUDGE	1	104.6	1800.1	179.1
+ Temp:DET	1	43.4	1652.2	179.5
+ Temp:PH	1	32.0	1663.5	179.8
+ TOC:PH	1	11.3	1684.2	180.3
+ Cl:Temp	1	10.2	1685.3	180.4
+ PH:SLUDGE	1	8.7	1686.9	180.4

+ PH:DET	1	2.4	1693.2	180.6
+ Cl:TOC	1	2.3	1693.2	180.6
+ TOC:Temp	1	2.2	1693.3	180.6
+ Temp:SLUDGE	1	1.7	1693.8	180.6
- TOC:DET	1	185.3	1880.8	180.9
- Cl:SLUDGE	1	195.7	1891.2	181.1
- Cl:DET	1	262.0	1957.5	182.5
- DET:SLUDGE	1	331.4	2026.9	183.9
- Temp	1	1500.8	3196.3	202.6

Step: AIC= 178.58

HAA ~ Cl + TOC + Temp + PH + DET + SLUDGE + Cl:DET + Cl:SLUDGE + TOC:DET + TOC:SLUDGE + DET:SLUDGE

	Df	Sum of Sq	RSS	AIC
- PH	1	64.4	1843.4	178.0
<none>			1779.0	178.6
+ Cl:PH	1	83.4	1695.5	178.6
- TOC:SLUDGE	1	127.0	1906.0	179.4
+ Temp:DET	1	37.1	1741.8	179.7
+ Temp:PH	1	22.6	1756.3	180.1
- Cl:SLUDGE	1	160.3	1939.3	180.1
+ Temp:SLUDGE	1	4.8	1774.2	180.5
+ TOC:PH	1	2.9	1776.0	180.5
+ PH:SLUDGE	1	1.2	1777.7	180.6
+ Cl:Temp	1	1.2	1777.8	180.6
+ PH:DET	1	1.1	1777.9	180.6
+ Cl:TOC	1	0.3	1778.6	180.6
+ TOC:Temp	1	0.3	1778.6	180.6
- TOC:DET	1	273.1	2052.1	182.4
- Cl:DET	1	284.0	2063.0	182.7
- DET:SLUDGE	1	295.4	2074.4	182.9
- Temp	1	1428.8	3207.8	200.8

Step: AIC= 178.04

HAA ~ Cl + TOC + Temp + DET + SLUDGE + Cl:DET + Cl:SLUDGE + TOC:DET + TOC:SLUDGE + DET:SLUDGE

	Df	Sum of Sq	RSS	AIC
<none>			1843.4	178.0
+ PH	1	64.4	1779.0	178.6
+ Temp:DET	1	51.2	1792.2	178.9
+ TOC:Temp	1	9.7	1833.6	179.8
+ Cl:Temp	1	9.2	1834.2	179.8
+ Cl:TOC	1	5.3	1838.1	179.9
+ Temp:SLUDGE	1	5.1	1838.2	179.9
- TOC:SLUDGE	1	203.8	2047.2	180.3

```

- Cl:SLUDGE      1      210.1 2053.5 180.5
- Cl:DET         1      241.8 2085.2 181.1
- TOC:DET       1      284.2 2127.6 181.9
- DET:SLUDGE    1      482.3 2325.7 185.6
- Temp          1     1545.3 3388.6 201.0
>
> # Demonstrate significance of the interaction terms
> m4 <- lm(HAA~Cl+TOC+Temp+PH+DET+SLUDGE, data=d1)
> m5 <- step(m4,direction="both")
Start: AIC= 190.64
      HAA ~ Cl + TOC + Temp + PH + DET + SLUDGE

              Df Sum of Sq      RSS      AIC
- SLUDGE     1          10.8 3057.7 188.8
<none>                               3046.8 190.6
- DET        1         216.9 3263.7 191.5
- Cl         1         219.6 3266.5 191.5
- TOC        1         239.2 3286.0 191.7
- PH         1         305.8 3352.6 192.6
- Temp       1        1770.2 4817.1 207.4

Step: AIC= 188.79
      HAA ~ Cl + TOC + Temp + PH + DET

              Df Sum of Sq      RSS      AIC
<none>                               3057.7 188.8
- DET        1         223.2 3280.9 189.7
- Cl         1         238.4 3296.1 189.9
- TOC        1         253.6 3311.3 190.1
- PH         1         295.0 3352.7 190.6
+ SLUDGE     1          10.8 3046.8 190.6
- Temp       1        1759.9 4817.5 205.4
> anova(m5,update(m3,~.+PH))
Analysis of Variance Table

Model 1: HAA ~ Cl + TOC + Temp + PH + DET
Model 2: HAA ~ Cl + TOC + Temp + DET + SLUDGE + PH + Cl:DET
+ Cl:SLUDGE + TOC:DET + TOC:SLUDGE + DET:SLUDGE
  Res.Df    RSS Df Sum of Sq      F Pr(>F)
1       35 3057.7
2       29 1779.0  6    1278.7 3.4742 0.01038 *
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 '
' 1
>
> # Summarizes the ideal model
> summary(m3)

```



Call:

```
lm(formula = HAA ~ Cl + TOC + Temp + DET + SLUDGE + Cl:DET  
+ Cl:SLUDGE + TOC:DET + TOC:SLUDGE + DET:SLUDGE, data = dl)
```

Residuals:

	Min	1Q	Median	3Q	Max
	-12.7329	-4.1254	0.4048	3.3377	20.4792

Coefficients:

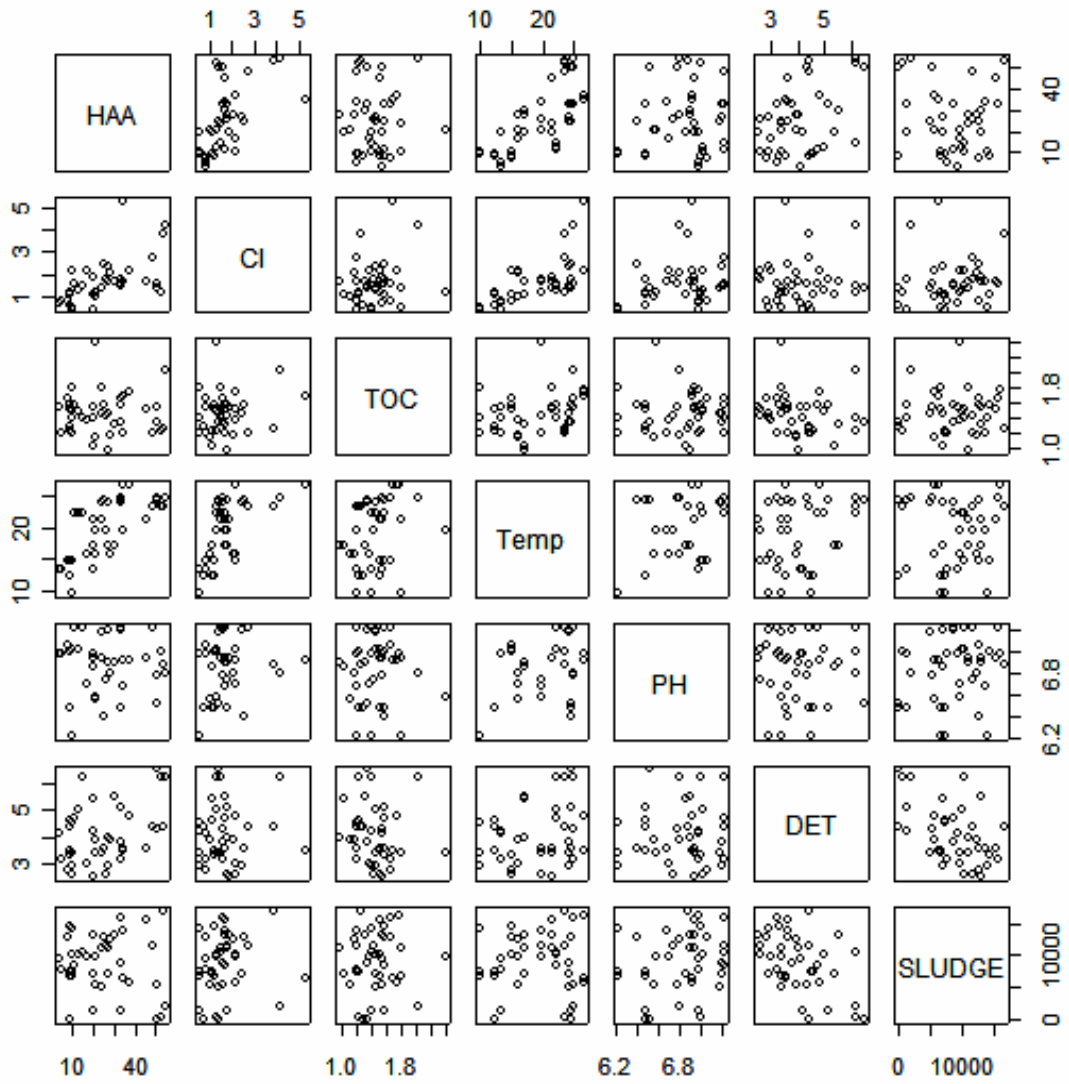
	Estimate	Std. Error	t value	Pr(> t )	
(Intercept)	-1.663e+02	7.391e+01	-2.250	0.03196	*
Cl	-2.256e+01	9.647e+00	-2.339	0.02621	*
TOC	1.113e+02	5.060e+01	2.199	0.03570	*
Temp	1.873e+00	3.734e-01	5.015	2.23e-05	***
DET	2.887e+01	1.190e+01	2.425	0.02153	*
SLUDGE	9.303e-03	4.487e-03	2.073	0.04681	*
Cl:DET	4.918e+00	2.479e+00	1.984	0.05651	.
Cl:SLUDGE	6.193e-04	3.349e-04	1.849	0.07433	.
TOC:DET	-2.046e+01	9.515e+00	-2.151	0.03969	*
TOC:SLUDGE	-4.849e-03	2.663e-03	-1.821	0.07858	.
DET:SLUDGE	-8.717e-04	3.111e-04	-2.802	0.00881	**

