Effect of Biofiltration on DBP Formation at Full-Scale and Pilot-Scale

by

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Abstract

Over the past century chlorine has been a reliable disinfectant to reduce transmission of waterborne diseases in drinking water. Concerns about chlorination have increased since it was discovered in the 1970s that use of chlorine in drinking water produces trihalomethanes (THMs), when chlorine reacts with natural organic matter (NOM), which has been observed in increased levels in surface water during the past decades. THM and other disinfection by-products (DBPs) such as some of the haloacetic acids (HAAs) and some nitrosamines are considered probable human carcinogens by USEPA.

Since DBPs are still formed even when using alternative disinfectants such as chloramines, treatment processes by which disinfection by-product precursors are removed continue to be studied. Many researchers have demonstrated that the use of pre-ozonation/biological processes in the production of drinking water has the potential to decrease levels of disinfection by-products in finished water more than conventional treatment alone.

Two of the parameters which affect the efficiency of DBP precursor removal in biofilters are filter media and filter flow rate. In this research, the biofiltration process was examined using pilot-scale filters receiving ozonated water to determine the relative effectiveness of these parameters for influencing the removal of natural organic matter. The research presented in this thesis initially focuses on determining the effects of flow rate and filter media including GAC (granular activated carbon) and anthracite on decreasing the levels of THM, HAA and nitrosamine precursors in biologically active filters. In the second part, the performances of full-scale and pilot-scale filters at the Mannheim Water Treatment Plant were compared.

THM and HAA precursor removal was found to decrease when loading rates were increased, likely due to associated shorter contact times in the filters. Also, higher THM and HAA precursor removal was always observed in the GAC filters than in the anthracite filters. However, removal of nitrosamines was not affected by flow rate or the type of filter media.

In general, the pilot-scale filter performance was representative of full-scale filter performance, especially in regards to THM precursor and chlorine demand removal. Statistical evaluation and interpretation of the data for HAA and NDMA precursor removal was more difficult, likely due to the low concentrations of these DBPs which was near their method detection limits (MDLs) and also because of some operational problems with pilot filter #1. Despite these limitations, the results of this study add to the literature concerning the use of different types of media to support biofiltration and reduce DBP precursor concentrations during drinking water treatment.

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List of Abbreviations

%	percent
ANOVA	analysis of variance
AOC	assimiable organic carbon
BAC	biological activated carbon
BDOC	biodegradable dissolved organic carbon
BOM	biodegradable organic matter
Br^-	bromide ion
Br2AA	dibromoacetic acid
Br2ClAA	dibromochloroacetic acid
Br3AA	tribromoacetic acid
BrAA	bromoacetic acid
BrCl2AA	dichlorobromoacetic acid
BrClAA	bromochloroacetic acid
CH2N2	diazomethane
CHBr3	bromoform
CHCl3	chloroform
$CHCl_2Br$	dichlorobromomethane
CHClBr2	dibromochloromethane
Cl^-	chloride ion
Cl2	chlorine

Cl2AA	dichloroacetic acid
Cl3AA	trichloroacetic acid
ClAA	chloroacetic acid
d6-NDMA	deuterated NDMA
DBP	disinfection by-product
DCM	dichloromethane
DMA	dimethylamine
DPD	N, N-diethyl-*p*-phenylenediamine
DWSP	Drinking water Surveillance Program (Ontario Ministry of Environment)
ECD	electron capture detector
FS	full-scale
GAC	Granular activated carbon
GC	gas chromatography
GC/MS	gas chromatograph/Mass spectrometer
H^{++}	hydrogen ion
H2O2	hydrogen peroxide
H2SO4	sulfuric acid
HAA	haloacetic acid
HAA6	total haloacetic acids (5 species)
HAA6	total haloacetic acids (6 species)
HOBr	hypobromous acid

HOCl	hypochlorous acid
HRT	hydraulic retention time
IMAC	interim maximum acceptable concentration
L/m	liters / minute
M Ω cm	mega-ohm centimeter
m/h	meter/ hour
MCL	maximum contaminant limit
MDL	minimum detection limit
Mg	milligram
mg/L	milligrams per liter
ML	million liters
MNNG	1-methyl-3-nitro-1-nitrosoguanidine
MOE	Ontario ministry of environmental
MTBE	Methyl *tert* butyl ether
$Na_2 S_2O_3$	sodium Thiosulfate
$Na_2 SO_4$	sodium Sulfate
NaOCl	sodium hypochlorite
NaOH	sodium hydroxide
NDBA	N-nitrosodibutylamine
NDEA	N-nitrosodiethylamine
NDMA	N-nitrosodimethylamine
ng	nanograms

ng/L	nanograms per Liter
NH_4Cl	ammonium chloride
NMEA	N-nitrosomethylethyl amine
NMOR	N-nitrosomorpholine
NOM	Natural organic matter
NPIP	N-nitrosopiperidine
NPRO	N-nitrosodi-n-propylamine
NPYR	N-nitrosopyrolidine
O_3	ozone
OBr^-	hypobromite ion
OCl^-	hypochlorite ion
$OH^\cdot$	hydroxyl radical
pH	negative logarithm of hydrogen ion concentration
POX	purgable organic halides
ppm	parts per million
PS	pilot-scale
R^2	correlation coefficient
SDS	simulation distribution system
THM	trihalomethane
THMFP	trihalomethane formation potential
TOX	total organic halides
TTHMs	total trihalomethanes

UC	uniformity coefficient
UDMH	1,1-dimethyl hydrazine
USEPA	United States Environmental Protection Agency
UV	ultraviolet
µg	microgram
µg/L	micrograms per liter
µL	microliter

Chapter 1 Introduction

1.1 Background

Since the early days of chlorine disinfection, water quality control criteria and regulations for drinking water have been related mainly to the biological safety parameters and appearance properties of water such as color, taste, and odor. After a Dutch water chemist found in the early 1970s that chlorination of drinking water produced chloroform, numerous researchers followed his work and by the end of the 1970s confirmed trihalomethanes as one of the most important groups of disinfection by-products (DBPs) to be formed due to water chlorination in the presence of NOM (Minear and Amy, 1996).

Some of these DBPs have been recognized as potentially carcinogenic substances. Accordingly, the maximum concentration levels (MCLs) set by the USEPA for TTHM and HAA5 (consisting of monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, dibromoacetic acid) are 80 and 60 μg/L, respectively. As a result, a need to know how to produce microbially safe water with a minimum possibility of formation of disinfection by-products arose.

The first attempts at decreasing DBP formation were focused on adopting an alternative disinfectant such as chloramines or ozone. However, since DBPs are formed by all different kinds of chemical disinfectants in the presence of NOM, and because there are also disadvantages associated with other types of disinfectants (which may include disinfection efficiency or cost, for example, depending on the system being considered), the most

efficient way to control DBPs has been the control and removal of NOM and, therefore, DBP precursors.

It has been demonstrated that the NOM in natural waters, which is comprised of humic acids and fulvic acids (Collins and Amy, 1986), is well removed through granular activated carbon (GAC) filters when operated biologically. In the biofiltration process, microorganisms that are present in water grow and develop into a biofilm on the filter media surface by utilizing organic substances from the water as carbon sources. The combination of pre-ozonation and GAC biofilters has been demonstrated to enhance biodegradable organic matter removal relative to other biofilters as ozone converts NOM into smaller biodegradable compounds (Langlais et al., 1991). A reduction in biodegradable organic matter results in a decrease in the DBP load of finished water and produces a more biologically stable water (Huck et al., 1992; Huck et al., 1994).

1.2 Objective and Scope

The first objective of this research was comparing the performance of the Mannheim Water Treatment Plant pilot-scale filters with its full-scale filters, which have similar types of media but not exactly same physical characteristics, to understand if they perform significantly differently in removing disinfection by-product formation potential. In other words, this research was performed to determine if the pilot filters represent the full-scale filter performance, and it was investigated by measuring the chlorine demand and subsequent disinfection by-products formed, including trihalomethanes (THMs), haloacetic acids (HAAs) and nitrosamines, in filters' influents and effluents. During these experiments, the pilot-scale filters were operated under the same conditions as the full-scale filters, i.e.,

running in biological mode and at similar loading rates, and backwashing with similar protocols. However, the range of loading rates that could be studied at full-scale and, therefore, in the pilot-scale filters was limited depending on the amount of water that Region was allowed to take from the Grand River in different weeks. In addition, different filter media (GAC vs. anthracite) performance was investigated as part of this research.

The second objective was a study focused on the pilot-scale filters to assess the effects of flow rate on the performance of filters containing different types of media for reducing the disinfection by-product formation potential. The aim was to determine the importance of flow rate in selecting an optimal filter media for biological drinking water treatment processes.

1.3 Thesis Organization

Chapter 2 contains a comprehensive review of different studies concerning the formation of disinfection by-products and their precursors in the water treatment industry. Then it reviews the importance and efficiency of different filter media on biofiltration with respect to disinfection by-product removal. Chapter 3 describes the materials and analytical methods used for analytical measurements, and also it explains the experimental details concerning performing the experiments. Chapters 4 and 5 discuss the experimental results and allow us to make several conclusions concerning the two main objectives of this thesis in Chapter 6.

Chapter 2 Literature Review

2.1 Overview

This chapter reviews the occurrence of chlorination and chloramination by-products in drinking water and their health impacts. These studies, consisting of research on disinfection by-product precursors and how biofiltration can remove them, will be considered in this chapter.

2.2 Chlorination, Chloramination By-products in Drinking Water

For over a century, disinfection processes in water treatment have been used with the aim of controlling waterborn diseases by eliminating associated microorganisms. To accomplish disinfection, chlorine is the most common disinfectant that is added to the water at or near the last step of water treatment in public drinking water treatment systems. This should ensure that the presence of a disinfectant residual in water distribution system keeps water free of pathogenic microorganisms.

To chlorinate water, chlorine in the form of chlorine gas, sodium hypochlorite, or calcium hypochlorite is added to water in a water treatment plant. They all hydrolyze and form hypochlorous acid such that HOCl and OCl^- will be produced. It is the HOCl portion of the dissociated acid which is most active and effective as a disinfectant (Hazen and Sawyer, 1992). In addition to inactivating pathogens, chlorine or its HOCl portion of it reacts with natural organic matter and forms specific by-products such as trihalomathanes**,** haloacetic acids, and nitrosamines. The type and the amount of DBPs formed depends on some factors

such as type and dose of disinfectant, contact time, concentration and characteristics of the precursors and water chemistry including pH and bromide (Trussell and Umphres, 1978).

Chloramines are another group of disinfectant for drinking water that has been used increasingly recently. Chloramines are formed by a series of substituting reactions in which HOCl and NH_3 (ammonia) react and Cl^{+1}substitute for H^+ in NH_3. The chloramine species distribution depends on ratio of reactants; however, for disinfection purposes the reaction conditions are controlled to ensure that monochloramine is the dominant species (Hazen and Sawyer, 1992).

Chloramines have lower disinfecting capability than chlorine since Cl^+ bonds strongly in the structure of the chloramine molecule which makes it less reactive than when it is in HOCl (Hazen and Sawyer, 1992). However, interest in using monochloramine in disinfection process is growing because it is recognized as a more stable disinfectant than chlorine, allowing residuals to be maintained for longer periods in drinking water distribution systems, which improves bacterial inactivation (Lechevallier et al., 1996). Also it has been observed that chloramines are less active than HOCl in reaction with natural organic matter leading to disinfection by-product formation. Consequently, they generally produce lower levels of trihalomethanes and halogenated acetic acids (Hazen and Sawyer, 1992; Topudurti and Haas, 1991).

2.2.1 Trihalomethanes (THMs)

2.2.1.1 Occurrence

Trihalomethanes are one of the common and well known DBPs in chlorinated and chloromainated water. According to Kranser et al. (1989), THM was presented as a largest group of DBPs in their study on 35 water treatment plants across the USA. These compounds are formed as a result of reaction of free chlorine or chloramines with bromide and natural organic matters (mainly humic materials) either in the water treatment plant or the water distribution network

There are four trihalomethane comprising THMs: trichloromethane or chloroform $CHCl_3$, bromodichloromethane $CHBrCl_2$, chlorodibromethane $CHClBr_2$, and tribormomethane or bromoform $CHBr_3$. Among these species chloroform was the first DBP identified and studied.

2.2.1.2 Influence of Bromide upon Trihalomethane Speciation

Chlorine is a stronger oxidant than bromide, and when it is in a form of $HOCl/OCl^-$ has the ability of oxidizing bromide (Br^-) to hypobromous acid/hypobromite ion ($HOBr/OBr^-$) in a very fast reaction (White, 1985).HOCl acts as a more effective oxidant while HOBr acts as a more efficient substitution agent, so when bromide-containing waters were chlorinated, oxidation of Br^- to $HOBr/OBr^-$ leads to formation brominated DBP compounds (Luong et al., 1982). As a result, presence of bromide and its concentration affect brominated trihalomethane species formation in chlorinated water.

Amy et al. (1991) reported that a substantial proportion of original bromide (50%) and a low portion of applied chlorine (5-10%) are contributed to form THM-Br and THM-Cl respectively.

Another factor which affects trihalomethane speciation is the ratio of Br^-/DOC. THM precursors, which are measured as dissolved organic carbon (DOC), are removed in activated carbon biofiltration which does not change bromide concentration. Therefore, increasing the ratio of Br^-/DOC in effluent, leads to increased brominated THM fraction in the effluent of the subsequent chlorination process (Amy et al., 1991).

2.2.1.3 Health Effect

Since chloroform is the THM found in the highest concentration, most health concerns are related to it and it has been studied more extensively than the other THMs. Chloroform may be absorbed to the body through ingestion, inhalation or through skin. It can be absorbed through skin during swimming in chlorinated pools or bathing. But the most significant source of exposure to chloroform for human is consumption of chlorinated water. The main health concern about chloroform is because of its carcinogenic potential.

While studies on animals give sufficient evidences of chloroform carcinogenicity and its effect on reproductivity of rats and mice, researches on humans show small increase in

Bladder cancer caused by exposure to chloroform and there is not adequate evidence regarding reproductive or cancer effects on humans (USEPA, 2007).

Acute or short term exposure to higher dosages of chloroform usually causes reversible effects including abnormalities in kidneys or liver and damage of nervous system. Cancer can arise from either acute or chronic exposure (exposure over a long period to low levels of

contaminant; Hazen and Sawyer, 1992). Finding such health impacts for THMs, EPA considers total trihalomethane (TTHM) as EPA's group B2, meaning probable human carcinogen (USEPA, 2007). TTHM maximum contaminant level (MCL) has been set by USEPA as 0.08 mg/L and individual MCL goals are 0.0 mg/L, 0.06 mg/L, and 0.0 mg/L for bromodichloromethane, bromochloromethane, and bromoform respectively (USEPA, 2001).

2.2.2 Halogenated Acetic Acids (HAAs)

2.2.2.1 Occurrence

Halogenated acetic acids are another major group of DBP following THMs in chlorinated chloroaminated drinking water. Kranser et al. (1989) identified HAA as the second significant disinfection by-product fraction among 35 utilities studied across the USA.

Similar to THMs, HAAs are the products of reaction between NOM, chlorine and bromide. There are nine common haloacetic acids, which are obtained by replacing hydrogen atoms of acetic acid with halogen atoms partially or completely. Monochloroacetic acid $CH_2ClCOOH$, monobromoacetic acid $CH_2BrCOOH$, dichloroacetic acid $CHCl_2COOH$, bromochloroacetic acid $CHBrClCOOH$, dibromoacetic acid $CHBr_2COOH$, trichloroacetic acid CCl_3COOH, bromodichloroacetic acid $CBrCl_2COOH$, Chlorodibromoacetic acid $CBr_2ClCOOH$, and tribromoacetic acid CBr_3COOH.

2.2.2.2 Health Effects

HAAs mainly exposure way to human occurs through drinking of chlorinated or chloraminated water. HAAs are very stable in water and they are absorbed into the blood system when water containing HAAs is consumed. More information are available on certain HAA's (such as dichloroacetic acid and trichloroacetic acid) than others. Studies on animals suggest that they can cause risk of cancer but they are not expected to produce acute health effects in the human body at the concentration found in drinking water. However, long term exposure can cause disorder in the brain, nervous system, liver and kidney. EPA classifies dichloro and trichloroacetic acid as likely to be carcinogen in human and group C (possible human carcinogen) due to inadequate data on human and limited evidence of carcinogenicity in animals (USEPA, 2007). As a result, regulation has been established by EPA on five of HAAs including monobromoacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, dibromoacetic acid. MCL of total of these five HAAs in drinking water is 0.06 mg/L. Also individual MCL goal has been established for dichloroacetic acid (0.0 mg/L) and for trichloroacetic acid (0.30 mg/L) (USEPA, 2001).

2.2.3 Nitrosamines

2.2.3.1 Occurrence

Nitrosamines have been found in many food products. However, most of the studies about nitrosamines have been conducted on the nitrosodimethyle amine (NDMA). From 1960s NDMA has been reported in the diet, various meat cures by nitrite, beer, and tobacco smoke (Mitch et al., 2003). According to Mitch et al. (2003), recently NDMA was discovered in the

ground water and drinking water wells adjacent to a rocket engine testing facility in California because of groundwater contamination with rocket fuel. It also appeared in locations where waste water treatment effluent was reused to recharge the aquifer since NDMA forms in chlorinated wastewater as well.

Concerns about NDMA increased when researchers could detect it in drinking water as disinfection (chloramination) by-product due to improved analytical techniques in recent years. Available studies suggest two major mechanisms in NDMA formation. Mitch and Sedlak (2002) described that NDMA formation via nitrosation, which involves nitrosyl cation (formed from nitrite acidification) reaction with ammonia, is not a probable pathway under the conditions present in water and waste water treatment. Instead, they proposed a second mechanism which is NDMA formation via oxidation of unsymmetrical dimethylhydrazine (UDMH) as an intermediate of monochloramine and dimethylamine (DMA) reaction. Choi and Valentine (2001) in their experiments found that for NDMA to be formed monochloramine and DMA as main organic nitrogen- containing precursor must be present.

Chlorination can also form NDMA to some extent when nitrogen precursors present, i.e., natural ammonia and nitrogen containing coagulants must be presented. This was confirmed by the results of surveys conducted in 1998 and 2001 in Canada and USA respectively and showed higher levels of NDMA in chloraminated drinking water systems than chlorinated ones (Mitch et al,. 2003).

In the present research, occurrence of eight nitrosamines including N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine (NDEA), N-nitrosodibutylamine (NDBA), N-nitrosodi-n-

propylamine (NPRO), N-nitrosopiperidine (NPIP), N-nitrosomorpholine (NMOR), N-nitrosopyrolidine (NPYR), and N-nitrosomethylethyl amine (NMEA) were investigated to assess the ability of biological filtration to remove organic nitrogen –containing nitrosamines precursors (including both NOM and amin-containing polymers), and on nitrosamines formation.

2.2.3.2 Health Effects

Nitrosamines are a chemical class recognized as probable human carcinogenic (group B2) by EPA (USEPA, 2007). Their cancer potencies are reported higher than those at trihalomethane (Mitch et al., 2003). This classification is based on animal studies which have shown induction of tumors in liver, kidney, and lungs in mammals exposed to it. There is inadequate human data to show relation between cancer in human and being exposed to nitrosamines; however, short-term effect such as irritated eyes, skin and respiratory tract and chronic effect such as liver and kidney malfunctions have been confirmed (USEPA, 2007).

In 2002 California Department of Health Service established 10ng/L for NDMA as notification level, not as a maximum contaminant level. Canada as a country does not regulate nitrosamines in drinking water, but the Ontario Ministry of the Environment (MOE) set an interim maximum acceptable concentration (IMAC) for NDMA in drinking water of 9ng/L.

2.3 Water Disinfection and Natural Organic Matter (NOM)

Natural waters contain a complex mixture of heterogeneous organic compounds varying in physical and chemical characteristics. Most of these compounds such as humic acid

substances, hydrophilic acids, carbohydrate, amino acids, and carboxylic acids result from decomposition of biological materials (Yavich et al., 2004). Humic acids and fulvic acids are multi component substances, historically considered major organic substances in natural water from a water treatment point of view because of their reaction with chlorine to form disinfection by-products (Collines et al., 1986).

Understanding of reactivity of NOM with disinfectants is very important in controlling disinfection by-products. pH is a parameter which influences NOM and aqueous chlorine reaction by influencing electron distribution of NOM structure as well as chlorine species distribution (Harrington et al., 1996). NOM structural nature is another important factor in chlorination reaction of NOM since the reactivity of NOM molecules with oxidants, such as chlorine, depends on their aromatic rings or aromaticity which, according to several researchers (Peters et al., 1980; Reckhow et al., 1990) comprise 30% of NOM molecules. Rook (1977) and Scully et al. (1988), demonstrated in their studies that organic compounds with electron rich organic structure such as activated aromatic rings strongly react with aqueous electrophil chlorine species. For example, Leenheer et al. (2001) demonstrated that THM and TOX yield significantly increased during chlorination due to phenol structure in natural fulvic acids of their research sample water. The rate and the extent of aqueous chlorine species and NOM reaction depends on chlorine dose and contact time as well. Temperature and presence of bromide or iodide are other variables that can also affect this reaction (Harrington et al., 1996).

NOM in drinking water increases chlorine demand and produces potential carcinogenic halogenated byproducts during disinfection process. Another disadvantage of presence of

NOM in drinking water is that NOM consumes chlorine and makes it unavailable to kill pathogenic microorganisms during disinfection process (Harrington et al., 1996). NOM also increases biological regrowth in distribution system because they act as nutrient for microorganisms to grow. Finally they can impact coagulation process and reduce adsorption performance of filters by blocking pores of granular activated carbon filters. The presence of NOM in drinking water is problematic due to the reasons mentioned and, since conventional water treatment processes fail to remove NOM, other technologies like biofiltration need to be used to remove NOM.

2.4 Biological Drinking Water Treatment

2.4.1 Basic Concepts of Biofiltration

Biological drinking water treatment is a technique in water treatment using a biofiltration process in which living materials (bacteria on the filter) oxidize dissolved organic substances in the water and remove them. In the oxidation reaction which happens, bacteria in drinking water use ambient oxygen in the water to oxidize and utilize carbonaceous organic matter as a substrate and source of nutrients for cell growth and replication. As a result, this fraction of organic matter, which is called the biodegradable organic matter (BOM), is eliminated and will not be available to react with chlorine and form disinfection by-products.

Biological processes for drinking water treatment are often of the biofilm type wherein bacteria cells are present and live as a biofilm community. They are retained in a filter and are attached to the surface of a solid media to grow. Typical carrier media for

microorganisms in drinking water biological treatment are gravel, sand, anthracite, and granular activated carbon (GAC). Sand and anthracite are considered to be nonporous and also inert materials because they do not interact chemically with organic matter. Granular activated carbon is a porous material that initially removes organic precursors through adsorption and then slightly more through biological activity. Once its adsorption capacity is exhausted and a biofilm accumulates, removal is achieved solely through substrate utilization (Camel and Bermond, 1998), and then the GAC will be called biologically activated carbon (BAC) and the process would be called biologically activated carbon filtration.

Studies show that GAC has a higher performance than anthracite and sand (Liu et al., 2001, Wang et al., 1995). This means that higher biomass concentrations accumulate on GAC media, which can be a result of GAC's rough surface. The rough surface and macrospores provide suitable sites in the GAC to protect bacteria from shear forces during filter operation and backwashing and, consequently, causes denser colonization of bacteria to be developed to provide more organic matter utilization (Urfer et al., 1997; Niquette, 1998). It has been also found that the most probable reason for GAC to be significantly more efficient in BOM removal is stronger attractive forces between GAC and bacteria than between bacteria and sand or anthracite, as bacteria have a higher adsorption rate constant on GAC than on sand (Uhl, 2000).

Ozonation effects on biological treatment will be discussed in next section in detail. Briefly, biological treatment following ozonation has these advantages. Natural organic matter is changed to biodegradable dissolved organic carbon (BDOC) during ozonation. These compounds along with assimiable organic carbon (AOC), a part of organic carbon converted

to biomass by specific bacteria and expressed as a carbon concentration (Huck 1990), are responsible for microorganism growth and regrowth in distribution systems. BDOC and AOC are removed during biofiltration following ozonation and, as a result, potential for bacterial regrowth in a distribution system is decreased and biologically stable water will be produced (Vanderkooij et al., 1992).

Another benefit is that ozonation by-products and a significant amount of dissolved organic carbon (DOC), which are precursors of disinfection by-products (such as THM and HAA) are well removed through biofiltration and consequently the chlorine demand of water and the risk of disinfection by-product formation is reduced (Huck et al., 1992). Langlais et al., 1991 also correlated removal of the hydrophilic fraction of NOM by BAC with decreasing of THMFP and TOX formation potential.

2.4.2 Role of Ozone

Among different oxidants, ozone (O_3) has been used widely in drinking water treatment due to its strong oxidation potential. It has been used for disinfection purposes, singly or in combination with UV and H_2O_2, as a chlorine replacement that does not produce halogenated by-products. It is also used in intermediate oxidation steps to modify natural organic substances which are disinfection (chlorination) by-product precursors through oxidization and transferring them to biodegradable organic matters (BOM). Furthermore, ozone degradation happens rapidly and it will not negatively affect the subsequent biofiltration step. Langlais et al., 1991 suggest in their study that the direct molecular ozone mechanism to attack THM precursors is more likely to happen than the radical reaction. However, water quality conditions determine which reaction is dominant in the typical water treatment.

(Trussell and Umphres, 1978) presented in their study that reduction in THM precursors is almost always possible by ozonation; however, the variation in THM precursor removal in different water types depends on the concentration and specific characteristics of the organic substances present, inorganic water quality, ozone contactor transfer efficiency, contact time after chlorination, and ozonation contact time before chlorination.

Shukairy et al. (1992) carried out experiments on two different source waters and investigated the preozonation impact on disinfection by-product formation. Their results show that ozone selectively targets parts of organic matter that are potential sites for chlorine substitution, especially those that form purgable organic halides (POX), and oxidizes them. As a result, POX formation potential is reduced and chlorine demand is decreased because preozonation oxidizes organic matter before they react with chlorine in a chlorination step.

Studies also give evidence that the biological filtration process is always enhanced and greater amount of organics are removed on GAC filters when they receive ozonated water. Anderson et al. (1986) showed that ozone breaks compounds with large molecular weight to smaller molecules by attacking their sensitive sites (aromatic parts or conjugated double bonds) and oxidizing them to lead to increased biodegradable matter. The fact is that these smaller molecules can pass through the bacterial cell wall readily and are more available to be used by microorganisms due to lower mass transfer resistance which can make them more accessible for enzymatic attack (Koechling et al,. 1996). In the other words, during ozonation natural organic matter (disinfection by-product precursors) are transformed to organic matters with high biodegradability which can be removed by bacteria in subsequent biofilters more efficiently (Gilbert, 1987; Camel and Bermond, 1998).

Also, Glaze et al. 1989 and Carlson et al. 1998 measured low molecular weight molecules including aldehydes, carboxylic acids, and ketoacids as ozonation by-products in their studies. Production of such low molecular weight, polar and highly oxidized molecules, which can be easily removed by biological activity, indicates that ozonation enhances the biodegradability of organic matters. However, in some studies changes in biodegradability depended on the origin and type of humic substances in the source water (Huck, 1990; Melin and Ødegaard, 2000).

2.4.3 NOM Removal by Biofiltration

It has been observed that granular activated carbon (GAC) filters can remove dissolved organic carbon (DOC) in most natural waters, even after their adsorption capacity is exhausted, because of biofilms developing on them. The principle of organic substances removal in biofiltration is the utilization of organic substances by bacteria which are attached to the surface of filter media. Basically, in ozonation/biofiltration processes biodegradable NOM, which are formed in the hydrophilic fraction of NOM with high polarity and low molecular size, are preferably utilized by microorganisms and removed (Koechling et al., 1996). However, even though a biofilm works mainly through biodegradation processes, it should be remembered that it will still be able to slightly adsorb solutes on its surface (Kaplan and Newbold, 1995).

Analysis of BDOC, which represent a biodegradable part of dissolved organic carbon, usually is used to define NOM removal. However, only rapidly biodegradable BDOC will be removed by biofiltration and there is an optimum dose of O_3 that controls the formation of rapidly degraded BDOC. In the other words, removal of the biodegradable fraction of natural

organic matter in a biofilter is limited by the formation of rapidly BDOC during ozonation (Calson and Amy, 2001).

Another parameter which is used for quantifying NOM removal in ozonation/biofiltration process is UV absorbance. UV absorbance provides information about the composition of NOM and is correlated with the aromaticity content of dissolved organic matter according to Weishaar et al., (2003). The electronic structure of a molecule is responsible for its potential to absorb of UV light. UV light between 200-380 nanometers is adsorbed by conjugated systems such as conjugated bonds in aromatic molecules (Silverstein et al., 1974). On the other hand, studies demonstrate that aromaticity of DOC molecules is an important indicator of DOC activity in biological processes such as biological filtration. For example, the reactivity of humic substances as a major organic constituent in natural water, with oxidants such as chlorine and ozone, strongly depends on their aromaticity since aromatic rings are Cl^- reactive sites to be substituted in the molecules (Li et al., 2000; Huixian et al., 1997; Boyces et al., 1993).

As a result, monitoring of UV absorbance as NOM surrogate in filter effluents during biofiltration processes shows changes in natural organic matter characteristics. Since the UV absorbance of a water sample is correlated with its NOM amount proportionally, UV absorbance can be correlated with the formation of disinfection by-products when water is chlorinated (Li et al., 2000). In addition, the specific UV absorbance (SUVA), which is UV absorbance of aquatic sample at 254 nanometer divided by DOC concentration (mg/L) of the sample (Li et al., 2000), is also a good estimate of aromaticity characteristic of aquatic humic substances and is used as surrogate for the NOM of a water sample.

Camel and Bermond (1998) summarized that ozonation causes a rapid decrease in UV absorbance and, therefore, reduction in disinfection by-product formation. However, it should be considered that not all organic compounds which contribute to overall UV react with chlorine and form THM Weishaar et al. (2003).

2.4.4 Biofiltration Process Configurations

2.4.4.1 Slow Sand and Bank Filtration

Historically, several forms of biofiltration processes have been used in the water treatment industry. Among them, slow sand biofiltration is a simple and reliable drinking water treatment which has been longer in use and has been applied in both big cities (such as European capital cities) water treatment systems and small-scale treatment plants. Slow sand filtration, which is run at low flow rate and high retention time, performs very well in removing particulates and microorganisms. In spite of the formation of a thin biological layer on the top of the sand bed, the filter displays a weak performance in terms of organic removal. However, when researchers combined a preozonation step with slow sand filtration they observed an improvement in organic matter removal (Cable and Jones, 1996).

Bank filtration is another configuration for biological process. It has been widely in use in European countries like Germany and Switzerland from the beginning of the 20th century. Bank filtration is a naturally occurring influx from surface water through wells or banks dug next to a surface body. It is a natural process in that water is filtered by passing through the banks' fine sediments and BOM, including THM precursors, are removed (Prevost et al., 2005).

2.4.4.2 GAC Biofiltration

Conventional GAC biological filtration was developed and has been in use since it was observed that GAC still removed organic matters after its adsorption capacity had been exhausted.

The use of rapid biological filtration on activated carbon (BAC filtration) has been recognized from the 1970's in European countries (Sontheimer et al., 1978; Sontheimer, 1979). Because of increasing concerns about health effects of disinfection by-products, use of biological rapid filtration to remove BOM and particles simultaneously in the same filter unit has attracted more attention in North America.

Bablon et al. (1988) investigated a combination of conventional rapid filter (loading rate of 5-6 m/h) and granular activation carbon column in the form of a dual layer with the aim of using biological oxidation to reduce chlorination by-product precursors. Their experiments showed that the dual layer sand-GAC filter running at 6m/h is more effective in removing chlorine demand and organic pollution than a sand filter alone.