---

Signif. codes: 0 '\*\*\*' 0.001 '\*\*' 0.01 '\*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 7.839 on 30 degrees of freedom  
Multiple R-Squared: 0.7972, Adjusted R-squared: 0.7297  
F-statistic: 11.8 on 10 and 30 DF, p-value: 6.717e-08

APPENDIX B FIGURE 1 HAA5 Pairwise Plot



## APPENDIX C: R code for TTHM model with ClO<sub>2</sub>

```
#R Code for TTHM model with ClO2
> # Read data
> d <- read.csv("hunter-indicator.csv")
>
> # Select variables from each basin
> attach(d)
>
> # Rear HAA
> # Rear THM
> # Front Cl
> # Front TOC
>
> t1 <-
data.frame(basin=rep(1,14),HAA=R1HAA,THM=R1THM,ClO2=ClO2,Cl
=F1Cl,TOC=F1TOC,Temp=Temp,PH=P1H,DET=D1ET,SLUDGE=S1ludge,
time=1:14)
>
> t2 <-
data.frame(basin=rep(2,14),HAA=R2HAA,THM=R2THM,ClO2=ClO2,Cl
=F2Cl,TOC=F2TOC,Temp=Temp,PH=P2H,DET=D2ET,SLUDGE=S2ludge,
time=1:14)
>
> t3 <-
data.frame(basin=rep(3,14),HAA=R3HAA,THM=R3THM,ClO2=ClO2,Cl
=F3Cl,TOC=F3TOC,Temp=Temp,PH=P3H,DET=D3ET,SLUDGE=S3ludge,
time=1:14)
>
> detach(d)
>
> # Stack data and format it into a single data set with a
column for basin
> d1 <- rbind(t1,t2,t3)
> rownames(d1) <- 1:NROW(d1)
> d1$basin <- as.factor(d1$basin)
>
> #> names(d1)
> # [1] "Basin" "Haa" "Thm" "Clo2" "Cl" "Toc"
"Temp" "Ph"
> # [9] "Det" "Sludge" "Time"
>
> # Visualize all factors that may influence Haa
> pairs(d1[,-c(1,2,11)])
>
> # Fit full model, including basin
```

```

> m0 <- lm(THM~basin + ClO2 + Cl + TOC + Temp + PH + DET +
SLUDGE +
# main effects
+ I(Cl^2) + I(Temp^2) +
# quadratic effects
+ ClO2:Cl + ClO2:TOC + ClO2:Temp + ClO2:PH + ClO2:DET +
ClO2:SLUDGE +
# ClO2 interactions
+ Cl:TOC + Cl:Temp + Cl:PH + Cl:DET + Cl:SLUDGE +
# Cl interactions
+ TOC:Temp + TOC:PH + TOC:DET + TOC:SLUDGE +
# TOC interactions
+ Temp:PH + Temp:DET + Temp:SLUDGE +
# Temp interactions
+ PH:DET + PH:SLUDGE +
# PH interactions
+ DET:SLUDGE,
# DET interactions
+ data=d1)
>
> # Refit m0, excluding basin
> m1 <- update(m0, ~ . - basin)
>
> # Demonstrate that basin is not significant
> anova(m0,m1)
Analysis of Variance Table

Model 1: THM ~ basin + ClO2 + Cl + TOC + Temp + PH + DET +
SLUDGE + I(Cl^2) + I(Temp^2) + ClO2:Cl + ClO2:TOC +
ClO2:Temp + ClO2:PH + ClO2:DET + ClO2:SLUDGE + Cl:TOC +
Cl:Temp + Cl:PH + Cl:DET + Cl:SLUDGE + TOC:Temp + TOC:PH +
TOC:DET + TOC:SLUDGE + Temp:PH + Temp:DET + Temp:SLUDGE +
PH:DET + PH:SLUDGE + DET:SLUDGE
Model 2: THM ~ ClO2 + Cl + TOC + Temp + PH + DET + SLUDGE +
I(Cl^2) + I(Temp^2) + ClO2:Cl + ClO2:TOC + ClO2:Temp +
ClO2:PH + ClO2:DET + ClO2:SLUDGE + Cl:TOC + Cl:Temp + Cl:PH
+ Cl:DET + Cl:SLUDGE + TOC:Temp + TOC:PH + TOC:DET +
TOC:SLUDGE + Temp:PH + Temp:DET + Temp:SLUDGE + PH:DET +
PH:SLUDGE + DET:SLUDGE
  Res.Df    RSS Df Sum of Sq      F Pr(>F)
1         8 339.68
2        10 398.60 -2      -58.92 0.6938 0.5274
>
> # AIC selected model for full model with all 2-way
interactions
> m2 <- step(m1,direction="both")
Start:  AIC= 155.25

```

THM ~ ClO2 + Cl + TOC + Temp + PH + DET + SLUDGE + I(Cl^2)  
+ I(Temp^2) + ClO2:Cl + ClO2:TOC + ClO2:Temp + ClO2:PH +  
ClO2:DET + ClO2:SLUDGE + Cl:TOC + Cl:Temp + Cl:PH + Cl:DET  
+ Cl:SLUDGE + TOC:Temp + TOC:PH + TOC:DET + TOC:SLUDGE +  
Temp:PH + Temp:DET + Temp:SLUDGE + PH:DET + PH:SLUDGE +  
DET:SLUDGE

	Df	Sum of Sq	RSS	AIC
- PH:SLUDGE	1	7.34	405.94	154.00
- PH:DET	1	7.68	406.28	154.03
- Cl:TOC	1	11.09	409.69	154.38
- TOC:DET	1	15.55	414.15	154.82
<none>			398.60	155.25
- Cl:DET	1	21.09	419.69	155.36
- Cl:SLUDGE	1	21.10	419.70	155.36
- ClO2:Temp	1	44.21	442.80	157.56
- I(Temp^2)	1	73.54	472.14	160.19
- Temp:SLUDGE	1	76.06	474.66	160.41
- ClO2:Cl	1	77.00	475.60	160.49
- TOC:Temp	1	78.53	477.13	160.62
- TOC:SLUDGE	1	84.13	482.73	161.10
- ClO2:PH	1	90.67	489.27	161.65
- Temp:PH	1	91.28	489.88	161.70
- ClO2:TOC	1	96.46	495.06	162.14
- Cl:PH	1	120.67	519.26	164.09
- TOC:PH	1	129.70	528.30	164.80
- ClO2:SLUDGE	1	143.39	541.99	165.85
- DET:SLUDGE	1	159.31	557.91	167.04
- Temp:DET	1	164.67	563.27	167.43
- ClO2:DET	1	171.72	570.32	167.94
- I(Cl^2)	1	181.52	580.12	168.64
- Cl:Temp	1	264.26	662.86	174.10

Step: AIC= 154

THM ~ ClO2 + Cl + TOC + Temp + PH + DET + SLUDGE + I(Cl^2)  
+ I(Temp^2) + ClO2:Cl + ClO2:TOC + ClO2:Temp + ClO2:PH +  
ClO2:DET + ClO2:SLUDGE + Cl:TOC + Cl:Temp + Cl:PH + Cl:DET  
+ Cl:SLUDGE + TOC:Temp + TOC:PH + TOC:DET + TOC:SLUDGE +  
Temp:PH + Temp:DET + Temp:SLUDGE + PH:DET + DET:SLUDGE