Carlson et al. (1996) in their study on anthracite media filters found that biomass accumulates faster at higher filter hydraulic loading rates (up to 9.7 m/h). However, when the BOM loading rate is increased above that at which biomass is colonized, removal of DOC decreases because biomass can not utilize the additional organic matter. This means when the biomass concentration is at a pseudo-steady-state, the BOM concentration will not decrease at loading rates higher than the acclimatization loading rate.

In another study on high rate biofiltration which was conducted by Womba et al. (1999) even higher flow rates were investigated. They reported a significant increase in removal of

ozonation by-products and HAA background in GAC biofilters running at a loading rate of 35 m/h. However, at the present, information on high rate deep bed filtration is not adequate and there is a need of more research to be done to obtain reliable conclusions about the efficiency of high rate deep bed filtration for removing disinfection by-product precursors.

Chapter 3 Material and Methods

3.1 Ultrapure Water and Chemical Reagents for THM, HAA and Nitrosamine Analyses

MilliQ UV® ultraviolet treated water (often called ultrapure water) with resistivity of 18.2 M Ω cm was used to prepare all blanks, reagents and quality control standards and to rinse labware. The system was purchased from Millipore (Missisauga, Ontario).

Sodium hypochlorite solution was purchased from VWR International (Mississauga, Ontario) and used to make sampling bottles chlorine-demand-free before doing chlorine demand tests and also to use in Simulated Distribution System (SDS) tests. Ammonium chloride was also purchased from VWR and used in SDS tests to quench further thrihalometane and haloacetic acids (THM and HAA) formation. Free and total chlorine DPD reagents powder were purchased from Cleartech (Mississauga, Ontario), and used to measure free and total chlorine concentrations of samples in SDS tests. Sodium thiosulfate ($Na_2S_2O_3$) and sodium sulfate (Na_2SO_4) were purchased from VWR for use in THM and HAA analytical methods. Concentrated sulfuric acid was also purchased from VWR and used for HAA analysis. 1,2-dibromopropane (1,2-DBP) was used as the internal standard for both the THM and HAA analytical methods. 2,3-dibromopropanoic acid (2,3-DBPA) and 2,3,5,6-tetrafluorobutanoic acid (2,3,5,6-TFBA) were used as surrogate standard solutions for the HAA analytical method. Methanol (CH_3OH 99.9%) for stock standard solution preparation and syringe rinsing, and 99.9% methyl tertiary-butyl ether (MtBE, 99.9%) the HAA extraction solvent

both were purchased from VWR while GC grade pentane (99.9%), the THM extraction solvent was purchased from Sigma-Aldrich (Oakville, Ontario).

The THM mixed standard (2000 μg/L) and HAA individual standards (1000 μg/L each) used for THM and HAA method calibration, respectively, and also diazald (N-methyl N- nitroso-p-toluensulfonamide), which is used as diazomethane generating reagent were obtained from Sigma-Aldrich.

Seven analytical grade nitrosamines, including N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine (NDEA), N-nitrosodibutylamine (NDBA), N-nitrosodi-n-propylamine (NPRO), N-nitrosopiperidine (NPIP), N-nitrosomorpholine (NMOR), N-nitrosopyrolidine (NPYR), were purchased from Sigma-Aldrich while N-nitrosomethylethyl amine (NMEA) was purchased from VWR. All were used to prepare standard solutions preparation for calibration and quality control purposes. N-nitrosodimethylamine-d_6 (d_6-NDMA), a surrogate standard in the nitrosamine analysis, was also purchased from Sigma-Aldrich.

Ambersorb XEN-572, which is used to extract nitrosamines from water, and 99.9% dichloromethane, which is used to extract nitrosamines from Ambersorb XEN-572, were purchased from Sigma-Aldrich and VWR, respectively.

3.2 Sample Preparation and Analytical Methods

3.2.1 Simulated Distribution System Testing and Chlorine Demand Measurement

Simulated Distribution System (SDS) Testing was performed to simulate the Mannheim Water Treatment Plant full- scale chlorination/chloramination regime to estimate the effects of filter media and configuration on subsequent DBP formation caused by the

chlorination/chloramination process followed by a 24 hour residence time in the distribution syatem.

At the Mannheim Water Treatment Plant, post-filtration water is chlorinated before it goes into a reservoir of 7.5 ML which is typically 85-95% full (Walton, 2006). The average flow rate through the plant is 600-800 L/sec. Therefore, the hydraulic retention time (HRT) of the reservoir is calculated to be approximately 2.2 to 3.3 hours. Water is chlorinated such that it achieves a post-reservoir free residual chlorine of 1.5 to 2 mg/L and 1.5 to 2 mg/L monochloramine after the subsequent addition of ammonia.

To carry out the SDS test on a water sample in a 650 mL bottle at room temperature, an appropriate amount of NaOCl (typically 35 to 40 μL) was added to the sample such that it would have a 1.5 to 2 mg/L free residual chlorine after 3 hours of chlorine contact time at room temperature and in the dark. The needed amount of NaOCl to achieve this specified amount of chlorine residual was detemined with a sample chlorine demand test which will be explained subsequently in this section. At the end of 3 hours, which is the contact time for THM and HAA formation, NH_4Cl was added to the sample to provide ammonia to convert free chlorine to monochloramine. The amount of NH_4Cl added was calculated to provide a Cl_2:N mass ratio of 3:1. It was calculated that this ratio in the sample can be achieved by adding 1 mL of 0.0234 mol/L NH_4Cl. This mass ratio converted free chlorine to monochloramine (1.5 to 2 mg/L as Cl_2) and effectively stopped THM and HAA formation, so samples were taken at this stage for THM and HAA analyses. The rest of the sample was kept in the dark for additional 20 to 24 hours to provide chloramine contact time for nitrosamine formation and then sample were analyzed for nitrosamines.

To measure chlorine demand, water sample that was collected in a 650 mL bottle was brought to room temperature by leaving them out of fridge and divided to eight portions in 40 mL vials before dosing it with chlorine. NaOCl 6% was used to prepare 4 different concentrations of chlorine and two replicates of each one. They were stored to stay for three hours in the dark for free chlorine contact time and free residual chlorine was measured at the end of three hours using a HACH DR/2010 colorimeter (Cleartech, Mississauga, Ontario) and free chlorine DPD reagent. The chlorine demand of the sample to be used in SDS tests was the one that was equal to the chlorine concentration which leaves free residual chlorine of 1.5-2 mg/L as Cl_2 after three hours.

The detection limit for the chlorine demand test was calculated according to the Method 1030C of Standard Methods (APHA-AWWA-WEF, 1999). Seven portions of water sample with known chlorine demand were dosed with chlorine and their free residual chlorine concentrations were measured after three hours. The standard deviation of replicated results was calculated to be 0.296 and the MDL (or the smallest amount that can be detected above the noise with in 99% confidence level) in the chlorine demand method, was determined by multiplying the standard deviation by 3.14 which is t value of 7-1=6 degrees of freedom and 99% confidence level.

3.2.2 THM Sample Preparation

THM sample preparation method was based on liquid-liquid extraction with pentane and subsequent GC/ECD analysis which was performed according to Method 6232 in Standard Methods (APHA-AWWA-WEF, 1999).

100 μL of $Na_2S_2O_3$ as a quenching agent and 5 grams of Na_2SO_4 were added to 20 mL of water sample and blanks. Then 4 mL of extraction solvent, which was pentane containing 100 μg/L of 1,2 DBP as internal standard, was added to the sample and the mixture in the vial was shaken for 7 minutes on the shaker. Solution was left to stay for 15 minutes in room temperature for organic and aqueous phase separation. Organic phase was transferred to the to GC vial containing oven dried Na_2SO_4 for GC analysis.

The gas chromatograph which has been used in this method was HP 5890 Series II with 30m x 025 mm x 0.25 μm film DB 1701 capillary column with retention gap and temperature programmable oven. Temperature of injector and detector were 220 ºC and 300 ºC, respectively.

Calibration curves were constructed for each of the four trihalomethanes. 10 mL of 200 mg/L stock solution was prepared using a mixed solution of THMs at 2000 μg/mL which had been obtained from Sigma-Aldrich. Standard solutions for calibration purposes were prepared using three replicates of each concentration level in the range of 0.5 to 200 μg/L, and in 20 mL of MilliQ water. Liquid –liquid extraction was carried out for standard samples same as described above for real samples. The extracts were injected into the GC/ECD and used to prepare calibration curves for the trihalomethanes. Calibration curves and R^2 (correlation coefficient) are shown in Appendix B.

The MDL of the THM analytical method used in these experiments was calculated according to section 1030C in Standard Methods (APHA-AWWA-WEF, 1999). A THM solution of 10 μg/L concentration was prepared and THM preparation method was carried out on seven 20 mL replicates. Subsequently, the MDLs for the four trihalomethane species we determined

by multiplying standard deviation of each compound by 3.14, which is t value of 7-1=6 degrees of freedom and 99% confidence level.

3.2.3 HAA Sample Preparation

HAA samples, along with method (lab) and travel blanks were prepared and analyzed according to method 6251B in Standard Method (APHA-AWWA-WEF, 1999) after some minor method modification. The principle was based on liquid–liquid extraction of the HAAs with MtBE at an acidic pH followed by diazomethane derivatization and GC/ECD analysis.

100 μL of $Na_2S_2O_3$ as quenching agent and 6 grams of oven dried Na_2SO_4 were added to 20 mL of water sample in a 40 mL vial. Concentrated sulfuric acid was added to the vial to maximize the extraction. 2,3-DBPA and 2,3,5,6-TFBA were added to the 40mL vial as surrogate additives and also 5 mL of MtBE as extraction solvent containing internal standard 1,2-DBP was added. The vial was placed on the shaker to be shaken seven minutes and then allowed to stand for 15 minutes at room temperature for phase separation. At this point, the organic phase was transferred to a test tube carefully without mixing with aqueous phase and the test tube was put in freezer for seven minutes.

Diazomethane (CH_2N_2) solution, which was generated as the derivatization reagent, was added to the cooled test tubes containing organic phase and they were left at 4ºC for 15 minutes and then another 15 minutes at room temperature. Extracts were washed with saturated sodium bicarbonate ($NaHCO_3$) and the organic phase was separated and transferred to a GC vial containing oven baked Na_2SO_4 to be analyzed by GC/ECD for HAAs.

Diazomethane, which is toxic carcinogenic and an explosion hazard (Aldrich-Sigma, 2007), was used in the HAA extraction method to methylate extracted organic acids and produce

methyl ester derivatives that can be separated chromatographically. Diazomethane was generated by means of MNNG (Figure 3.1) apparatus which is setup in an ice-filled beaker under the fume hood. Diazald was added to the inner tube of the generator while MtBE was added to the outer tube. It had to be ensured that the glass joints of the inner and outer tubes were sealed for maximum diazomethane generation and recovery. After the set up cooled on the ice bath for 10 minutes, 600 µL of 20 % NaOH was added dropwise to the inner tube using a gas tight syringe. Diazomethane gas was formed in 30-45 minutes, escaped from the inside tube hole and was collected in MtBE in the outside tube. It changed the MtBE color to yellow. The resulting CH_2N_2 in MtBE was transferred to a 4 mL vial using a flamed Pasteur pipette and stored in an explosion-free fridge.

Figure 3.1 MNNG diazomethane generation apparatus (Sigma-Aldrich online catalogue)

The gas chromatograph which used was a HP 5890 Series II with 30m x 025 mm x 0.25 μm film DB 1701 capillary column with relation gap and temperature programmable oven. The injector and detector temperatures were 200 ºC and 300 ºC, respectively.

A 20 μg/mL mixed HAAs stock solution was prepared from 1000 μg/mL individual HAA standards. Calibration standards were prepared using three replicates at each concentration level and for a concentration range of 0.5 to 90 μg/L by injecting appropriate amounts of stock solution directly into 20 mL of water. Extraction/esterification procedure was performed the same as what was carried out for real samples, and standards were analyzed under the same conditions as samples. Calibration curves which were obtained can be seen in Appendix B.

The MDL of the HAA method was determined according to the Section 1030C in Standard Methods (APHA-AWWA-WEF, 1999). An HAAs solution of 10 μg/L was prepared and divided evenly into seven 20 mL portions in 40 mL vials. All replicates went through liquid-liquid extraction and GC analysis, and standard deviations of the measurements were calculated for each of the 6 target HAA compounds (including monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, bromochloroacetic acid, trichloroacetic acid, dibromoacetic acid). Other HAAs were not included in this research because they either were not regulated or had not been detected by this method. Subsequently, an MDL for each of the 6 mentioned HAA compounds was calculated by multiplying the standard deviation of the associated compound results by 3.14, which is t value for 7-1=6 degrees of freedom at a 99% of confidence level (Appendix B).

3.2.4 Nitrosamines Sample Preparation

Nitrosamines sample preparation method was carried out according to Taguchi et al. (1994). Sample was collected in 500 mL bottles and approximately 300 μg of solid ascorbic acid was added if a free residual was present in the samples. 20 μL of d_6-NDMA was added as an internal standard to the sample to achieve to 25 ng/L concentration. Also, 200 mg of Ambersorb XEN-572 was added to the sample. The sample was filtered under vacuum through filter paper Whatman No.4 and nitrosamine-sorbed Ambersorb XEN-572 was collected on the filter paper. Filter paper was placed in an aluminum dish after one minute, and the Ambersorb XEN-572 was allowed to be dried in the air (under fume hood) for 30-60 minutes until the Ambersorb beads were no longer clumped together. Then, the Ambersorb beads were transferred to a 400 μL flat bottom GC vial insert, and 350 μL of pure dichloromethane was added to the vial insert using a 1 mL syringe. The vial insert was placed in a GC vial to be analyzed by GC/MS for nine nitrosamines (NDMA, NDEA, NDBA, NPRO, NPIP, NMOR, NPYR, NMEA, and d_6-NDMA).

A Varian 4000 GC/MS with CP 8400 autosampler equipped with VF-5 mass spectrometer, 30m x 0.25 mm x 0.25 μm DB1 710 column, temperature programmable oven, with filament delay of 2.5 min and elect ionization (EI) of 70ev was used for nitrosamines analysis.

Calibration standards were prepared from a 100 μg/L mixed working solution (which had been made from individual 1000 mg/L stocks) at seven levels from 1 to 100 ng/L. Standard samples went through the same preparation procedure as real samples and were analyzed by means of GC/MS for use in the calibration curves which can be seen in Appendix B.

The MDL of the nitrosamines method was determined according to Section 1030C in Standard Methods (APHA-AWWA-WEF, 1999). Seven replicate samples from a 10 ng/L standard were processed using the above method and analyzed by GC/MS for nine nitrosamines. The standard deviation of each compound was calculated and multiplied by a factor of 3.14 (t-value of 6 degrees for freedom and 99% confidence interval) to result in the MDLs of the compounds which are given in Appendix B. These MDLs were accepted in this method because they were less than experimental results of this research and less than Ontario Drinking Water IMAC 9 ng/L.

3.2.5 UV Absorbance Analytical Methods

The UV absorption of UV-absorbing constituents in a sample, which was in proportion to their concentration, is measured at 254 nm. Ultraviolet absorbance measurements were carried out according to method 65910B in Standard Methods (APHA-AWWA-WEF, 1999). The sample was filtered to remove particulate interferences. Sample absorbance was measured with a spectrophotometer (Hach DR 2010) that was first adjusted to read zero absorbance with the organic-free water (blank) and 2 to 3 mL of sample was transferred to the 1-cm cell so that its UV absorbance could be measured at 254 nm.

3.2.6 Quality Assurance /Quality Control Measures

Quality Control and Quality Assurance measures were included in this research to monitor and maintain method performance. Samples were taken for chlorine demand and DBPs experiments in chlorine demand free bottles. Also samples were taken in duplicate to monitor analytical precision.

Lab and travel blanks were prepared and analyzed along with each set of samples to check and eliminate any contamination of analyte of interest in solvents and reagent water.

Standards were processed with each set of samples and used for control charts (Appendix II) to check the consistency of the preparation method and the stability of GC performance.

The area of the peak of the internal standard, which was added to the samples, was used to correct for any deviation in sample extraction efficiency and check GC performance. Also, as explained in the previous sections, calibration curves were generated and the MDL was determined for each method as another quality control element.

3.3 Mannheim Water Treatment Plant

The Mannheim Water Treatment Plant is located in Kitchener, Ontario and provides treated drinking water for the cities of Kitchener and Waterloo. Its source water is from the Grand River, which receives agricultural runoff and is also affected by an upstream wastewater treatment plant. It has a bromide (Br^-) concentration of 50μg/L (Peldszus et al., 2004) and a relatively high organic content (TOC or DOC) (6mg/L; Emelko et al., 2006).

3.3.1 Full Scale-Filter Configuration and Media Specification

Raw water from the Grand River is first stored in a reservoir of about 38 million gallons before entering the water treatment plant. In the water treatment facility, water enters two identical treatment trains which consist of coagulation, flocculation and sedimentation processes followed by ozonation, biological conventional filtration (two filters in each train). Disinfection is the last process at the Mannheim Water Treatment Plant and chlorination is

followed by ammonia addition to enable chloramination for distribution system disinfection. Figure 3.2 is a schematic of the treatment processes at the Mannheim Water Treatment Plant.

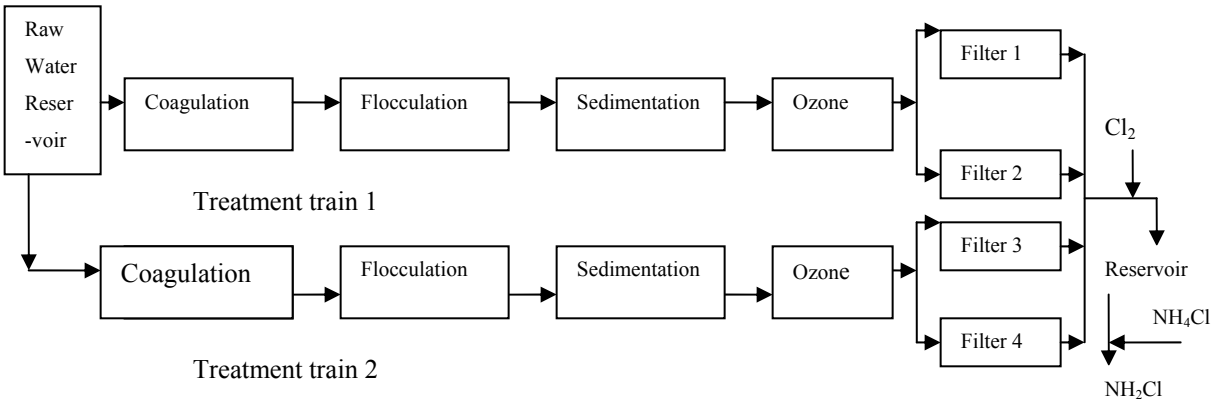

Figure 3.2 Schematic of processes at the Mannheim Water Treatment Plant

Filter #1 (F1) and filter #2 (F2) were dual media filters consisting of 137 cm GAC over 30 cm sand during this project. Filter #3 (F3) and Filter #4 (F4) used to be dual media filters of 122 cm anthracite over 30 cm sand (Emelko et al., 2006) but they were changed to new GAC and anthracite media, respectively, similar to the GAC and anthracite in the pilot filters at the beginning of this project (on Mar 2/07 and Apr 28/07). All biological full-scale filters ran in conventional mode with a loading rate of 530 to 780 L/s (7 to 10 m/h) during this project, the actual values depending on the demands exerted on the upstream (determined and controlled by plant staff).

3.3.2 Pilot-Scale Filter Description and Media Specification

Pilot-scale filters (Figure 3.3) were designed to be operated at the Mannheim Water Treatment Plant to study optimum filter configurations by comparing new media with different specifications with the existing conventional filters. Figure 3.4 is a schematic showing the pilot filter position and that it received post-ozonated water from the full-scale treatment train on side two of the plant so that there were similar water conditions for both the full-scale and pilot-scale filter influents. Pilot filter specifications are summarized in Table 3.1 (Wojcicka , 2007).

P1 P2 P3 P4

Figure 3.3 Pilot-Scale Filters at the Mannheim Water Treatment Plant

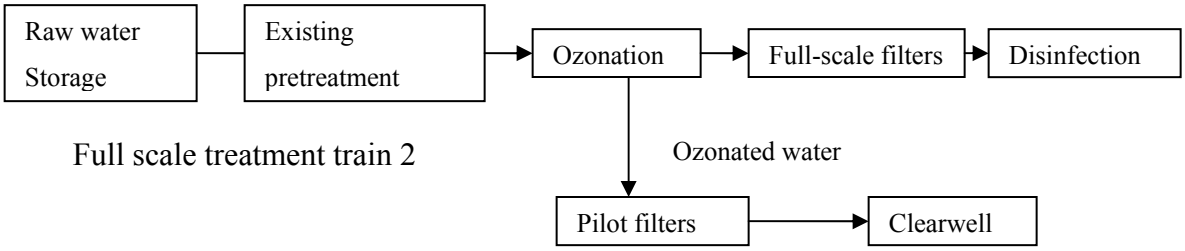

Figure 3.4 Schematic showing the position of pilot filters at the Mannheim Water Treatment Plant

Table 3.1 Pilot Filter Media Specifications (Wojcicka, 2007)

Filter	Media type	U.C. (if available)	Effective size	Depth
P1	GAC Sand	N/A	0.45-0.65 mm 0.45-0.65 mm	1300 mm 300 mm
P2	GAC Sand	1.4 max 1.5	1.3-1.5 mm 0.67 mm	1300 mm 300 mm
P3	Anthracite Sand	1.6 1.5	1.3 mm 0.67 mm	1300 mm 300 mm
P4	Anthracite Sand	1.3 1.5	1.3 mm 0.67 mm	1300 mm 300 mm

3.4 Filter Sampling Procedures and Experimental Plans

3.4.1 General Filter Sampling Procedure from Mannheim Water Treatment Plant

Filter sampling plans were prepared in three stages. The first sampling phase, or preliminary phase, included samples from two influents and the full-scale and pilot-scale filters. It was just used to estimate the expected DBP range in chlorinated or chloraminated filter effluents and as background information. It was performed from May to June 2007 during which time the pilot filters ran at about 7 L/m. The data that were collected during this phase are not included in this thesis since they did not contribute to the overall study of flow and media effects on DBP formation.

The second stage of sampling was accomplished in July 2007. Samples were taken from the pilot filters along with their influent (ozonation effluent on side 2 of the treatment plant) when pilot filters had been acclimated. This was following approximately 4 months of operation during which time it was expected that biofilm had become established on the filter media.

In the last stage of sampling in August 2007, samples were taken every week from influents and full-sale and pilot-scale filter effluents to compare performance of pilot-scale and full-scale filters when they were operated at same loading rate.

Samples for chlorine demand and DBPs measurements were taken in 650 mL chlorine demand free bottles and were headspace free. Bottles were made chlorine demand free by filling them with deionized water and adding 1 mL of NaOCl 6%, and then they were left for

3 hours and rinsed with deionized water. Sampling bottles also were rinsed with the sample water before filling with filter influent and effluent samples.

All samples were transferred to the lab in a cooler, where they went through chlorine demand, trihalomathane, haloacetic acids, and nitrosamines analyses.

3.4.2 Pilot-Scale Filter Flow Rate Experiments

To assess impact of the flow rate in the performance of different filter media in regard to DBP formation, pilot filters were operated at flow rates from 1 L/m to 13 L/m randomly. Flow rate changes in the pilot filters are summarized in Table 3.2.

Table 3.2 Pilot Filter Flow Rates (L/m) During Flow Rate Experiments

Sampling Date / Filter	Jul 19	Jul 13	Jul 16	Jul 3	Jul 9	Jul 23
P1		10.2	8.6	5	1	
P2	8.5	8	7.7	5	1	
P3		11.2	9	5	1	
P4		12.8	7.5	4.3		2

Monitoring of flow rate and head loss variation at the pilot filters using data collected by the pilot control panel helped to estimate the required frequency of filter backwashing at each different flow rate. Analyzing head loss data and flow rate profiles indicated that filters had shorter runs and head loss was built sooner when they were run at higher flow rates. The filters were backwashed when the head loss started to build. Their backwash frequency was lower when they were run at a lower flow rate.

Filters were backwashed according to the Collapse-Pulsing protocol which was provided by (Wojcicka, 2007). Samples were taken from pilot filters after at least 2 filter cycles to let the filters adjust to the new flow rate, and 24 hours before the next backwashing to avoid sampling when filters reach their terminal head loss and/or when the flow rate had been reduced significantly from its target value.

3.4.3 Comparison of Full-Scale and Pilot-Scale Filter Performance

Pilot-scale filters were operated under the same loading conditions as the full-scale filters in this round of experiments, so that the performance of pilot-scale and full-scale filters would be more directly comparable. Pilot-scale and full-scale filters were divided into comparable subgroups (i.e. same influents, and same media type with similar or slightly different media specification). Chlorination of samples was done in the lab to simulate DBP formation. Then variations in water quality parameters including chlorine demand, UV absorbance, THMs, HAAs, and nitrosamines in the filter effluents in each group were measured and compared.

As mentioned above, during this phase of the experiments the pilot filter loading rates were adjusted to meet the changes in loading rate at full-scale. The final loading rates are shown in the Table 3.3. Corresponding flow rates are given in Chapter 5.

Table 3.3 Pilot-Scale and Full-Scale Filter Loading Rates During FS/PS Comparison Experiments

Sampling date	**Aug 7**	**Aug 13**	**Aug 20**	**Aug 27**	**Sep 4**
Filters loading rate m/h	10.3	8	8	7.05	7.05

3.4.4 Statistical Analyses

For each set of comparison to be made, a single factor (involving filter media of filter scale) analysis of variance test (ANOVA table; Montgomery, 1991) was performed first to determine if there were gross differences within a specific set of filters. Data sets were checked to see if they were normally distributed prior to running ANOVA. Normal probability plots were used to determine if sample data followed normal distributions. If they did, then the data followed a straight line pattern on the normal probability plots (Montgomery, 1991). Following ANOVA, independent (regular) t-test and paired t-test (which makes comparisons within of matched pairs of data points in two sets of data) calculations were performed where appropriate. Finally, the Least Significant Difference (LSD) method (Montgomery, 1991) was used to make additional comparisons between each pair of filters to determine if the filters performed significantly differently. Of these statistical tests, the paired t-tests were considered to provide the most reliable comparisons given that they provide a means of evaluating that separate performance trends from changes in influent water quality.

Chapter 4 Pilot-Scale Filters Flow Rate Experiment Results

As described in the Materials and Methods Chapter, pilot filters were operated at different targeted flow rates, from a low value of 1 L/m which corresponds to a (1.9 m/h loading rate) to high value of 13 L/m (24.1 m/h loading rate) during a period of one month to investigate the effect of flow rate on the ability of these filters to influence chlorine demand and DBP formation. Before this round of experiments, the pilot filters had been operated for three months to acclimatize and establish biological activity.

4.1 Chlorine Demand Variation in Pilot-Scale Filters During Flow Rate Experiment

Samples were taken from influent II and all filter effluents and their chlorine demands were measured in the lab. Table 4.1 shows the flow rate of each filter, which was recorded during sampling, and its corresponding chlorine demand. The results, which are plotted in Figure 4.1, showed identical trends for chlorine demand in all types of filter media. Although probably not considerably, the data showed that the chlorine demand of the filter effluent increased very slightly by increasing the flow rate except at the lowest flow rates that were tested. In fact, this increase occurred regardless of the type of the filter media. It was also observed that the chlorine demands of the effluent samples from the anthracite filters (designated as P3 and P4 for filters #3 and # 4) were always similar to each other and higher than the GAC filter (designated as P1 and P2 for filters #1 and # 2) effluent chlorine demands at any flow rate. This observation was anticipated because the coarser surface of GAC relative to anthracite which provides a better surface area for bacteria to grow.

Table 4.1 Chlorine demand of chlorinated pilot plant filter effluents at different flow rates

Influent II	
Sampling Date and Target Flow Rate	**Chlorine Demand mg/L as Cl_2**
9-Jul-07 (1L/m)	4.5
3-Jul-07 (5L/m)	4.5
16-Jul-07 (9L/m)	4.5
12-Jul-07 (13L/m)	4.5
23-Jul-07 (1.85L/m)	4.5

P1		P2	
Sampling Date and Flow Rate	**Chlorine Demand mg/L as Cl_2**	**Sampling Date and Flow Rate**	**Chlorine Demand mg/L as Cl_2**
9-Jul-07 (1L/m)	3.3	9-Jul-07 (1L/m)	3.2
3-Jul-07 (5L/m)	3.2	3-Jul-07 (5L/m)	3.2
16-Jul-07 (8.6L/m)	3.2	16-Jul-07 (7.7L/m)	3.1
12-Jul-07 (10.2L/m)	3.4	12-Jul-07 (8L/m)	3.4
P3		**P4**	
Sampling Date and Flow Rate	**Chlorine Demand mg/L as Cl_2**	**Sampling Date and Flow Rate**	**Chlorine Demand mg/L as Cl_2**
9-Jul-07 (1L/m)	3.7	23-Jul-07 (1.85L/m)	3.9
3-Jul-07 (5L/m)	3.5	3-Jul-07 (4.3L/m)	3.7
16-Jul-07 (9L/m)	3.6	16-Jul-07 (7.5L/m)	3.5
12-Jul-07 (12.8L/m)	3.8	12-Jul-07 (11.2L/m)	3.8

Influent II= influent to pilot filters from side 2 of water treatment plant.

P1, P2, P3, P4= effluent from pilot filter columns #1, #2, #3, #4

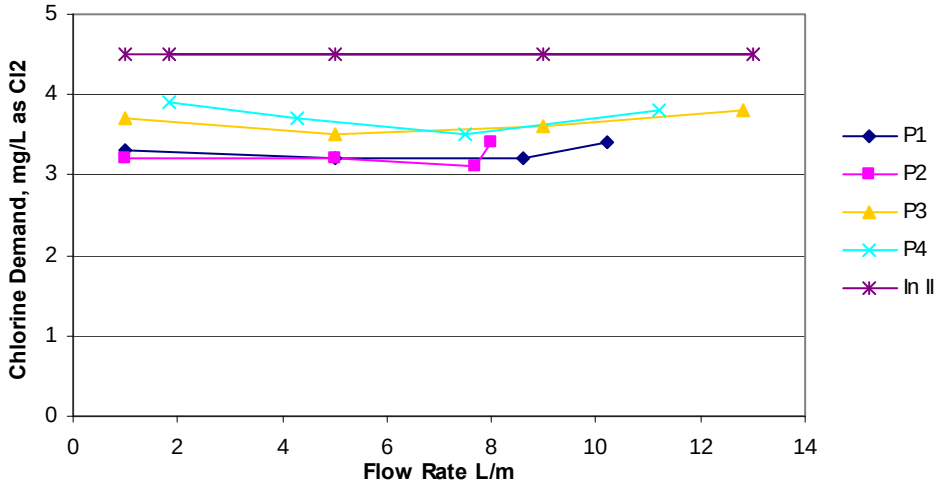

Figure 4.1 Chlorine demand variation in chlorinated pilot filter influent and effluents at different flow rates (influent values are plotted against target flow rates)

Considering the fact that the influent chlorine demand did not change during the flow rate experiments, it can be concluded that the chlorine demand removal was independent from flow rate in the different types of filter media that were tested.

4.2 UV254 Absorbance in Pilot Filters During Flow Rate Experiments

UV254 absorbance was measured (1 cm path length) as an indicator of the aromatic part of NOM molecules which is the active part of DOC in reactions with chlorine to form disinfection by-products. As mentioned in Chapter 2, not all aromatic molecules which contribute to UV254 absorbance may react with chlorine as THM precursors and some THM precursors may not contribute to the overall UV absorbance. Nevertheless, UV254 absorbance still provides a good indication of the THMFP of the water.