	Df	Sum of Sq	RSS	AIC
- TOC:DET	1	16.68	422.61	153.65
- Cl:TOC	1	19.61	425.55	153.93
<none>			405.94	154.00
- PH:DET	1	25.69	431.63	154.51
- Cl:DET	1	30.25	436.18	154.94
+ PH:SLUDGE	1	7.34	398.60	155.25

- Cl:SLUDGE	1	38.41	444.35	155.70
- ClO2:Temp	1	39.50	445.44	155.81
- TOC:Temp	1	71.33	477.27	158.63
- ClO2:Cl	1	71.78	477.72	158.67
- I(Temp^2)	1	72.40	478.34	158.73
- TOC:SLUDGE	1	77.67	483.60	159.18
- Temp:SLUDGE	1	80.74	486.68	159.44
- ClO2:PH	1	83.40	489.33	159.66
- Temp:PH	1	85.03	490.97	159.79
- ClO2:TOC	1	90.31	496.25	160.23
- Cl:PH	1	114.67	520.60	162.20
- TOC:PH	1	123.03	528.96	162.85
- ClO2:SLUDGE	1	145.94	551.87	164.59
- DET:SLUDGE	1	151.98	557.92	165.04
- ClO2:DET	1	165.80	571.74	166.04
- Temp:DET	1	174.35	580.28	166.65
- I(Cl^2)	1	174.62	580.56	166.67
- Cl:Temp	1	263.68	669.62	172.52

Step: AIC= 153.65

THM ~ ClO2 + Cl + TOC + Temp + PH + DET + SLUDGE + I(Cl^2)  
+ I(Temp^2) + ClO2:Cl + ClO2:TOC + ClO2:Temp + ClO2:PH +  
ClO2:DET + ClO2:SLUDGE + Cl:TOC + Cl:Temp + Cl:PH + Cl:DET  
+ Cl:SLUDGE + TOC:Temp + TOC:PH + TOC:SLUDGE + Temp:PH +  
Temp:DET + Temp:SLUDGE + PH:DET + DET:SLUDGE

	Df	Sum of Sq	RSS	AIC
- Cl:TOC	1	11.76	434.37	152.77
- PH:DET	1	13.42	436.03	152.93
- Cl:DET	1	14.36	436.97	153.02
<none>			422.61	153.65
- ClO2:Temp	1	23.71	446.32	153.89
+ TOC:DET	1	16.68	405.94	154.00
+ PH:SLUDGE	1	8.46	414.15	154.82
- Cl:SLUDGE	1	36.49	459.11	155.04
- TOC:Temp	1	54.71	477.32	156.64
- I(Temp^2)	1	66.19	488.81	157.61
- Temp:SLUDGE	1	69.16	491.78	157.86
- ClO2:TOC	1	73.80	496.42	158.25
- TOC:SLUDGE	1	74.04	496.66	158.27
- ClO2:Cl	1	74.32	496.93	158.29
- ClO2:PH	1	82.90	505.52	158.99
- Temp:PH	1	89.84	512.46	159.55
- Cl:PH	1	102.77	525.38	160.57
- TOC:PH	1	112.98	535.59	161.36
- DET:SLUDGE	1	136.90	559.52	163.15
- ClO2:SLUDGE	1	138.68	561.29	163.28

```

- ClO2:DET      1      157.77 580.38 164.65
- Temp:DET      1      161.30 583.91 164.90
- I(Cl^2)       1      164.85 587.47 165.15
- Cl:Temp       1      268.70 691.31 171.83

```

Step: AIC= 152.77

```

THM ~ ClO2 + Cl + TOC + Temp + PH + DET + SLUDGE + I(Cl^2)
+ I(Temp^2) + ClO2:Cl + ClO2:TOC + ClO2:Temp + ClO2:PH +
ClO2:DET + ClO2:SLUDGE + Cl:Temp + Cl:PH + Cl:DET +
Cl:SLUDGE + TOC:Temp + TOC:PH + TOC:SLUDGE + Temp:PH +
Temp:DET + Temp:SLUDGE + PH:DET + DET:SLUDGE

```

	Df	Sum of Sq	RSS	AIC
<none>			434.37	152.77
- PH:DET	1	23.98	458.35	152.98
- Cl:DET	1	26.10	460.48	153.17
+ PH:SLUDGE	1	14.82	419.55	153.35
- Cl:SLUDGE	1	31.06	465.43	153.61
+ Cl:TOC	1	11.76	422.61	153.65
- ClO2:Temp	1	32.27	466.64	153.71
+ TOC:DET	1	8.83	425.55	153.93
- TOC:SLUDGE	1	63.00	497.37	156.33
- ClO2:Cl	1	70.22	504.59	156.92
- TOC:Temp	1	74.56	508.94	157.27
- I(Temp^2)	1	84.64	519.01	158.07
- ClO2:TOC	1	85.39	519.77	158.13
- ClO2:PH	1	85.98	520.36	158.18
- Temp:SLUDGE	1	96.63	531.01	159.01
- Temp:PH	1	102.20	536.57	159.44
- TOC:PH	1	104.96	539.34	159.65
- Cl:PH	1	105.15	539.52	159.66
- ClO2:SLUDGE	1	130.10	564.47	161.52
- ClO2:DET	1	146.02	580.40	162.66
- Temp:DET	1	152.57	586.94	163.12
- DET:SLUDGE	1	165.31	599.69	164.00
- I(Cl^2)	1	204.30	638.68	166.58
- Cl:Temp	1	289.00	723.37	171.68

>

```

> # Demonstrate significance of the interaction terms,
almost significant at 0.05 (which still
> # think definitely justifies including them in the larger
model)

```

```

> m3 <- lm(THM~ClO2 + Cl + TOC + Temp + PH + DET + SLUDGE +
+ I(Cl^2) + I(Temp^2), data=d1) # main and quadratic
effects included in m2

```

```

> anova(m3,m2)

```

Analysis of Variance Table

```
Model 1: THM ~ ClO2 + Cl + TOC + Temp + PH + DET + SLUDGE +
I(Cl^2) + I(Temp^2)
```

```
Model 2: THM ~ ClO2 + Cl + TOC + Temp + PH + DET + SLUDGE +
I(Cl^2) + I(Temp^2) + ClO2:Cl + ClO2:TOC + ClO2:Temp +
ClO2:PH + ClO2:DET + ClO2:SLUDGE + Cl:Temp + Cl:PH + Cl:DET
+ Cl:SLUDGE + TOC:Temp + TOC:PH + TOC:SLUDGE + Temp:PH +
Temp:DET + Temp:SLUDGE + PH:DET + DET:SLUDGE
```

	Res.Df	RSS	Df	Sum of Sq	F	Pr(>F)
1	31	1903.28				
2	13	434.37	18	1468.91	2.4423	0.05313

---

```
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

>

```
> # One last check to verify basin was not significant
```

```
> anova(m2,update(m2, ~ . + basin))
```

```
Analysis of Variance Table
```

```
Model 1: THM ~ ClO2 + Cl + TOC + Temp + PH + DET + SLUDGE +
I(Cl^2) + I(Temp^2) + ClO2:Cl + ClO2:TOC + ClO2:Temp +
ClO2:PH + ClO2:DET + ClO2:SLUDGE + Cl:Temp + Cl:PH + Cl:DET
+ Cl:SLUDGE + TOC:Temp + TOC:PH + TOC:SLUDGE + Temp:PH +
Temp:DET + Temp:SLUDGE + PH:DET + DET:SLUDGE
```

```
Model 2: THM ~ ClO2 + Cl + TOC + Temp + PH + DET + SLUDGE +
I(Cl^2) + I(Temp^2) + basin + ClO2:Cl + ClO2:TOC +
ClO2:Temp + ClO2:PH + ClO2:DET + ClO2:SLUDGE + Cl:Temp +
Cl:PH + Cl:DET + Cl:SLUDGE + TOC:Temp + TOC:PH + TOC:SLUDGE
+ Temp:PH + Temp:DET + Temp:SLUDGE + PH:DET + DET:SLUDGE
```

	Res.Df	RSS	Df	Sum of Sq	F	Pr(>F)
1	13	434.37				
2	11	411.27	2	23.10	0.309	0.7404

>

```
> # Examine fit of m2 -- some influential points, but not
super serious
```

```
> formula(m2)
```

```
THM ~ ClO2 + Cl + TOC + Temp + PH + DET + SLUDGE + I(Cl^2)
+ I(Temp^2) + ClO2:Cl + ClO2:TOC + ClO2:Temp + ClO2:PH +
ClO2:DET + ClO2:SLUDGE + Cl:Temp + Cl:PH + Cl:DET +
Cl:SLUDGE + TOC:Temp + TOC:PH + TOC:SLUDGE + Temp:PH +
Temp:DET + Temp:SLUDGE + PH:DET + DET:SLUDGE
```

```
> summary(m2)
```

```
Call:
```

```
lm(formula = THM ~ ClO2 + Cl + TOC + Temp + PH + DET +
SLUDGE + I(Cl^2) + I(Temp^2) + ClO2:Cl + ClO2:TOC +
```



C1O2:Temp + C1O2:PH + C1O2:DET + C1O2:SLUDGE + C1:Temp + C1:PH + C1:DET + C1:SLUDGE + TOC:Temp + TOC:PH + TOC:SLUDGE + Temp:PH + Temp:DET + Temp:SLUDGE + PH:DET + DET:SLUDGE, data = d1)

Residuals:

	Min	1Q	Median	3Q	Max
	-9.8848	-1.0433	0.4464	1.5720	6.7949

Coefficients:

	Estimate	Std. Error	t value	Pr(> t )
(Intercept)	-1.531e+03	8.685e+02	-1.763	0.1013
C1O2	-6.770e+02	3.710e+02	-1.825	0.0911 .
C1	-2.285e+02	1.373e+02	-1.664	0.1201
TOC	5.659e+02	3.058e+02	1.851	0.0871 .
Temp	7.587e+01	4.191e+01	1.810	0.0934 .
PH	2.370e+02	1.428e+02	1.660	0.1209
DET	-1.154e+01	5.347e+01	-0.216	0.8325
SLUDGE	8.414e-03	6.132e-03	1.372	0.1932
I(C1^2)	8.907e+00	3.602e+00	2.473	0.0280 *
I(Temp^2)	7.949e-01	4.995e-01	1.592	0.1355
C1O2:C1	1.836e+01	1.266e+01	1.450	0.1709
C1O2:TOC	-6.718e+01	4.202e+01	-1.599	0.1339
C1O2:Temp	-6.361e+00	6.473e+00	-0.983	0.3437
C1O2:PH	1.189e+02	7.412e+01	1.604	0.1327
C1O2:DET	1.315e+01	6.288e+00	2.090	0.0568 .
C1O2:SLUDGE	-3.849e-03	1.951e-03	-1.973	0.0701 .
C1:Temp	-5.001e+00	1.700e+00	-2.941	0.0115 *
C1:PH	3.740e+01	2.109e+01	1.774	0.0995 .
C1:DET	3.191e+00	3.610e+00	0.884	0.3928
C1:SLUDGE	4.768e-04	4.946e-04	0.964	0.3526
TOC:Temp	8.969e+00	6.004e+00	1.494	0.1591
TOC:PH	-9.646e+01	5.442e+01	-1.772	0.0998 .
TOC:SLUDGE	-4.402e-03	3.205e-03	-1.373	0.1929
Temp:PH	-1.423e+01	8.137e+00	-1.749	0.1039
Temp:DET	-2.223e+00	1.040e+00	-2.137	0.0522 .
Temp:SLUDGE	3.216e-04	1.891e-04	1.701	0.1128
PH:DET	7.770e+00	9.172e+00	0.847	0.4122
DET:SLUDGE	-1.374e-03	6.177e-04	-2.224	0.0445 *

---

Signif. codes: 0 '\*\*\*' 0.001 '\*\*' 0.01 '\*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 5.78 on 13 degrees of freedom  
 Multiple R-Squared: 0.9294, Adjusted R-squared: 0.7827  
 F-statistic: 6.335 on 27 and 13 DF, p-value: 0.0005727

## APPENDIX D: R code for HAA5 model with ClO<sub>2</sub>

```
#R Code for HAA5 model with ClO2
> # Read data
> d <- read.csv("hunter-indicator.csv")
>
> # Select variables from each basin
> attach(d)
>
> # Rear HAA
> # Rear THM
> # Front Cl
> # Front TOC
>
> t1 <-
data.frame(basin=rep(1,14),HAA=R1HAA,THM=R1THM,ClO2=ClO2,Cl
=F1Cl,
+
TOC=F1TOC,Temp=Temp,PH=P1H,DET=D1ET,SLUDGE=S1ludge,time=1:1
4)
>
> t2 <-
data.frame(basin=rep(2,14),HAA=R2HAA,THM=R2THM,ClO2=ClO2,Cl
=F2Cl,
+
TOC=F2TOC,Temp=Temp,PH=P2H,DET=D2ET,SLUDGE=S2ludge,time=1:1
4)
>
> t3 <-
data.frame(basin=rep(3,14),HAA=R3HAA,THM=R3THM,ClO2=ClO2,Cl
=F3Cl,
+
TOC=F3TOC,Temp=Temp,PH=P3H,DET=D3ET,SLUDGE=S3ludge,time=1:1
4)
>
> detach(d)
>
> # Stack data and format it into a single data set with a
column for basin
> d1 <- rbind(t1,t2,t3)
> rownames(d1) <- 1:NROW(d1)
> d1$basin <- as.factor(d1$basin)
>
> #> names(d1)
> # [1] "Basin" "Haa" "Thm" "Clo2" "Cl" "Toc"
"Temp" "Ph"
> # [9] "Det" "Sludge" "Time"
```

```

>
> # Visualize all factors that may influence Haa
> pairs(d1[,-c(1,3,11)])
>
> # Fit full model, including basin
> m0 <- lm(HAA~basin + ClO2 + Cl + TOC + Temp + PH + DET +
SLUDGE +
# main effects
+ ClO2:Cl + ClO2:TOC + ClO2:Temp + ClO2:PH + ClO2:DET +
ClO2:SLUDGE + # ClO2 interactions
+ Cl:TOC + Cl:Temp + Cl:PH + Cl:DET + Cl:SLUDGE +
# Cl interactions
+ TOC:Temp + TOC:PH + TOC:DET + TOC:SLUDGE +
# TOC interactions
+ Temp:PH + Temp:DET + Temp:SLUDGE +
# Temp interactions
+ PH:DET + PH:SLUDGE +
# PH interactions
+ DET:SLUDGE,
# DET interactions
+ data=d1)
>
> # Refit m0, excluding basin
> m1 <- update(m0, ~ . - basin)
>
> # Demonstrate that basin is not significant
> anova(m0,m1)
Analysis of Variance Table