UV254 absorbance results of chlorinated pilot filter influent and effluents during the flow rate experiments are shown in Table 4.2 and Figure 4.2. These results show that UV254 absorbance increased as the flow rate increased for flow rates below approximately 8 L/m, which does not support the trends observed when chlorine demand was measured. This suggests that while the bulk of the dissolved NOM is not affected by flow rate the fraction of organic matter which can absorb UV254 (and therefore may contain DBP precursors) is affected by flow rate. In addition, UV254 absorbance showed higher values in anthracite filter effluents than in GAC filter effluents at any flow rate because GAC out-performs anthracite in removing NOM and consequently in decreasing UV254 absorbance.

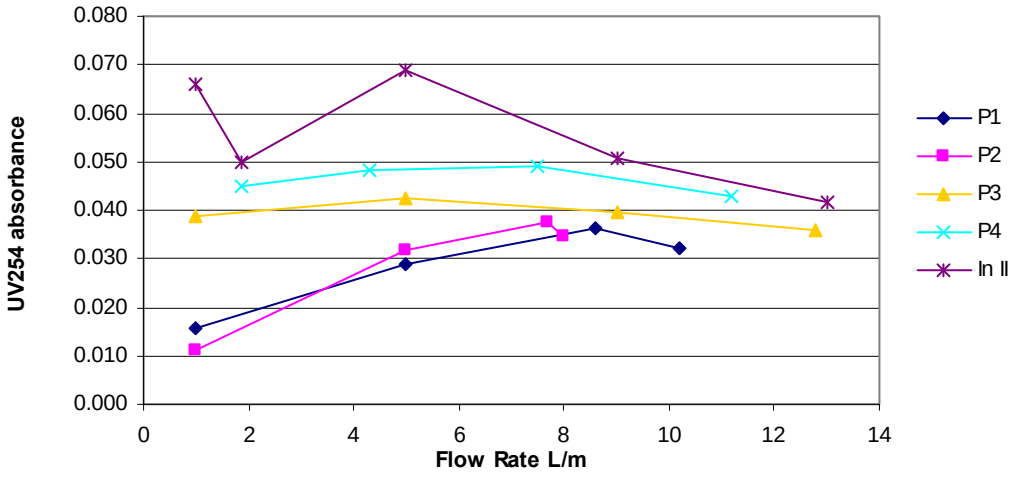

Figure 4.2 UV254 absorbance in chlorinated pilot filter influent and effluents at different flow rates (influent values are plotted against target flow rates)

Table 4.2 UV254 absorbance and %reductions of UV245 absorbance of chlorinated pilot filter effluents at different flow rates during flow rate experiment

Influent II	
Sampling Date and Target Flow Rate	**UV absorbance**
9-Jul-07 (1L/m)	0.066
3-Jul-07 (5L/m)	0.069
16-Jul-07 (9L/m)	0.051
12-Jul-07 (13L/m)	0.042
23-Jul07 (1.85L/m)	0.05

P1			P2		
Sampling Date and Flow Rate	**UV absorbance**	**%R of UV absorbance**	**Sampling Date and Flow Rate**	**UV absorbance**	**%R of UV absorbance**
9-Jul-07 (1L/m)	0.016	75.9	9-Jul-07 (1L/m)	0.011	82.9
3-Jul-07 (5L/m)	0.029	58.4	3-Jul-07 (5L/m)	0.032	53.9
16-Jul-07 (8.6L/m)	0.036	28.0	16-Jul-07 (7.7L/m)	0.038	25.8
12-Jul07 (10.2L/m)	0.032	22.6	12-Jul-07 (8L/m)	0.035	16.5
P3			**P4**		
Sampling Date and Flow Rate	**UV absorbance**	**%R of UV absorbance**	**Sampling Date and Flow Rate**	**UV absorbance**	**%R of UV absorbance**
9-Jul-07 (1L/m)	0.039	40.9	23-Jul07 (1.85L/m)	0.045	21.7
3-Jul-07 (5L/m)	0.043	38.1	3-Jul-07 (4.3L/m)	0.048	28.4
16-Jul-07 (9L/m)	0.040	21.6	16-Jul-07 (7.5L/m)	0.049	4.6
12-Jul07 (12.8L/m)	0.036	13.4	12-Jul07 (11.2L/m)	0.043	-3.3

Influent II= influent to pilot filters from side 2 of water treatment plant.

P1, P2, P3, P4= effluent from pilot filter columns #1, #2, #3, #4

Considering the variability in influent UV254 values, filter effluent UV254 absorbance data were normalized by dividing them by the corresponding influent UV254 absorbance values and percentage reductions were calculated. The results are illustrated in Figure 4.3. UV254 absorbance removal occurred in all filters in the range of 4% to 80%. The maximum percentage reduction was seen in filter #2 (GAC) at flow rate 1 L/m (82%) and the minimum was -3.3% in filter #4 (anthracite) at flow rate 11.2 L/m. It is possible that at high flow rates organic matter is sloughed off from the filter media and contributes to the UV254 absorbance of filter effluent, even increasing the UV254 absorbance to higher value than in the influent and causing an overall percentage increase (negative percentage reduction) as happened in filter #4 at 11.2 L/m.

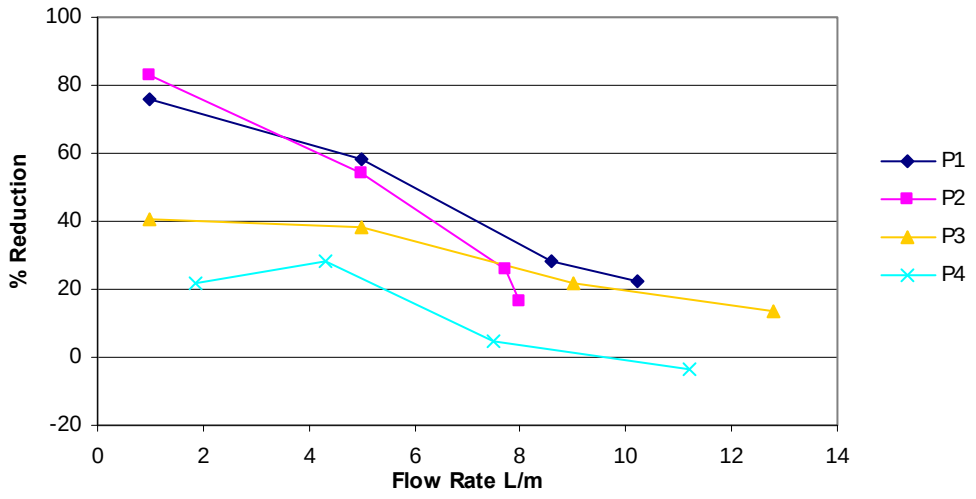

Figure 4.3 %Reductions of UV254 absorbance in chlorinated pilot filter effluents at different flow rates

4.3 Trihalomethane Formation Potential (THMFP) Removal in Pilot Filters During Flow Rate Experiments

As described in Chapter 3, THMPF tests were conducted on pilot filter influent and effluent samples. Four trihalomethane species along with total trihalomethane concentrations (TTHM) were measured in pilot filter effluent samples as the 4 pilot filters were operated at different flow rates. The concentrations of the individual THM species and TTHM values for pilot filter #1 are presented in Table 4.3 and Figure 4.4. Filter #1 was selected to be shown in this section as a typical filter among the pilot filters. THM data for the other filters are given in Appendix A.

Table 4.3 THM species and TTHM concentrations (µg/L) in chlorinated pilot filter #1 effluent during flow rate experiment

Flow Rate (L/m)	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	TTHM
1	5.6	10.9	17.1	12.3	99.1
5	7.1	15.3	29.5	16.5	68.4
8.6	12.9	24.7	33.1	16.8	87.4
10.2	15.0	27.7	42.1	18.2	103

In Figure 4.4 a consistent trend for all species can be observed. The THM species concentrations, and therefore TTHM concentrations, increased as the flow rates were increased. Individual THM concentrations ranged from approximately 5 µg/L to 40 µg/L and TTHM ranged from 40 µg/L to 100 µg/L in these experiments. It should be mentioned that although the higher concentrations are above the current regulations, they are decreased

before the drinking water enters the distribution system because finished water from this water treatment plant is mixed with ground water before distribution.

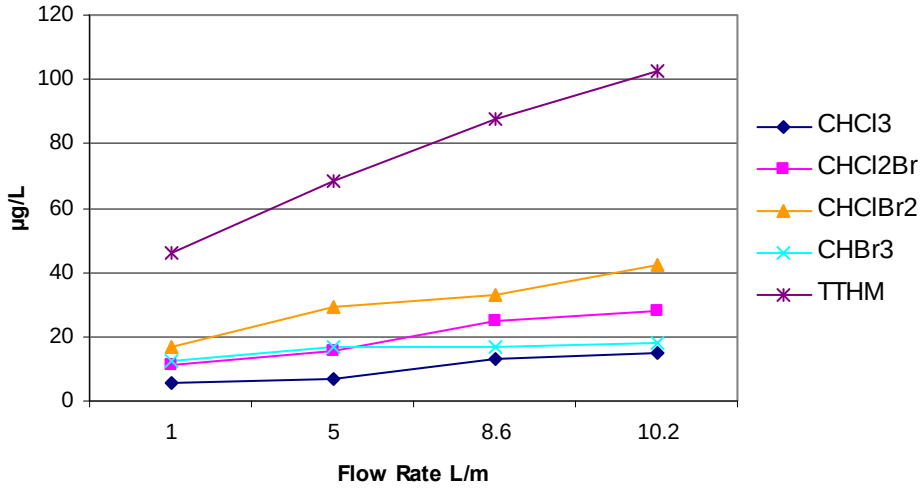

Figure 4.4 THM concentrations in chlorinated pilot filter #1 effluent at different flow rates

In regards to relative species concentrations, the formation of chloroform had the lowest level among all THM species (which is consistent with published DWSP data) and brominated species contributed more to the TTHM. This was because bromide concentration in Grand River is moderately high (50 µg/L; Peldszus et al., 2004) and it is not affected by filtration, unlike organic compounds. Chlorine in the form of hypochlorous acid oxidizes bromide to hypobromous acid (HOBr) in a very fast reaction, therefore the yield of THM species shifts to more brominated THMs when the parallel bromination reactions occur with THM precursor compounds**.** Experimental results showed that very similar amounts of $CHBr_3$ were

formed in the influent and all filter effluents at any specific flow rate, and also that the $CHBr_3$ concentration increased slightly as flow rates were increased.

In addition in the presence of ozone, which is a unit process at this water treatment plant, bromide is oxidized to $HOBr/OBr^-$ and then can be oxidized further to form bromate which is a pH dependent reaction. However, in the presence of both humic substances and bromide ion (similar to the Mannheim pilot filter conditions), HOBr tends to react with humic substances to form organic DBPs like THMs rather than forming bromate (Amy et al., 1991).

Percentage reductions of THM species concentrations in chlorinated filter #1 effluent samples relative to the influent THM concentrations are given in Table 4.4. Figure 4.5 illustrates THM percentage reduction vs. flow rate in filter #1 and shows that all THM species and TTHM percentage reductions decreased with increasing flow rate, which confirms the trend shown in Figure 4.4. It illustrates the poorer filter performance in regard to THMPF removal at high flow rates due to the lower contact time of the water in the filter and therefore less removal of organic precursors at such flow rates.

Chloroform always showed the highest percentage removal (80% to 5%) at different flow rates among the THM species in filter #1, and minimum percentage reductions or even increases in species concentrations were associated with $CHBr_3$ and $CHClBr_2$ (which showed increases of approximately 20% at 8.6 L/m).

Table 4.4 THM %reductions in chlorinated pilot filter #1 effluent and related influent concentration during flow rate experiment

THM Concentrations µg/L (Influent II)					
Sampling Date	**$CHCl_3$**	**$CHCl_2Br$**	**$CHClBr_2$**	**$CHBr_3$**	**TTHM**
9-Jul-07	5.6	10.9	17.1	12.3	45.9
3-Jul-07	14.2	23.1	30.2	14.2	81.7
16-Jul-07	22.6	27.7	26.6	13.7	90.6
12-Jul-07	15.9	29.4	39.4	18.6	103
% Reduction in THM Concentrations (P1)					
Sampling Date and Flow Rate	**$CHCl_3$**	**$CHCl_2Br$**	**$CHClBr_2$**	**$CHBr_3$**	**TTHM**
9-Jul-07 (1 L/m)	78.7	63.8	40.3	11.8	53.7
3-Jul-07 (5 L/m)	50.0	33.8	2.3	-16.2	16.3
16-Jul-07 (8.6 L/m)	43.1	11.0	-24.4	-22.6	3.5
12-Jul-07 (10.2 L/m)	5.7	5.6	-6.9	2.4	0.3

Influent II= influent to pilot filters from side 2 of water treatment plant.

P1= effluent from pilot filter column #1

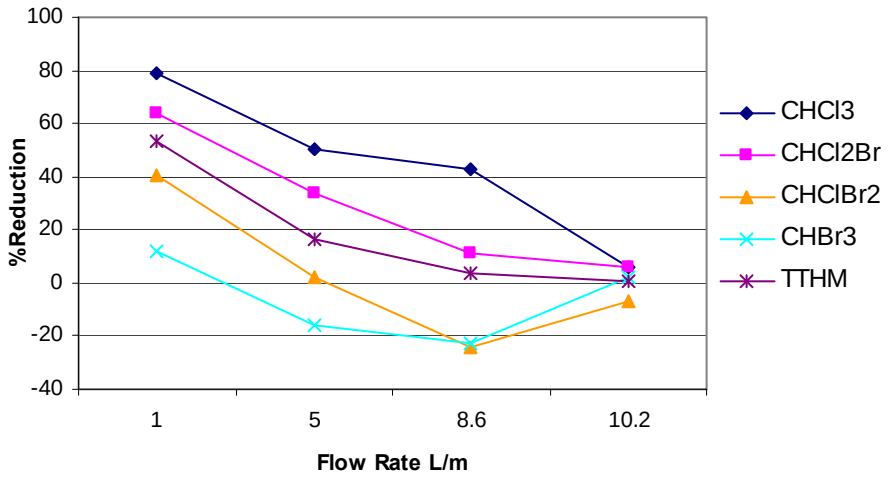

Figure 4.5 THM %reductions in chlorinated pilot filter #1 at different flow rates

TTHM concentrations and percentage reductions for all pilot filters were compared together as flow rates were changed in Figure 4.6 and 4.7, respectively. These figures suggest that flow rate increases have significant effects on TTHM levels in filter effluents and on TTHM percentage reductions for any of the types of filter media that were studied.

As is presented in Figure 4.6, the overall trend is for decreases in TTHM percentage reductions to result from increases in flow rate. Figure 4.7 also shows that P1 and P2 (GAC filters) performed more efficiently in TTHMFP removal than P3 and P4 (anthracite filters). This can be explained by the fact that GAC acts as a better media for THM precursor removal than anthracite in both biological and adsorption mechanisms.