Model 1: HAA ~ basin + ClO2 + Cl + TOC + Temp + PH + DET +
SLUDGE + ClO2:Cl + ClO2:TOC + ClO2:Temp + ClO2:PH +
ClO2:DET + ClO2:SLUDGE + Cl:TOC + Cl:Temp + Cl:PH + Cl:DET
+ Cl:SLUDGE + TOC:Temp + TOC:PH + TOC:DET + TOC:SLUDGE +
Temp:PH + Temp:DET + Temp:SLUDGE + PH:DET + PH:SLUDGE +
DET:SLUDGE
Model 2: HAA ~ ClO2 + Cl + TOC + Temp + PH + DET + SLUDGE +
ClO2:Cl + ClO2:TOC + ClO2:Temp + ClO2:PH + ClO2:DET +
ClO2:SLUDGE + Cl:TOC + Cl:Temp + Cl:PH + Cl:DET + Cl:SLUDGE
+ TOC:Temp + TOC:PH + TOC:DET + TOC:SLUDGE + Temp:PH +
Temp:DET + Temp:SLUDGE + PH:DET + PH:SLUDGE + DET:SLUDGE
  Res.Df      RSS Df Sum of Sq      F Pr(>F)
1       10   794.07
2       12 1250.99 -2    -456.92 2.8771 0.1030
>
> # AIC selected model for full model with all 2-way
interactions
> m2 <- step(m1,direction="both")
Start: AIC= 198.14

```

HAA ~ ClO2 + Cl + TOC + Temp + PH + DET + SLUDGE + ClO2:Cl + ClO2:TOC + ClO2:Temp + ClO2:PH + ClO2:DET + ClO2:SLUDGE + Cl:TOC + Cl:Temp + Cl:PH + Cl:DET + Cl:SLUDGE + TOC:Temp + TOC:PH + TOC:DET + TOC:SLUDGE + Temp:PH + Temp:DET + Temp:SLUDGE + PH:DET + PH:SLUDGE + DET:SLUDGE

	Df	Sum of Sq	RSS	AIC
- PH:SLUDGE	1	0.71	1251.70	196.17
- Temp:DET	1	1.34	1252.33	196.19
- Cl:TOC	1	1.63	1252.62	196.20
- TOC:DET	1	1.89	1252.88	196.20
- PH:DET	1	3.02	1254.01	196.24
- Temp:PH	1	7.31	1258.30	196.38
- TOC:SLUDGE	1	9.72	1260.71	196.46
- TOC:PH	1	14.02	1265.01	196.60
- DET:SLUDGE	1	14.27	1265.26	196.61
- Cl:SLUDGE	1	22.93	1273.92	196.89
- Cl:PH	1	23.16	1274.15	196.89
- Cl:Temp	1	23.57	1274.56	196.91
- ClO2:SLUDGE	1	26.55	1277.54	197.00
- Temp:SLUDGE	1	27.76	1278.75	197.04
- ClO2:TOC	1	30.42	1281.41	197.13
- ClO2:PH	1	31.68	1282.67	197.17
<none>			1250.99	198.14
- TOC:Temp	1	67.86	1318.85	198.31
- ClO2:DET	1	88.11	1339.10	198.93
- ClO2:Temp	1	89.10	1340.09	198.96
- ClO2:Cl	1	112.86	1363.85	199.68
- Cl:DET	1	289.98	1540.97	204.69

Step: AIC= 196.17

HAA ~ ClO2 + Cl + TOC + Temp + PH + DET + SLUDGE + ClO2:Cl + ClO2:TOC + ClO2:Temp + ClO2:PH + ClO2:DET + ClO2:SLUDGE + Cl:TOC + Cl:Temp + Cl:PH + Cl:DET + Cl:SLUDGE + TOC:Temp + TOC:PH + TOC:DET + TOC:SLUDGE + Temp:PH + Temp:DET + Temp:SLUDGE + PH:DET + DET:SLUDGE

	Df	Sum of Sq	RSS	AIC
- Temp:DET	1	1.95	1253.64	194.23
- TOC:DET	1	2.06	1253.75	194.23
- Cl:TOC	1	2.39	1254.08	194.24
- PH:DET	1	9.69	1261.38	194.48
- TOC:SLUDGE	1	10.88	1262.57	194.52
- Temp:PH	1	11.44	1263.13	194.54
- DET:SLUDGE	1	13.69	1265.39	194.61
- TOC:PH	1	15.82	1267.52	194.68
- Cl:PH	1	23.08	1274.78	194.92

- Cl:Temp	1	28.32	1280.02	195.08
- Cl:SLUDGE	1	30.63	1282.33	195.16
- ClO2:TOC	1	35.84	1287.54	195.32
- ClO2:SLUDGE	1	40.07	1291.76	195.46
- ClO2:PH	1	45.87	1297.57	195.64
<none>			1251.70	196.17
- Temp:SLUDGE	1	63.69	1315.39	196.20
- TOC:Temp	1	75.55	1327.25	196.57
- ClO2:DET	1	90.07	1341.77	197.01
- ClO2:Temp	1	115.94	1367.64	197.80
+ PH:SLUDGE	1	0.71	1250.99	198.14
- ClO2:Cl	1	153.38	1405.08	198.91
- Cl:DET	1	359.93	1611.63	204.53

Step: AIC= 194.23

HAA ~ ClO2 + Cl + TOC + Temp + PH + DET + SLUDGE + ClO2:Cl + ClO2:TOC + ClO2:Temp + ClO2:PH + ClO2:DET + ClO2:SLUDGE + Cl:TOC + Cl:Temp + Cl:PH + Cl:DET + Cl:SLUDGE + TOC:Temp + TOC:PH + TOC:DET + TOC:SLUDGE + Temp:PH + Temp:SLUDGE + PH:DET + DET:SLUDGE

	Df	Sum of Sq	RSS	AIC
- Cl:TOC	1	1.33	1254.98	192.27
- TOC:DET	1	1.80	1255.44	192.29
- PH:DET	1	7.78	1261.42	192.48
- DET:SLUDGE	1	11.76	1265.40	192.61
- Temp:PH	1	14.64	1268.28	192.71
- TOC:SLUDGE	1	14.71	1268.35	192.71
- TOC:PH	1	16.33	1269.97	192.76
- Cl:PH	1	21.48	1275.12	192.93
- Cl:SLUDGE	1	28.69	1282.33	193.16
- ClO2:TOC	1	34.45	1288.09	193.34
- ClO2:SLUDGE	1	42.46	1296.11	193.60
- Cl:Temp	1	43.16	1296.80	193.62
- ClO2:PH	1	46.68	1300.32	193.73
- Temp:SLUDGE	1	61.90	1315.54	194.21
<none>			1253.64	194.23
- TOC:Temp	1	73.61	1327.26	194.57
- ClO2:Temp	1	114.60	1368.24	195.82
+ Temp:DET	1	1.95	1251.70	196.17
+ PH:SLUDGE	1	1.31	1252.33	196.19
- ClO2:Cl	1	183.40	1437.04	197.83
- ClO2:DET	1	300.04	1553.68	201.03
- Cl:DET	1	360.16	1613.81	202.58

Step: AIC= 192.27

HAA ~ ClO2 + Cl + TOC + Temp + PH + DET + SLUDGE + ClO2:Cl + ClO2:TOC + ClO2:Temp + ClO2:PH + ClO2:DET + ClO2:SLUDGE + Cl:Temp + Cl:PH + Cl:DET + Cl:SLUDGE + TOC:Temp + TOC:PH + TOC:DET + TOC:SLUDGE + Temp:PH + Temp:SLUDGE + PH:DET + DET:SLUDGE

	Df	Sum of Sq	RSS	AIC
- TOC:DET	1	1.02	1255.99	190.31
- PH:DET	1	10.98	1265.96	190.63
- DET:SLUDGE	1	14.13	1269.11	190.73
- Temp:PH	1	19.02	1274.00	190.89
- Cl:PH	1	20.35	1275.33	190.93
- TOC:PH	1	20.36	1275.34	190.93
- TOC:SLUDGE	1	22.46	1277.44	191.00
- ClO2:TOC	1	36.81	1291.79	191.46
- Cl:Temp	1	43.10	1298.08	191.66
- ClO2:SLUDGE	1	51.48	1306.45	191.92
- Cl:SLUDGE	1	54.63	1309.60	192.02
- ClO2:PH	1	59.21	1314.19	192.16
- Temp:SLUDGE	1	61.44	1316.41	192.23
<none>			1254.98	192.27
- TOC:Temp	1	73.49	1328.47	192.61
- ClO2:Temp	1	123.31	1378.29	194.12
+ PH:SLUDGE	1	1.80	1253.18	194.21
+ Cl:TOC	1	1.33	1253.64	194.23
+ Temp:DET	1	0.90	1254.08	194.24
- ClO2:Cl	1	182.22	1437.19	195.83
- ClO2:DET	1	336.10	1591.08	200.00
- Cl:DET	1	370.57	1625.55	200.88

Step: AIC= 190.31

HAA ~ ClO2 + Cl + TOC + Temp + PH + DET + SLUDGE + ClO2:Cl + ClO2:TOC + ClO2:Temp + ClO2:PH + ClO2:DET + ClO2:SLUDGE + Cl:Temp + Cl:PH + Cl:DET + Cl:SLUDGE + TOC:Temp + TOC:PH + TOC:SLUDGE + Temp:PH + Temp:SLUDGE + PH:DET + DET:SLUDGE

	Df	Sum of Sq	RSS	AIC
- PH:DET	1	10.10	1266.09	188.63
- DET:SLUDGE	1	13.42	1269.42	188.74
- TOC:PH	1	19.66	1275.65	188.94
- Cl:PH	1	19.79	1275.79	188.95
- Temp:PH	1	23.51	1279.51	189.07
- Cl:Temp	1	42.46	1298.45	189.67
- ClO2:TOC	1	46.52	1302.52	189.80
- TOC:SLUDGE	1	46.61	1302.60	189.80
- ClO2:SLUDGE	1	55.45	1311.45	190.08
- Cl:SLUDGE	1	62.32	1318.31	190.29

<none>			1255.99	190.31
- ClO2:PH	1	63.84	1319.83	190.34
- Temp:SLUDGE	1	79.92	1335.91	190.84
- TOC:Temp	1	91.37	1347.36	191.19
+ PH:SLUDGE	1	1.75	1254.24	192.25
+ TOC:DET	1	1.02	1254.98	192.27
+ Temp:DET	1	0.99	1255.00	192.27
+ Cl:TOC	1	0.55	1255.44	192.29
- ClO2:Temp	1	133.03	1389.02	192.43
- ClO2:Cl	1	181.81	1437.80	193.85
- Cl:DET	1	393.30	1649.30	199.48
- ClO2:DET	1	424.64	1680.64	200.25

Step: AIC= 188.63

HAA ~ ClO2 + Cl + TOC + Temp + PH + DET + SLUDGE + ClO2:Cl + ClO2:TOC + ClO2:Temp + ClO2:PH + ClO2:DET + ClO2:SLUDGE + Cl:Temp + Cl:PH + Cl:DET + Cl:SLUDGE + TOC:Temp + TOC:PH + TOC:SLUDGE + Temp:PH + Temp:SLUDGE + DET:SLUDGE

	Df	Sum of Sq	RSS	AIC
- DET:SLUDGE	1	9.37	1275.46	186.94
- Cl:PH	1	10.29	1276.38	186.97
- TOC:PH	1	10.97	1277.06	186.99
- Temp:PH	1	23.09	1289.18	187.38
- ClO2:TOC	1	40.40	1306.49	187.92
- TOC:SLUDGE	1	48.70	1314.79	188.18
- ClO2:PH	1	53.76	1319.85	188.34
- ClO2:SLUDGE	1	57.38	1323.47	188.45
- Cl:Temp	1	57.83	1323.92	188.47
<none>			1266.09	188.63
- Cl:SLUDGE	1	73.32	1339.41	188.94
- TOC:Temp	1	83.62	1349.71	189.26
- Temp:SLUDGE	1	105.69	1371.78	189.92
+ PH:DET	1	10.10	1255.99	190.31
+ PH:SLUDGE	1	10.01	1256.08	190.31
- ClO2:Temp	1	122.94	1389.03	190.43
+ Cl:TOC	1	3.34	1262.76	190.53
+ Temp:DET	1	0.42	1265.67	190.62
+ TOC:DET	1	0.13	1265.96	190.63
- ClO2:Cl	1	187.31	1453.40	192.29
- Cl:DET	1	388.64	1654.73	197.61
- ClO2:DET	1	414.57	1680.66	198.25

Step: AIC= 186.94

HAA ~ ClO2 + Cl + TOC + Temp + PH + DET + SLUDGE + ClO2:Cl + ClO2:TOC + ClO2:Temp + ClO2:PH + ClO2:DET + ClO2:SLUDGE + Cl:Temp + Cl:PH + Cl:DET + Cl:SLUDGE + TOC:Temp + TOC:PH +

TOC:SLUDGE + Temp:PH + Temp:SLUDGE

	Df	Sum of Sq	RSS	AIC
- Cl:PH	1	6.17	1281.63	185.14
- TOC:PH	1	39.91	1315.37	186.20
- Cl:Temp	1	58.39	1333.86	186.77
<none>			1275.46	186.94
- Temp:PH	1	63.97	1339.43	186.94
- Cl:SLUDGE	1	64.00	1339.47	186.94
- ClO2:SLUDGE	1	69.49	1344.96	187.11
- ClO2:TOC	1	82.76	1358.22	187.51
+ DET:SLUDGE	1	9.37	1266.09	188.63
+ PH:DET	1	6.05	1269.42	188.74
+ Cl:TOC	1	5.21	1270.25	188.77
+ PH:SLUDGE	1	4.87	1270.59	188.78
+ Temp:DET	1	2.14	1273.33	188.87
+ TOC:DET	1	0.01	1275.45	188.94
- Temp:SLUDGE	1	133.17	1408.63	189.01
- ClO2:PH	1	157.54	1433.00	189.71
- TOC:Temp	1	185.22	1460.68	190.50
- TOC:SLUDGE	1	189.99	1465.45	190.63
- ClO2:Cl	1	247.70	1523.16	192.21
- ClO2:Temp	1	271.57	1547.03	192.85
- ClO2:DET	1	476.61	1752.07	197.95
- Cl:DET	1	1035.95	2311.41	209.31

Step: AIC= 185.14

HAA ~ ClO2 + Cl + TOC + Temp + PH + DET + SLUDGE + ClO2:Cl  
 + ClO2:TOC + ClO2:Temp + ClO2:PH + ClO2:DET + ClO2:SLUDGE +  
 Cl:Temp + Cl:DET + Cl:SLUDGE + TOC:Temp + TOC:PH +  
 TOC:SLUDGE + Temp:PH + Temp:SLUDGE

	Df	Sum of Sq	RSS	AIC
- TOC:PH	1	50.38	1332.02	184.72
<none>			1281.63	185.14
- Cl:SLUDGE	1	70.15	1351.78	185.32
- Cl:Temp	1	78.15	1359.78	185.56
- ClO2:SLUDGE	1	78.59	1360.22	185.57
- ClO2:TOC	1	113.24	1394.87	186.61
- Temp:PH	1	123.45	1405.08	186.91
+ Cl:PH	1	6.17	1275.46	186.94
+ DET:SLUDGE	1	5.25	1276.38	186.97
+ Temp:DET	1	2.08	1279.56	187.07
+ Cl:TOC	1	1.20	1280.43	187.10
+ PH:DET	1	0.51	1281.13	187.12
+ TOC:DET	1	0.09	1281.55	187.13
+ PH:SLUDGE	1	0.01	1281.63	187.13



- Temp:SLUDGE	1	160.28	1441.91	187.97
- ClO2:PH	1	175.18	1456.81	188.39
- TOC:SLUDGE	1	193.06	1474.70	188.89
- TOC:Temp	1	244.44	1526.08	190.29
- ClO2:Cl	1	306.92	1588.55	191.94
- ClO2:Temp	1	318.12	1599.76	192.23
- ClO2:DET	1	524.21	1805.85	197.19
- Cl:DET	1	1082.97	2364.60	208.25

Step: AIC= 184.72

HAA ~ ClO2 + Cl + TOC + Temp + PH + DET + SLUDGE + ClO2:Cl  
+ ClO2:TOC + ClO2:Temp + ClO2:PH + ClO2:DET + ClO2:SLUDGE +  
Cl:Temp + Cl:DET + Cl:SLUDGE + TOC:Temp + TOC:SLUDGE +  
Temp:PH + Temp:SLUDGE

	Df	Sum of Sq	RSS	AIC
- ClO2:SLUDGE	1	62.02	1394.04	184.58
- ClO2:TOC	1	66.49	1398.51	184.71
<none>			1332.02	184.72
- Cl:Temp	1	73.11	1405.13	184.91
+ TOC:PH	1	50.38	1281.63	185.14
- Temp:PH	1	90.18	1422.20	185.40
+ DET:SLUDGE	1	33.75	1298.26	185.66
- Cl:SLUDGE	1	105.73	1437.74	185.85
+ Cl:PH	1	16.65	1315.37	186.20
+ PH:DET	1	16.10	1315.92	186.22
+ PH:SLUDGE	1	8.77	1323.25	186.45
- ClO2:PH	1	128.70	1460.72	186.50
+ Cl:TOC	1	4.51	1327.51	186.58
+ Temp:DET	1	1.12	1330.90	186.68
+ TOC:DET	1	0.002277	1332.02	186.72
- Temp:SLUDGE	1	163.23	1495.25	187.46
- ClO2:Temp	1	267.78	1599.80	190.23
- TOC:SLUDGE	1	269.92	1601.93	190.28
- ClO2:Cl	1	279.90	1611.92	190.54
- TOC:Temp	1	309.29	1641.31	191.28
- ClO2:DET	1	524.74	1856.75	196.33
- Cl:DET	1	1050.34	2382.36	206.55

Step: AIC= 184.58

HAA ~ ClO2 + Cl + TOC + Temp + PH + DET + SLUDGE + ClO2:Cl  
+ ClO2:TOC + ClO2:Temp + ClO2:PH + ClO2:DET + Cl:Temp +  
Cl:DET + Cl:SLUDGE + TOC:Temp + TOC:SLUDGE + Temp:PH +  
Temp:SLUDGE

	Df	Sum of Sq	RSS	AIC
- ClO2:TOC	1	37.82	1431.85	183.68

- Cl:Temp	1	58.03	1452.07	184.25
<none>			1394.04	184.58
+ ClO2:SLUDGE	1	62.02	1332.02	184.72
- Temp:PH	1	88.68	1482.72	185.11
+ DET:SLUDGE	1	37.75	1356.28	185.46
- ClO2:PH	1	103.38	1497.41	185.51
+ TOC:PH	1	33.82	1360.22	185.57
+ Cl:PH	1	25.45	1368.59	185.83
+ PH:DET	1	14.47	1379.57	186.15
+ Cl:TOC	1	11.13	1382.91	186.25
- Cl:SLUDGE	1	138.27	1532.31	186.46
+ Temp:DET	1	2.53	1391.51	186.51
+ TOC:DET	1	1.57	1392.47	186.54
+ PH:SLUDGE	1	0.70	1393.33	186.56
- Temp:SLUDGE	1	143.45	1537.48	186.60
- ClO2:Temp	1	212.06	1606.10	188.39
- TOC:SLUDGE	1	218.29	1612.33	188.55
- ClO2:Cl	1	221.13	1615.16	188.62
- TOC:Temp	1	247.27	1641.31	189.28
- ClO2:DET	1	467.89	1861.92	194.45