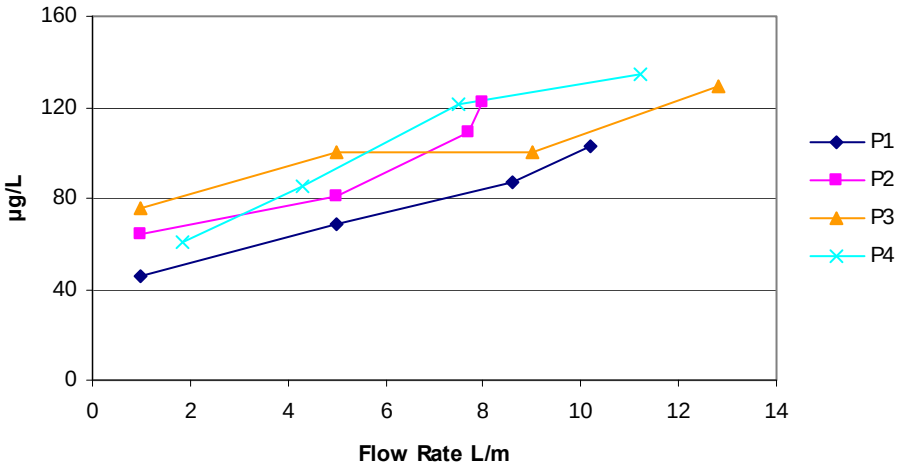

Figure 4.6 TTHM concentrations in chlorinated pilot filter effluents at different flow rates

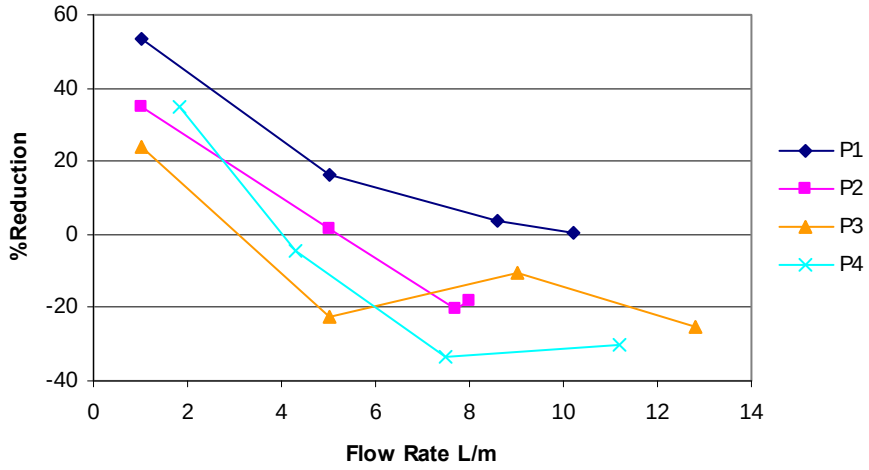

Figure 4.7 TTHM %reductions in chlorinated pilot filter effluents at different flow rates

At high flow rates (higher than approximately 5 L/m), there was not any percentage reduction in TTHM in filters # 2, 3 and 4. The negative percentage reductions at high flow rates indicate that organic matter is sloughed off from the filter media and contributes to the TTHM formation in the filter effluent, causing an overall percentage increase (negative TTHM percentage reduction) similar what was observed for UV254 absorbance measurements.

4.4 HAA Formation Potential Removal in Pilot Filters During Flow Rate Experiments

Concentrations of six haloacetic acids (including chloroacetic acid, bromoacetic acid, dichloroacetic acid, trichloroacetic acid, bromochloroacetic acid, and dibromoacetic acid) along with HAA6 were measured in pilot filter influent and effluents at different flow rates.

Flow rate range and HAA species concentrations in pilot filter #1 effluent are shown in Table 4.5 and Figure 4.8. All HAA species and HAA6 concentrations increased at high flow rates except, for chloroacetic acid and bromoaacetic acid which were consistently non-existent in samples or their concentrations were lower than their method detection limits. Concentrations of the four other HAAs that have been quantified were very close to each other and varied between 1.5 μg/L to 4.2 μg/L. Dichloacetic acid was observed at the maximum concentration level at all flow rates (2.5 μg/L to 4.5 μg/L), which was higher than its EPA MCL goal of 0.0 mg/L.

Since HAA species concentrations ranges in others filters were similar to those for filter #1, filter #1 was selected to be shown in this section as a typical filter among the pilot filters. HAA data for the other filters are given in Appendix I.

Table 4.5 HAA concentrations (µg/L) in chlorinated pilot filter #1 effluent during flow rate experiment

Flow Rate (L/m)	ClAA	BrAA	Cl_2AA	Cl_3AA	BrClAA	Br_2AA	HAA6
1	0	0	2.5	1.8	1.4	1.9	7.6
5	0	0	2.6	2	1.9	2.8	8.9
8.6	0	0	3.7	2.1	3.3	2.8	11.9
10.2	0	0	4.2	2.3	3.9	3.8	14.2

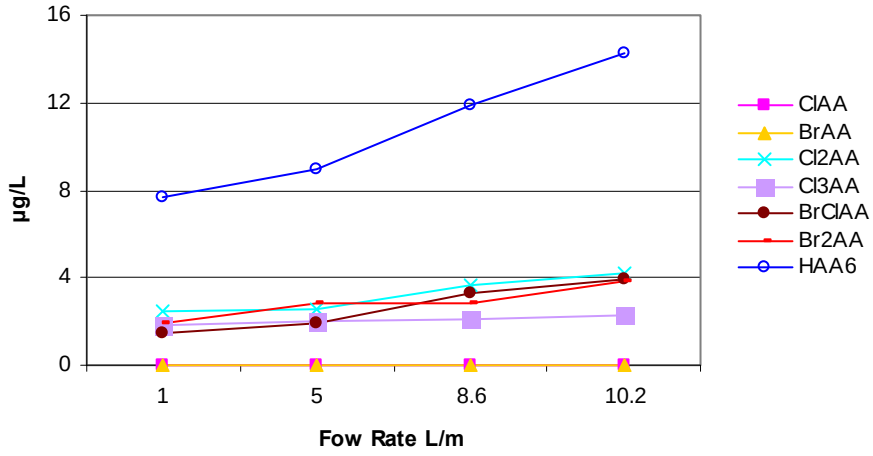

Figure 4.8 HAA concentrations in chlorinated pilot filter #1 effluent at different flow rates

HAA concentrations were normalized by dividing by the influent concentration obtained for each sampling date to express results in the form of percentage reduction (Table 4.6 and Figure 4.9).

Table 4.6 HAA %reductions in chlorinated pilot filter # 1 effluent and related influent concentrations during flow rate experiment

HAA concentration µg/L (Influent II)							
Sampling Date	**ClAA**	**BrAA**	**Cl_2AA**	**Cl_3AA**	**BrClAA**	**Br_2AA**	**HAA_6**
9-Jul-07	0	0	9.1	8.7	7.1	3.5	28.4
3-Jul-07	0	0	4.9	5.1	4.9	4	19
16Jul-07	0	0	4.7	3.1	5.5	2.9	16.2
12-Jul-07	0	0	5.8	4.2	3.7	2.7	16.4
%Reduction in HAA concentrations (P1)							
Sampling Date and Flow Rate	**ClAA**	**BrAA**	**Cl_2AA**	**Cl_3AA**	**BrClAA**	**Br_2AA**	**HAA_6**
9-Jul-07 (1 L/m)	0	0	60.8	79.4	79.6	45.7	69.4
3-Jul-07 (5 L/m)	0	0	55.5	60.9	60.7	30.9	53
16-Jul-07 (8.6 L/m)	0	0	21.3	12.9	35.4	3.4	21.3
12-Jul-07 (10.2 L/m)	0	0	27.6	45.9	-6.7	-40.7	13.4

Influent II= influent to pilot filters from side 2 of water treatment plant.

P1= effluent from pilot filter column #1

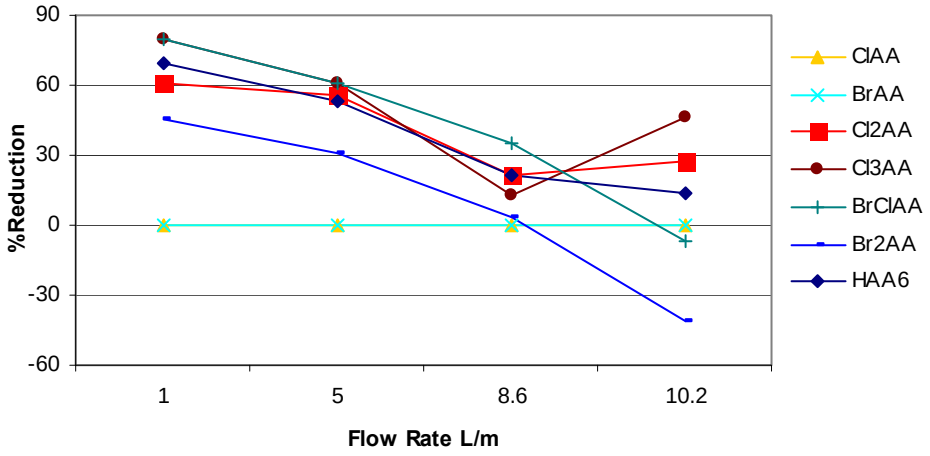

Figure 4.9 HAA %reductions in chlorinated pilot filter #1 effluent at different flow rates

It would appear that the percentage reduction of HAA species in chlorinated filter #1 effluent decreased with increasing flow rate which supports the general trend in all pilot filter effluents for HAA concentrations. These results suggest that there is less organic precursor removal and therefore lower HAA percentage reduction in filters when they are operated at higher flow rates, which is in agreement with THMFP removal results. This result can be explained by the longer filter run times at low flow rates, which increases contact time of the water within the filters and improves organic removal by the filters. On the other hand HAA concentrations in the influent were higher when filters were operated at 1 L/m flow rate relative to other flow rates (i.e. other sampling dates), which can be another reason for higher organic removal at that flow rate (Urfer et al., 1997).

The HAA6 concentrations and percentage reductions in the four pilot filters at different flow rates are shown in Figures 4.10 and 4.11, respectively. The overall trend in Figure 4.10 is for

the HAA6 concentrations to increase with increasing flow rate in all types of filter media. The exception is a higher HAA6 formation in filter #2 at the lowest flow rate (1 L/m); however, at the flow rates above approximately 4 L/m HAA6 reduction in filter #2 follows the general trend. The anomaly may be due to a higher influent HAA6 concentration because the anomaly disappears once the data are converted to % reduction (Figure 4.11).

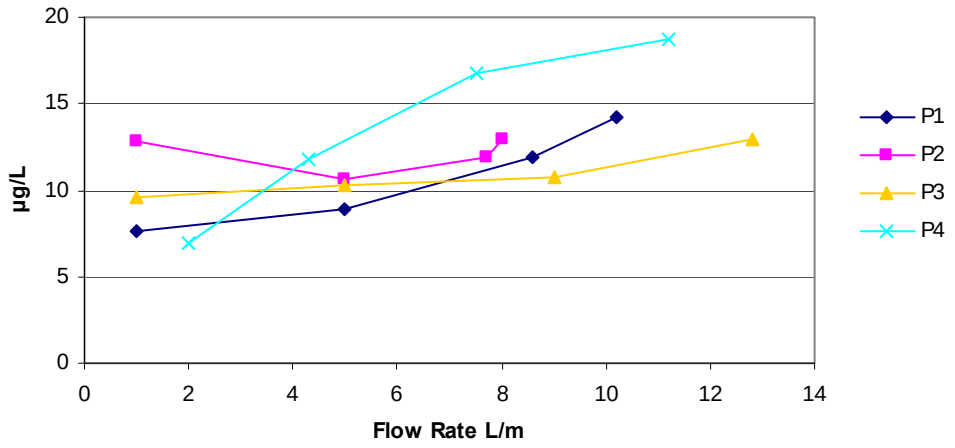

Figure 4.10 HAA6 concentrations in chlorinated pilot filter effluents at different flow rates

Figure 4.11 compares percentage reductions of HAA6 in all chlorinated pilot filters effluent during the flow rate experiments. Maximum percentage reduction (80%) and minimum percentage reduction (-13%, or a 13% increase) were observed in P1 and P4 at 1 L/m and 11.2 L/m, respectively.

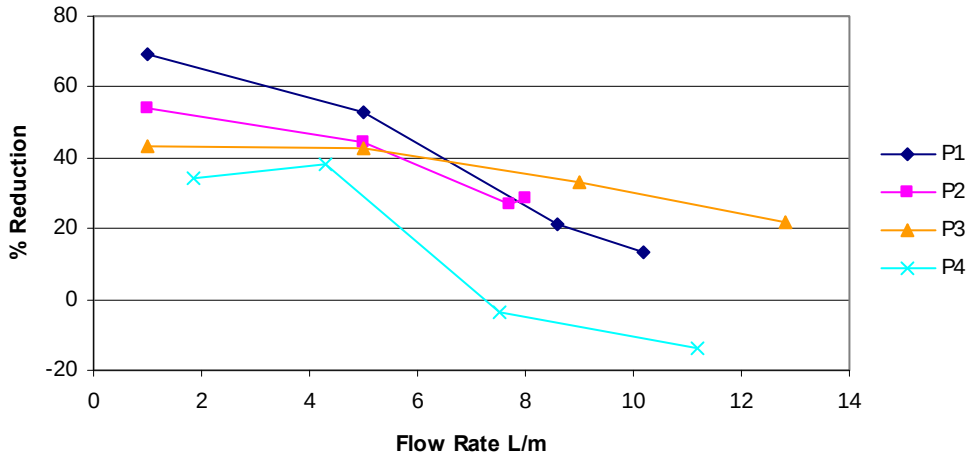

Figure 4.11 HAA6 %reductions in chlorinated pilot filter effluents at different flow rates

As illustrated in Figure 4.11, HAA6 percentage reductions decreased as flow rates were increased, similar to the TTHM percentage reduction trend. Filters #1 and #2 reduced HAA6 more efficiently (showed higher percentage reduction) relative to filter #3 and #4. This is likely because filters #1 and #2 are GAC filters and provide better media for organic precursors to be removed through either adsorption or biological processes. However, it is not clear why data for filter # 3 (one of the anthracite filters) showed higher percentage reduction than GAC filters at high flow rates.

HAA6 production (negative percentage reduction) in pilot filter #4 effluent at high flow rates was in agreement with its corresponding TTHM results. It helps to support the hypothesis that organic matter was sloughing off from the filter media at higher flow rates and

increasing the HAA6 precursor level in the filter effluent to more than the concentration that could be present in filter influent water.

4.5 Nitrosamines Formation Potential Removal in Pilot Filters During Flow Rate Experiments

Eight nitrosamine compounds were measured in chloraminated pilot filter effluent samples during the flow rate experiments. N-nitrosodiethylamine (NDEA), N-nitrosodibutylamine (NDBA), N-nitrosodi-n-propylamine (NPRO), N-nitrosopiperidine (NPIP), and N-nitrosopyrolidine (NPYR) were not detected in any chloraminated filter effluent samples in these experiments while N-nitrosodimethylamine (NDMA), N-nitrosomethylethylamine (NMEA), and N-nitrosomorpholine (NMOR) were observed at low concentrations, in the range of 0.5 to 4 ng/L in all chloraminated pilot filter effluents. Filter #1 effluent showed the highest levels of NDMA, NMEA, and NMOR (among pilot filters) at 3.8 ng/L, 1.4 ng/L, and 2.7 ng/L, respectively, at the flow rate of 8.6 L/m. Also, both NDMA and NMEA showed the lowest level at the 5 L/m flow rate while NMOR appeared at its lowest level at the 1L/m flow rate in chloraminated pilot filter #1 effluent.

The concentrations of all 8 nitrosamines detected in chloraminated filter #1 effluent are shown in Table 4.7. They are plotted against flow rate in Figure 4.12. Filter #1 was selected to be shown in this section as a typical filter among the pilot filters. Nitrosamines data for the other filters are given in Appendix I.

Table 4.7 Nitrosamine concentrations (ng/L) in chloraminated pilot filter #1 effluent during flow rate experiments

Flow Rate (L/m)	NDMA	NMEA	NDEA	NPRO	NPIP	NPYR	NDBA	NMOR
1	1.9	1.3	0	0	0	0	0	1.4
5	0.8	0.9	0	0	0	0	0	2.7
8.6	3.8	1.4	0	0	0	0	0	2.7
10.2	2.0	1.3	0	0	0	0	0	1.5

0= Less than the method detection limit (Appendix C)

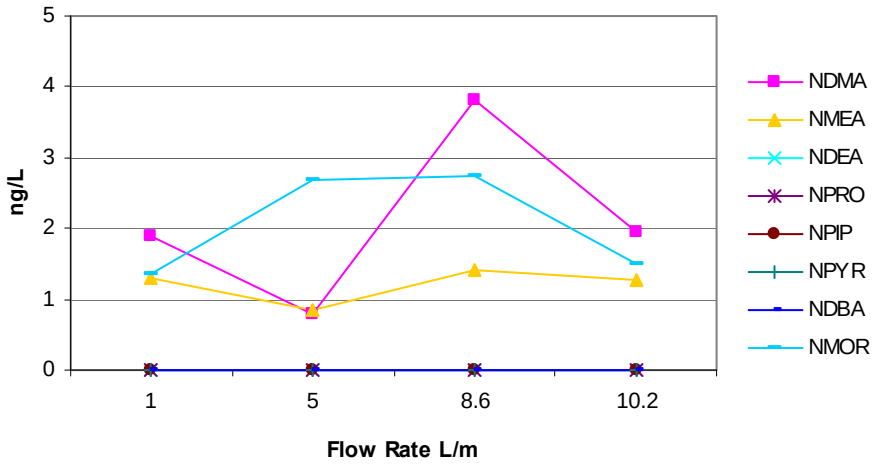

Figure 4.12 Nitrosamine concentrations in chloraminated pilot filter #1 effluent at different flow rates

Maximum and minimum levels for NDMA, NMEA, and NMOR occurred at 5 L/m and 8.6 L/m in filter #1, respectively. However, no consistent trend was observed in the concentration variations of these compounds as the flow rate changed in any type of filter media. This lack of definite trends may be due to the low concentrations observed (all near

MDLs). At these low concentrations it is difficult to separate trends from background variations.