- Cl:DET	1	988.60	2382.64	204.56

Step: AIC= 183.68

HAA ~ ClO2 + Cl + TOC + Temp + PH + DET + SLUDGE + ClO2:Cl  
+ ClO2:Temp + ClO2:PH + ClO2:DET + Cl:Temp + Cl:DET +  
Cl:SLUDGE + TOC:Temp + TOC:SLUDGE + Temp:PH + Temp:SLUDGE

	Df	Sum of Sq	RSS	AIC
- Temp:PH	1	64.15	1496.01	183.48
<none>			1431.85	183.68
- Cl:Temp	1	72.24	1504.09	183.70
- ClO2:PH	1	76.22	1508.07	183.81
+ Cl:PH	1	41.38	1390.48	184.48
+ ClO2:TOC	1	37.82	1394.04	184.58
+ DET:SLUDGE	1	34.87	1396.98	184.67
+ ClO2:SLUDGE	1	33.35	1398.51	184.71
+ TOC:DET	1	22.62	1409.23	185.03
+ Temp:DET	1	14.01	1417.84	185.28
+ PH:DET	1	6.60	1425.26	185.49
+ TOC:PH	1	1.27	1430.58	185.64
+ PH:SLUDGE	1	0.40	1431.46	185.67
+ Cl:TOC	1	0.31	1431.54	185.67
- ClO2:Temp	1	174.27	1606.12	186.39
- Temp:SLUDGE	1	174.97	1606.83	186.41
- Cl:SLUDGE	1	183.09	1614.95	186.61
- TOC:SLUDGE	1	234.40	1666.26	187.90
- ClO2:Cl	1	252.79	1684.64	188.35

- TOC:Temp	1	281.82	1713.67	189.05
- ClO2:DET	1	582.34	2014.19	195.67
- Cl:DET	1	1038.11	2469.96	204.03

Step: AIC= 183.48

HAA ~ ClO2 + Cl + TOC + Temp + PH + DET + SLUDGE + ClO2:Cl  
+ ClO2:Temp + ClO2:PH + ClO2:DET + Cl:Temp + Cl:DET +  
Cl:SLUDGE + TOC:Temp + TOC:SLUDGE + Temp:SLUDGE

	Df	Sum of Sq	RSS	AIC
- ClO2:PH	1	12.07	1508.08	181.81
+ Cl:PH	1	87.67	1408.34	183.00
+ DET:SLUDGE	1	72.58	1423.42	183.44
<none>			1496.01	183.48
+ Temp:PH	1	64.15	1431.85	183.68
+ ClO2:SLUDGE	1	40.35	1455.66	184.36
- ClO2:Temp	1	110.21	1606.22	184.39
+ TOC:DET	1	36.52	1459.49	184.46
+ PH:DET	1	21.65	1474.35	184.88
+ ClO2:TOC	1	13.29	1482.72	185.11
+ Temp:DET	1	9.50	1486.51	185.22
+ Cl:TOC	1	3.76	1492.25	185.37
+ TOC:PH	1	0.66	1495.35	185.46
+ PH:SLUDGE	1	0.44	1495.56	185.46
- TOC:SLUDGE	1	191.58	1687.58	186.42
- Temp:SLUDGE	1	226.20	1722.20	187.25
- Cl:Temp	1	265.02	1761.03	188.16
- Cl:SLUDGE	1	265.92	1761.93	188.18
- TOC:Temp	1	316.02	1812.03	189.33
- ClO2:Cl	1	391.96	1887.97	191.02
- ClO2:DET	1	567.49	2063.50	194.66
- Cl:DET	1	1128.31	2624.31	204.52

Step: AIC= 181.81

HAA ~ ClO2 + Cl + TOC + Temp + PH + DET + SLUDGE + ClO2:Cl  
+ ClO2:Temp + ClO2:DET + Cl:Temp + Cl:DET + Cl:SLUDGE +  
TOC:Temp + TOC:SLUDGE + Temp:SLUDGE

	Df	Sum of Sq	RSS	AIC
- PH	1	2.89	1510.97	179.88
+ DET:SLUDGE	1	84.63	1423.45	181.44
<none>			1508.08	181.81
- ClO2:Temp	1	98.19	1606.27	182.39
+ PH:DET	1	32.01	1476.06	182.93
+ TOC:DET	1	29.17	1478.91	183.01
+ ClO2:SLUDGE	1	22.67	1485.40	183.18
+ Cl:PH	1	16.17	1491.91	183.36

+ ClO2:PH	1	12.07	1496.01	183.48
+ Temp:DET	1	10.99	1497.08	183.51
+ ClO2:TOC	1	10.65	1497.42	183.52
+ Cl:TOC	1	7.57	1500.51	183.60
+ TOC:PH	1	1.80	1506.28	183.76
+ PH:SLUDGE	1	0.54	1507.53	183.79
+ Temp:PH	1	0.002942	1508.07	183.81
- TOC:SLUDGE	1	184.07	1692.15	184.53
- Cl:Temp	1	258.89	1766.96	186.30
- Temp:SLUDGE	1	295.11	1803.19	187.13
- TOC:Temp	1	304.23	1812.31	187.34
- Cl:SLUDGE	1	305.59	1813.66	187.37
- ClO2:Cl	1	390.99	1899.07	189.26
- ClO2:DET	1	563.21	2071.28	192.82
- Cl:DET	1	1124.65	2632.73	202.65

Step: AIC= 179.88

HAA ~ ClO2 + Cl + TOC + Temp + DET + SLUDGE + ClO2:Cl + ClO2:Temp + ClO2:DET + Cl:Temp + Cl:DET + Cl:SLUDGE + TOC:Temp + TOC:SLUDGE + Temp:SLUDGE

	Df	Sum of Sq	RSS	AIC
+ DET:SLUDGE	1	87.42	1423.54	179.44
<none>			1510.97	179.88
- ClO2:Temp	1	110.77	1621.74	180.78
+ TOC:DET	1	29.33	1481.64	181.08
+ ClO2:SLUDGE	1	25.07	1485.89	181.20
+ ClO2:TOC	1	12.09	1498.88	181.56
+ Temp:DET	1	11.80	1499.17	181.56
+ Cl:TOC	1	8.47	1502.50	181.65
+ PH	1	2.89	1508.08	181.81
- TOC:SLUDGE	1	182.65	1693.62	182.56
- Cl:Temp	1	296.99	1807.96	185.24
- TOC:Temp	1	302.69	1813.66	185.37
- Cl:SLUDGE	1	373.98	1884.94	186.95
- Temp:SLUDGE	1	384.72	1895.69	187.18
- ClO2:Cl	1	444.71	1955.68	188.46
- ClO2:DET	1	680.91	2191.88	193.14
- Cl:DET	1	1195.47	2706.44	201.78

Step: AIC= 179.44

HAA ~ ClO2 + Cl + TOC + Temp + DET + SLUDGE + ClO2:Cl + ClO2:Temp + ClO2:DET + Cl:Temp + Cl:DET + Cl:SLUDGE + TOC:Temp + TOC:SLUDGE + Temp:SLUDGE + DET:SLUDGE

	Df	Sum of Sq	RSS	AIC
- TOC:SLUDGE	1	18.14	1441.68	177.96

- ClO2:Temp	1	65.97	1489.52	179.30
<none>			1423.54	179.44
- DET:SLUDGE	1	87.42	1510.97	179.88
+ TOC:DET	1	38.39	1385.16	180.32
+ ClO2:SLUDGE	1	27.60	1395.94	180.64
+ ClO2:TOC	1	23.71	1399.83	180.75
+ Temp:DET	1	4.27	1419.27	181.32
+ Cl:TOC	1	0.59	1422.95	181.42
+ PH	1	0.10	1423.45	181.44
- Temp:SLUDGE	1	151.10	1574.64	181.58
- TOC:Temp	1	220.52	1644.06	183.35
- Cl:Temp	1	272.71	1696.26	184.63
- ClO2:Cl	1	348.92	1772.46	186.43
- Cl:SLUDGE	1	373.69	1797.23	187.00
- Cl:DET	1	499.27	1922.82	189.77
- ClO2:DET	1	581.43	2004.97	191.48

Step: AIC= 177.96

HAA ~ ClO2 + Cl + TOC + Temp + DET + SLUDGE + ClO2:Cl + ClO2:Temp + ClO2:DET + Cl:Temp + Cl:DET + Cl:SLUDGE + TOC:Temp + Temp:SLUDGE + DET:SLUDGE

	Df	Sum of Sq	RSS	AIC
- ClO2:Temp	1	57.31	1498.99	177.56
<none>			1441.68	177.96
+ TOC:DET	1	56.50	1385.18	178.32
+ ClO2:TOC	1	31.75	1409.93	179.05
+ ClO2:SLUDGE	1	18.47	1423.21	179.43
+ TOC:SLUDGE	1	18.14	1423.54	179.44
- Temp:SLUDGE	1	134.57	1576.25	179.62
+ Temp:DET	1	3.25	1438.43	179.87
+ Cl:TOC	1	0.33	1441.35	179.95
+ PH	1	0.05	1441.63	179.96
- TOC:Temp	1	202.41	1644.09	181.35
- DET:SLUDGE	1	251.94	1693.62	182.56
- Cl:Temp	1	254.58	1696.26	182.63
- ClO2:Cl	1	339.84	1781.52	184.64
- Cl:SLUDGE	1	365.72	1807.40	185.23
- ClO2:DET	1	572.52	2014.20	189.67
- Cl:DET	1	949.52	2391.19	196.71

Step: AIC= 177.56

HAA ~ ClO2 + Cl + TOC + Temp + DET + SLUDGE + ClO2:Cl + ClO2:DET + Cl:Temp + Cl:DET + Cl:SLUDGE + TOC:Temp + Temp:SLUDGE + DET:SLUDGE

	Df	Sum of Sq	RSS	AIC
--	----	-----------	-----	-----