Table 4.8 and Figure 4.13 show percentage reductions of nitrosamines in chloramonated filter #1 effluent. NDMA, NMEA, and NMOR percentage reductions in filter #1 ranged approximately from 60% to 80% as the flow rate changed but, similar to the nitrosamine concentrations themselves, the percentage reductions did not have any specific trend and they changed randomly with increasing flow rate. High NDMA percentage reduction (approximately 80%) in all filters indicates good filter performance for the removal of organic-nitrogen-containing precursors, especially considering that the NDMA concentrations in all filter effluents were less than the Ontario interim maximum acceptable concentration IMAC of 9 ng/L. The %100 removal of NDEA is not a very surprising percentage reduction since the NDEA concentration in the influent was very low (at approximately the detection limit). However, again, because of the very low measured concentrations it is difficult to make a definite judgment about the different filter media effects on the nitrosamine formation potential.

Comparison of nitrosamine concentrations and nitrosamine percentage reductions for the different types of filter media was also inconclusive as is shown in Figures 4.14 and Figure 4.15 for NDMA. NDMA percentage reductions for all filter media (Figure 4.15) were in the range of 60-95% for the range of flow rates that were tested. The experimental results do not show any consistent preference between GAC and anthracite filters for the removal of nitrosamine formation potential throughout the range of operated flow rates, unlike what was observed for THM and HAA removals in the filters.

Table 4.8 Nitrosamine %reductions in chloraminated pilot filter #1 effluent and related influent concentrations during flow rate experiment

Nitrosamine Concentrations (ng/L) Influent II								
Sampling Date	**NDMA**	**NMEA**	**NDEA**	**NPRO**	**NPIP**	**NPYR**	**NDBA**	**NMOR**
9-Jul-07	11.9	5.6	1.9	0	0	0	0	8.4
3-Jul-07	4.7	3.0	1.4	0	0	0	0	5.7
16-Jul-07	13.2	5.6	1.4	0	0	0	0	8.6
12-Jul-07	12.1	7.7	1.5	0	0	0	0	9.8
%Reductions in nitrosamine concentrations (P1)								
Sampling Date and Flow Rate	**NDMA**	**NMEA**	**NDEA**	**NPRO**	**NPIP**	**NPYR**	**NDBA**	**NMOR**
9-Jul-07 (1L/m)	84	76	100	_	_	_	_	83
3-Jul-07 (5L/m)	83	71	100	_	_	_	_	52
16-Jul-07 (8.6L/m)	71	74	100	_	_	_	_	68
12-Jul-07 (10.2L/m)	83	83	100	_	_	_	_	84

Influent II= influent to pilot filters from side 2 of water treatment plant.

P1= effluent from pilot filter column #1

0= Less than the method detection limit (Appendix C)

- = %Reduction was not calculated because of zero in influent

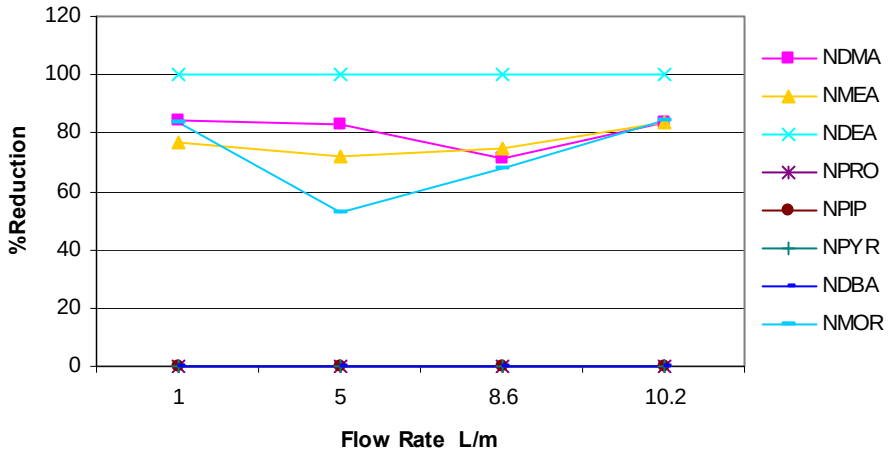

Figure 4.13 Nitrosamine %reductions in chloraminated pilot filter #1 effluent at different flow rates

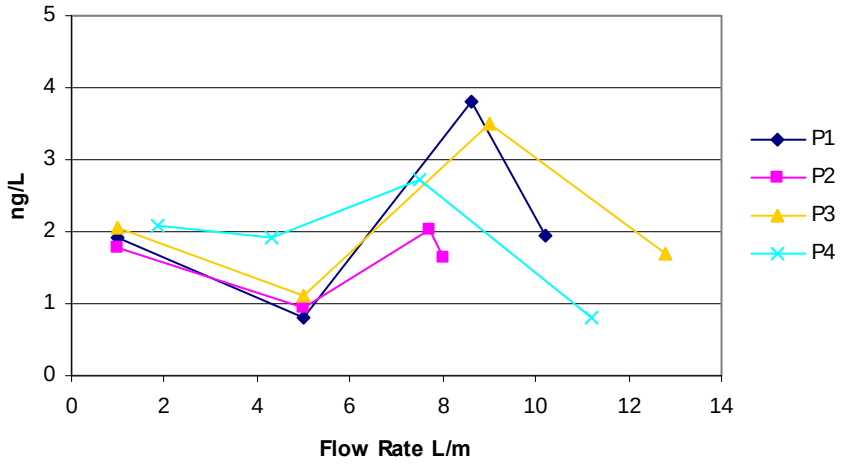

Figure 4.14 NDMA concentrations in chloraminated pilot filter effluents at different flow rate

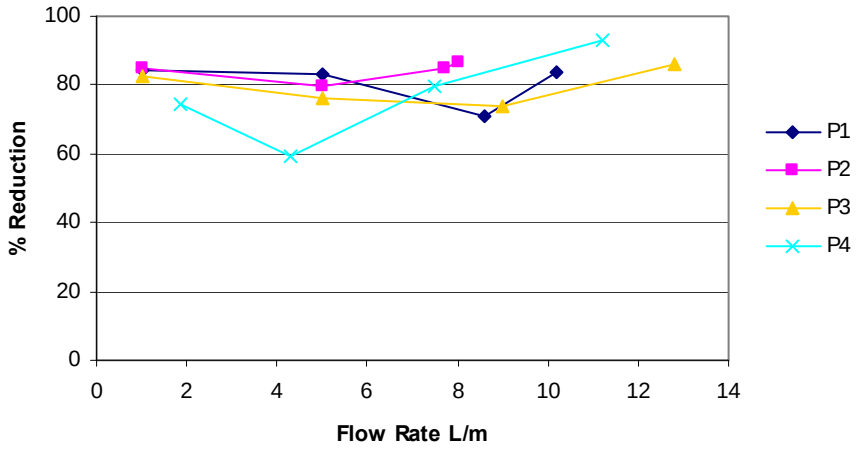

Figure 4.15 NDMA % reductions in chloraminated pilot filter effluents at different flow rate

Chapter 5 Full-Scale, Pilot-Scale Comparison Experiment Results

During this round of experiments, which took about one month, the biomass in the pilot filters was estimated to be approximately in steady state after having operated the pilot filters from February 2007 for approximately six months. The comparability of results obtained at pilot-scale (PS) and full-scale (FS) was investigated by means of different statistical procedures. Analysis of Variance (ANOVA table; Montgomery, 1991) was performed first to show if there was any significant difference between a specific set of filters. Then, independent (regular) t-test and paired t-test (which makes comparisons within matched pairs in two sets of data) calculations were performed where appropriate and, finally, the Least Significant Difference method (LSD) (Montgomery, 1991) was used to make additional comparisons between each pair of filters to determine if the filters performed significantly differently.

The pilot filter operating flow rates were calculated to match the full-scale filter loading rates as closely as possible. A table summarizing the corresponding full-scale and pilot-scale flow rates and loading rates is included in Appendix C (Emelko, 2007). Samples from the filter influents full-scale filter effluents and pilot-scale filter effluents were taken every week for five weeks and examined for several water quality parameters including, chlorine demand, UV254 absorbance, thrihmalomethanes, haloacetic acids and nitrosamines. This chapter presents the results of these experiments.

5.1 Chlorine Demand Variations During the FS/PS Experiments

Chlorine demand measurements were the first tests that were completed. Table 5.1 summarizes the 3-hour chlorine demand results and Figure 5.1 shows these results in graphical format.

Table 5.1 Chlorine demand concentrations during FS/PS experiments (mg/L as Cl_2)

Sampling date / Sample name	Aug 7/07 Loading rate at 10.3 m/h	Aug 13/07 Loading rate at 8 m/h	Aug 20/07 Loading rate at 8 m/h	Aug 27/07 Loading rate at 7.05 m/h	Sep 04/07 Loading rate at 7.05 m/h
Influent 1	4.5	4.2	4.2	4.5	4.6
Influent 2	4.5	4.2	4.2	4.5	4.6
F.S. Filter 1	3.2	3.0	3.4	3.3	3.4
F.S. Filter 2	3.2	3.0	3.4	3.3	3.6
F.S. Filter 3	3.6	3.3	3.6	3.6	3.7
F.S. Filter 4	3.6	3.5	3.6	3.6	3.7
P.S. Filter 1	3.3	3.2	-	-	3.4
P.S. Filter 2	3.3	3.3	3.5	3.5	3.7
P.S. Filter 3	3.6	3.6	3.7	3.8	3.9
P.S. Filter 4	3.6	3.6	3.6	3.8	3.9

- : filter #1 was plugged and no sample was taken

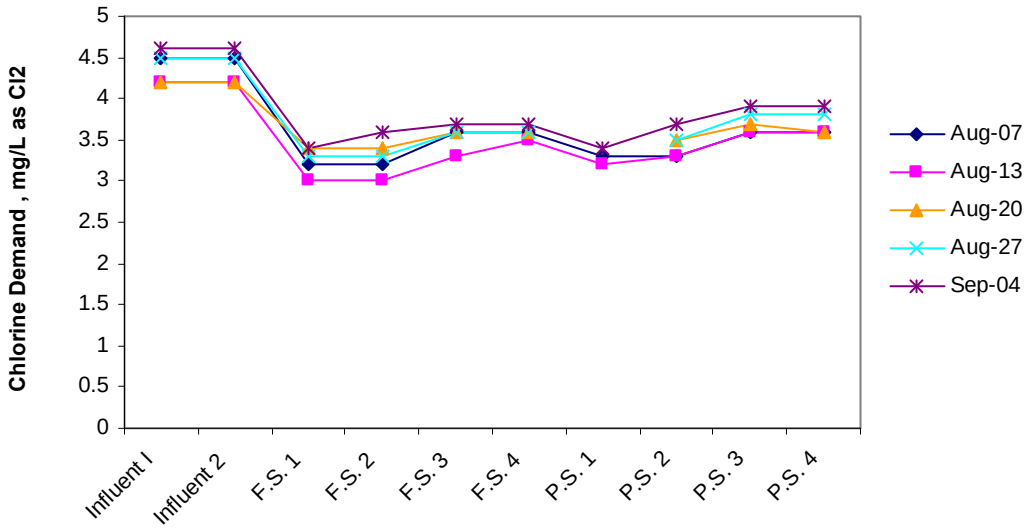

Figure 5.1 Chlorine demand variation during the FS/PS experiments

The chlorine demand range for all full-scale and pilot-scale filter effluents was from 3 to 3.9 mg/L as Cl_2. As well, the chlorine demand of each filter effluent did not change considerably during these experiments, which can be related to the consistent influent chlorine demand of 4.2 to 4.6 mg/L as Cl_2 and the steady performance of the filters.

From Figure 5.1 it is evident that chlorine demand was reduced by all full-scale and pilot-scale filters. As expected, it was reduced more in the GAC filters than in the anthracite filters at both full-scale and pilot-scale, likely because of better biomass growth on the GAC media than on anthracite and also the possibility of some residual adsorptive capacity of the GAC. The chlorine demands of the pilot-scale anthracite filter effluents (P3, P4) were similar to those obtained from the full-scale anthracite filter effluent (F4), and the chlorine demand of the full-scale GAC filter effluents (F1, F2) were similar to those obtained from the pilot-scale GAC filter effluents (P1, P2). However, full-scale filter #3, which had fresh GAC compared

to the other full-scale GAC filters (F1 and F2), appeared to have consistently higher chlorine demand than F1 and F2. F3's lower ability for removing chlorine demand may be because of the fact that it had not been acclimatized for a long period like the other GAC filters, having been in service for only 4 months, and so it just removed chlorine demand by adsorption and not by a combination of biological and adsorption mechanisms.

5.1.1 Chlorine Demand Removal Comparisons for Pilot-Scale Filters

In order to provide a means to compare filter performance from a common perspective, the data were normalized relative to filter influent values to account for variations or changes in water quality that was entering the filters over the series of sampling runs. Therefore, the first set of data comparisons was carried out between the different pilot filter chlorine demand percentage removals. Results from the five sampling runs are shown in Table 5.2 and Figure 5.2.

Table 5.2 Chlorine demand % reduction results in chlorinated pilot filter effluents

	P1	P2	P3	P4
Aug 7/07	26	26	20	20
Aug 13/07	23	21	14	14
Aug 20/07	-	16	11	14
Aug 27/07	-	22	15	15
Sep 4/07	26	19	15	15

- : filter #1 was plugged and no sample was taken

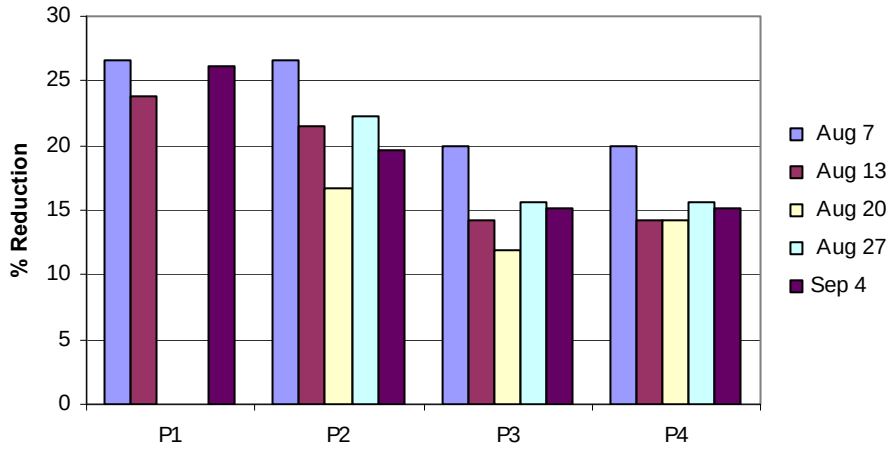

Figure 5.2 Chlorine demand %reduction in chlorinated pilot filter effluents

From Figure 5.2 it would appear that the anthracite filters (P3, P4) performed more consistently and similarly than the GAC filters (P1, P2) during the FS/PS experiments. In order to confirm that the above performance differences were statistically significant, an F-test was performed using an ANOVA table (Table 5.3; Montgomery, 1991). The normality of the data distribution was checked and confirmed prior to performing the ANOVA to compare chlorine demand removals observed in the different pilot filters. The normal probability plot is shown in Appendix D.