```

<none>                1498.99  177.56
+ ClO2:Temp           1      57.31 1441.68  177.96
+ TOC:DET             1      40.57 1458.42  178.43
+ Temp:DET            1      20.99 1478.00  178.98
+ ClO2:TOC            1      11.53 1487.46  179.24
- Temp:SLUDGE         1     143.06 1642.05  179.30
+ TOC:SLUDGE          1       9.47 1489.52  179.30
+ Cl:TOC              1       8.32 1490.67  179.33
+ PH                  1       1.66 1497.33  179.51
+ ClO2:SLUDGE         1       0.23 1498.75  179.55
- TOC:Temp            1     153.58 1652.57  179.56
- Cl:Temp             1     270.85 1769.84  182.37
- ClO2:Cl             1     297.93 1796.91  182.99
- DET:SLUDGE          1     304.43 1803.41  183.14
- Cl:SLUDGE           1     411.48 1910.47  185.50
- ClO2:DET            1     515.30 2014.29  187.67
- Cl:DET              1     893.00 2391.98  194.72
>
> # Demonstrate significance of the interaction terms
> m3 <- lm(HAA~ClO2 + Cl + TOC + Temp + DET + SLUDGE,
data=d1) # main effects included in m2
> anova(m3,m2)
Analysis of Variance Table

Model 1: HAA ~ ClO2 + Cl + TOC + Temp + DET + SLUDGE
Model 2: HAA ~ ClO2 + Cl + TOC + Temp + DET + SLUDGE +
ClO2:Cl + ClO2:DET + Cl:Temp + Cl:DET + Cl:SLUDGE +
TOC:Temp + Temp:SLUDGE + DET:SLUDGE
  Res.Df    RSS Df Sum of Sq    F    Pr(>F)
1      34 3234.9
2      26 1499.0  8    1735.9 3.7637 0.004745 **
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
>
> # One last check to verify basin was not significant
> anova(m2,update(m2, ~ . + basin))
Analysis of Variance Table

Model 1: HAA ~ ClO2 + Cl + TOC + Temp + DET + SLUDGE +
ClO2:Cl + ClO2:DET + Cl:Temp + Cl:DET + Cl:SLUDGE +
TOC:Temp + Temp:SLUDGE + DET:SLUDGE
Model 2: HAA ~ ClO2 + Cl + TOC + Temp + DET + SLUDGE +
basin + ClO2:Cl + ClO2:DET + Cl:Temp + Cl:DET + Cl:SLUDGE +
TOC:Temp + Temp:SLUDGE + DET:SLUDGE
  Res.Df    RSS Df Sum of Sq    F    Pr(>F)
1      26 1498.99

```

```

2      24 1399.02  2      99.97 0.8575 0.4368
>
> # Examine fit of m2 -- some influential points, but not
super serious

HAA ~ ClO2 + Cl + TOC + Temp + DET + SLUDGE + ClO2:Cl +
ClO2:DET + Cl:Temp + Cl:DET + Cl:SLUDGE + TOC:Temp +
Temp:SLUDGE + DET:SLUDGE
> summary(m2)

Call:
lm(formula = HAA ~ ClO2 + Cl + TOC + Temp + DET + SLUDGE +
ClO2:Cl + ClO2:DET + Cl:Temp + Cl:DET + Cl:SLUDGE +
TOC:Temp + Temp:SLUDGE + DET:SLUDGE, data = d1)

Residuals:
      Min       1Q   Median       3Q      Max
-14.0690  -2.8883   0.2904   2.9034  17.6785

Coefficients:
              Estimate Std. Error t value Pr(>|t|)
(Intercept) -3.372e+01  5.068e+01  -0.665 0.511707
ClO2          8.230e+01  2.567e+01   3.206 0.003550 **
Cl           -5.838e+01  1.874e+01  -3.115 0.004443 **
TOC          2.959e+01  2.714e+01   1.090 0.285575
Temp         3.600e+00  2.310e+00   1.559 0.131120
DET          1.267e+00  5.250e+00   0.241 0.811171
SLUDGE       3.403e-03  1.589e-03   2.142 0.041718 *
ClO2:Cl      -2.273e+01  9.999e+00  -2.273 0.031511 *
ClO2:DET     -1.080e+01  3.612e+00  -2.990 0.006035 **
Cl:Temp       1.713e+00  7.905e-01   2.167 0.039542 *
Cl:DET        7.604e+00  1.932e+00   3.936 0.000553 ***
Cl:SLUDGE     1.224e-03  4.580e-04   2.672 0.012855 *
TOC:Temp     -2.388e+00  1.463e+00  -1.632 0.114707
Temp:SLUDGE  -1.370e-04  8.695e-05  -1.575 0.127288
DET:SLUDGE   -7.490e-04  3.260e-04  -2.298 0.029865 *
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

```

Residual standard error: 7.593 on 26 degrees of freedom  
Multiple R-Squared: 0.8351, Adjusted R-squared: 0.7464  
F-statistic: 9.407 on 14 and 26 DF, p-value: 6.676e-07

APPENDIX E: Supplemental figures

FIGURE 1 Predicted HAA5 values using chlorine dioxide model when ClO<sub>2</sub> is absent

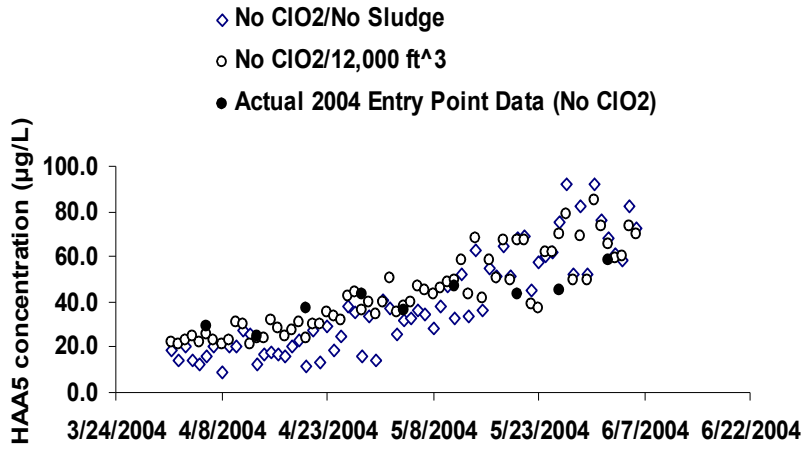
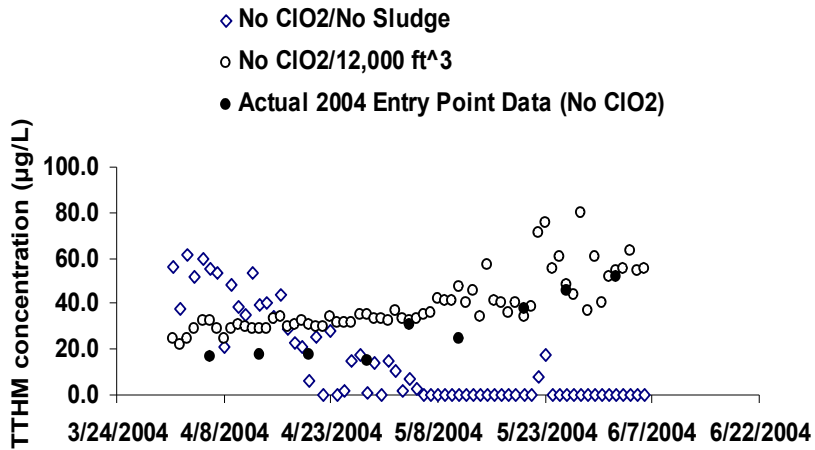


FIGURE 2 Predicted TTHM values using chlorine dioxide model when ClO<sub>2</sub> is absent





## **VITA**

William Hunter Carson was born to Dan and Sandy Carson on February 1<sup>st</sup>, 1978 in Roanoke, Virginia. He attended North Carolina State University in Raleigh, North Carolina where he received a Bachelors of Science in Environmental Sciences in 2000. Hunter began his graduate work in the fall of 2003 at Virginia Polytechnic Institute and State University and received a Masters of Science in Environmental Engineering in 2006.