The null hypothesis for this set of comparisons is:

Ho: $\mu_{P1} = \mu_{P2} = \mu_{P3} = \mu_{P4}$ in which μ is the mean of each set of filter results.

Table 5.3 ANOVA table for comparison of chlorine demand removal in the pilot filters

Source	df	SS	MS	$F_{observed}$
Filters	3	268	89.3	10.8
Within filters	14	116	8.3	
Total	17	383		

$F_{3,14,0.05} = F_{tabulated} = 3.35 \rightarrow F_{obs} > F_{tabulated}$

Since the observed F of 10.8 is greater than the tabulated F of 3.35, we can therefore reject the null hypothesis and conclude that there are significant differences between the variances in the performances of the pilot filters in regard to chlorine demand removal at a 95 % confidence level.

Then, to determine how the filters are different, the means of comparable filters were compared using the independent (regular) t-test, paired t-test, and the Least Significant Difference (LSD) methods (Montgomery, 1991). In this chapter, before performing an independent t-test between any pair of filters, an F-test was performed to compare the variances of the data sets for two filters, to determine if the variances could be assumed equal to allow use of the pooled variance for subsequent t-test calculations. In cases where the F-test result showed that the compared variances were not equal, Smith-Satterthwaite's approximation was used to determine an appropriate degrees of freedom and a slightly modified version of the t-test was used (Montgomery, 1991). For example, for the pilot GAC filters (P1 and P2) variances comparison, the null hypothesis is *Ho:* $S_1^2 = S_2^2$. Since $F_{observed} = (S_1/S_2)^2 = 6.08$ is less than $f_{4,\ 2,\ 0.005} = 19.25$ (from F table), the null hypothesis can not be

rejected. This confirms that the two variances are not significantly different and as a result, pooled variance was used in the independent t-test calculations.

The null hypothesis for the T-test for the comparison of P1 and P2 comparison is ***Ho:*** $\mu_{P1} = \mu_{P2}$ and the summary of the calculation is as follows:

	P1	P2
Ave	25.5	21.3
STDEV	1.5	3.7
S^2 (Variance)	2.3	13.5

S^2p (pooled variance) = 9.8 → Sp = 3.1 and $T_{obs} = 1.8$

From t-Table:

$T_{0.025,6} = 2.45 \quad \rightarrow \quad T_{obs} < T_{0.025,6}$

Therefore, since the observed T value is less than the tabulated value, the null hypothesis is accepted, which means there was no significant difference between the performance of the different filter media in pilot filters #1 and #2 (GAC filters) in regard to chlorine demand removal at a 95% confidence level. This result was supported by the paired t-test; however the Least Significant Difference (LSD) method showed differences between the performance of P1 and P2. It should be considered that the differences detected by the statistical tests in comparisons involving P1 might be influenced by the smaller number of samples obtained from P1 effluent relative to the other effluents.

The Independent t-test was also used to compare the pair of anthracite pilot filters (P3, P4). Calculations are summarized as follows:

Ho: $\mu_{P3} = \mu_{P4}$

	P3	P4
Ave	15.4	15.9
STDEV	2.9	2.4
S^2 (Variance)	8.7	5.7

S^2p (pooled variance) = 7.2 → Sp = 2.7 and T_{obs} = -0.28

From T–table:

$T_{0.025,8}$ =2.31 → $T_{obs} < T_{0.025,8}$

As was observed for the pair P1 and P2, the null hypothesis for the comparison of P3 and P4 could not be rejected. Therefore, it was concluded that the different uniformity coefficients of anthracite media in P3 and P4 do not affect their performance in terms of their chlorine demand removal at a 95% confidence level.

In order to check if there were significant differences between the performance of the GAC and anthracite pilot filters for removing chlorine demand, all the GAC filter effluent chlorine demand data were pooled together and the anthracite filter effluent chlorine demands were pooled together to make following table to be used in the t-test calculations:

	GAC Filters	Anthracite Filters
Ave	22.9	15.6
STDEV	3.6	2.5
S^2 (Variance)	13.1	6.4

S^2p (pooled variance) = 9.8 → Sp = 3.1 and T_{obs} = 4.9

From t-Table:

$T_{0.025,16}$ =2.12 → $T_{obs} > T_{0.025,16}$

As expected, the t-test result confirms that there was a significant difference between the GAC and anthracite filter performance in regard to chlorine demand removal, confirming what was observed in Figure 5.2 in which the GAC pilot filters appeared to remove a higher percentage of chlorine demand. This result was also confirmed by the paired t-test, and the LSD methods.

5.1.2 Chlorine Demand Removal Comparisons for FS and PS GAC Filters

The performance of the pilot-scale GAC filters (P1 and P2) for removing chlorine demand was compared with that of the full-scale GAC filter that received the same influent water (F3). F3 was chosen for the comparison instead of F1 and F2 because F3 receives the same influent water as P1 and P2. Chlorine demand percentage reductions from the five sampling runs are shown in Table 5.4 and Figure 5.3. Unfortunately, P1 was not operational for two of the sampling runs.

Table 5.4 Chlorine demand %reduction results in chlorinated GAC filter effluents

	P1	P2	F3
Aug 7	26.7	26.7	20.0
Aug 13	23.8	21.4	21.4
Aug 20	-	16.7	14.3
Aug 27	-	22.2	20.0
Sep 4	26.1	19.6	19.6

- : filter #1 was plugged and no sample was taken

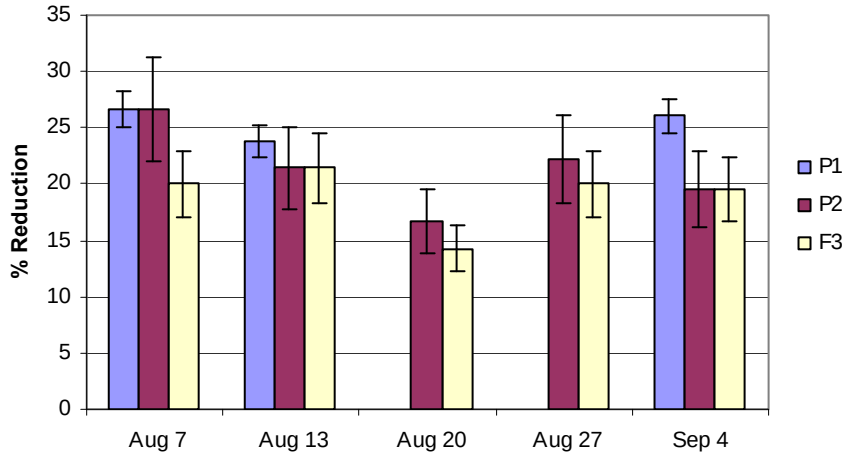

Figure 5.3 Chlorine demand %reduction in chlorinated GAC filter effluents (error bars are %standard deviation calculated from replicate samples)

Figure 5.3 shows P2 and F3 chlorine demand values were very close but it must be verified statistically. P1 also performed similarly to P2, although there were fewer data with which to make comparisons.

To confirm that above performance differences were statistically significant, ANOVA was first performed on the data. Performing an F-Test by means of following ANOVA Table (Table 5.5) demonstrated significant difference between the performance of the GAC filters at a 95% confidence level because the $F_{observed}$ value is greater than the tabulated value of F. Then the chlorine demand results from each pair of filters in this set were compared using the independent t-test, paired t-test, and LSD method. The following independent t-test for P1 and F3 comparison shows that the $T_{observed}$ value is greater than the tabulated value of T, therefore, the null hypothesis is rejected and it can be considered that there was a significant

difference between P1 and F3 performance in regard to chlorine demand removal at a 95% confidence level.

Table 5.5 ANOVA table for comparison of chlorine demand removal in GAC filters

Ho: $\mu_{P1} = \mu_{P2} = \mu_{F3}$

Source	df	SS	MS	$F_{observed}$
Filters	2.0	78.5	39.2	4.4
Within filter	10.0	89.1	8.9	
Total	12.0	167.6		

$F_{2,10,0.05} = 4.10 \quad \rightarrow \quad F_{obs} > F_{tabulated}$

Ho: $\mu_{P1} = \mu_{F3}$

	P1	F3
Ave	25.5	19.1
STDEV	1.5	2.8
S^2 (Variance)	2.3	7.6

$S^2p = 5.83 \rightarrow Sp = 2.41$ and $T_{obs} = 3.66$

From t-Table:

$T_{0.025, 6} = 2.45 \rightarrow T_{obs} > T_{0.025, 6}$

The LSD test result also supported the t-test result. However, the paired t-test showed no difference between the performance of the different GAC media in F3 and P1 in regard to chlorine demand removal. As mentioned before, there were only three data points dataset for P1 that could be used since it was out of service for two sampling runs.

In contrast to the comparison of P1 and P3, independent and paired t-tests and the LSD results showed that there is no significant difference between the performance of P2 and F3 in regard to chlorine demand removal at a 95% confidence level. The following table shows the independent T-test for the comparison between the performance of P2 and F3.

Ho: $\mu_{P2} = \mu_{F3}$

	P2	F3
Ave	21.3	19.1
STDEV	3.7	2.8
S^2 (Variance)	13.5	7.6

$S^2p = 10.57 \rightarrow Sp = 3.25$ and $T_{obs} = 1.1$

From t-Table:

$T_{0.025,8} = 2.31 \rightarrow T_{obs} < T_{0.025,8} \rightarrow$ Ho is accepted

The comparison of the GAC pilot-scale filters (P1and P2) with each other was described in Section 5.1.1 and indicated that there was no significant difference in the performance of these filters with respect to chlorine demand removal.

5.1.3 Chlorine Demand Removal Comparisons for FS and PS Anthracite Filters

In this set of comparisons, the chlorine demand percentage removal in the anthracite full-scale (F4) and pilot-scale (P3 and P4) filters was evaluated. Results are given in Table 5.6 and Figure 5.4.

Table 5.6 Chlorine demand %reduction results in chlorinated anthracite filter effluents

	P3	P4	F4
Aug 7	20.0	20.0	20.0
Aug 13	14.3	14.3	16.7
Aug 20	11.9	14.3	14.3
Aug 27	15.6	15.6	20.0
Sep 4	15.2	15.2	19.6

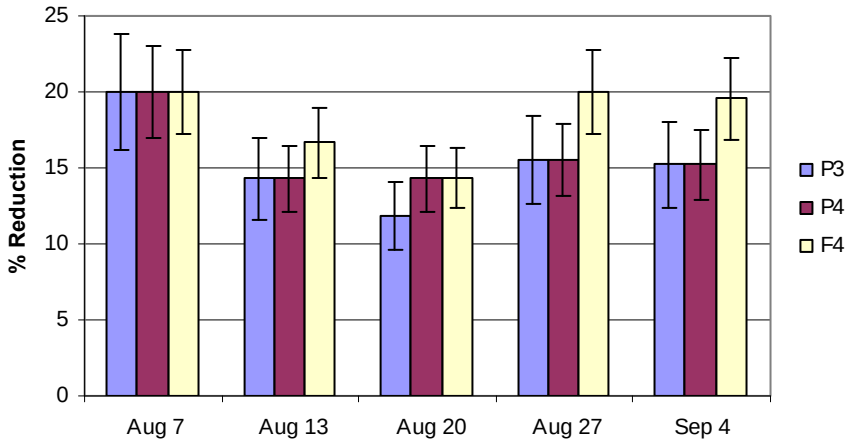

Figure 5.4 Chlorine demand %reduction in chlorinated anthracite filter effluents (error bars are %standard deviation calculated from replicate samples)

To confirm that above performance differences were statistically significant, ANOVA was first performed on the data. Unlike the results from the FS/PS GAC filters, results from the ANOVA Table (Table 5.7) identified no significant difference between the anthracite filter performances to achieve chlorine demand removal at a 95% confidence level.

Table 5.7 ANOVA table for comparison of chlorine demand removal in anthracite filters

Ho: $\mu_{P3} = \mu_{P4} = \mu_{F4}$

Source	df	SS	MS	$F_{observed}$
filters	2.0	20.9	10.5	1.5
Within filter	12.0	83.2	6.9	
Total	14.0	104.2		

$F_{2,12,0.05} = 3.89 \quad \rightarrow \quad F_{obs} < F_{tabulated}$

Information for the independent t-test for the pair P3 and F4 is as follows:

Ho: $\mu_{P3} = \mu_{F4}$

	P3	F4
Ave	15.4	18.1
STDEV	2.9	2.5
S^2 (Variance)	8.7	6.5

$S^2p = 7.58 \rightarrow Sp = 2.75$ and $T_{obs} = -1.56$

From t-Table:

$T_{0.025,8} = 2.31 \rightarrow T_{obs} < T_{0.025,8} \rightarrow$ Ho is accepted

The null hypothesis failed to be rejected; therefore, there was no considerable difference between the performance of the different anthracite media in P3 and F4 in regard to chlorine demand removal at a 95% confidence level. However, the result from the paired t-test was opposite to the independent T-test result.

Three different statistical tests were carried out to compare P4 and F4 and all results showed that there was no considerable difference between their performances at a 95% confidence level in regard to chlorine demand removal. Following is the calculation for comparison of P2 and F4 using the independent T-test.

Ho: $\mu_{P4} = \mu_{F4}$

	P4	F4
Ave	15.9	18.1
STDEV	2.4	2.5
S^2 (Variance)	5.7	6.5

$S^2p = 6.07 \rightarrow Sp = 2.46$ and $T_{obs} = -1.43$

From t-Table:

$T_{0.025,8} = 2.31 \rightarrow$ T obs$< T_{0.025,8} \rightarrow$ Ho is accepted

Statistical test results for P3 comparing and P4 comparison were explained in Section 5.1.1, and showed that there was no significant difference in the performance of these filters with respect to chlorine demand removal.

5.1.4 Chlorine Demand Removal Comparisons for Full-Scale GAC Filters

Chlorine demand removal in full-scale GAC filters were also compared as the last set of comparisons (Table 5.8 and Figure 5.5).

Table 5.8 Chlorine demand %reduction results in chlorinated full-scale GAC filter effluents

	F1	F2	F3
Aug 7	29	29	20
Aug 13	29	29	21
Aug 20	19	19	14
Aug 27	27	27	20
Sep 4	26	22	20

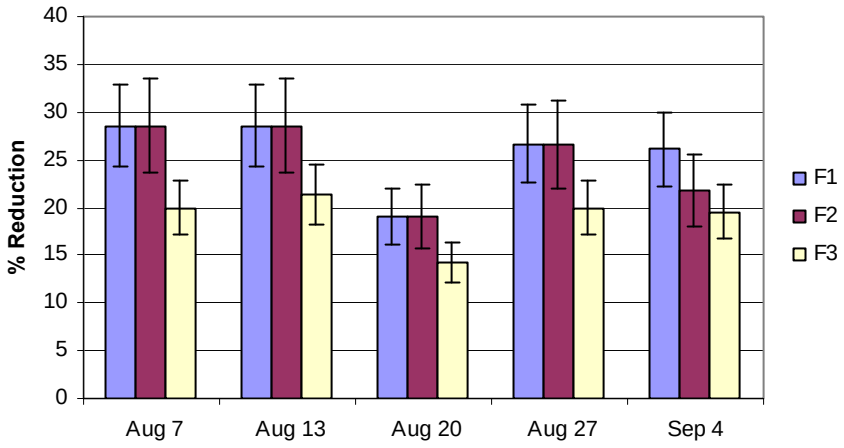

Figure 5.5 Chlorine demand %reduction in chlorinated full-scale GAC filter effluents (error bars are % standard deviation calculated from replicate samples)

Figure 5.5 shows that older GAC full-scale filters (F1 and F2) performed quite similarly and more efficiently than the fresh GAC (F3) in regard to chlorine demand removal. To confirm that above performance differences were statistically significant, ANOVA was first performed on the data. Analysis of variance (ANOVA Table 5.9) was carried out to

distinguish any overall differences in their performance and, subsequently t-tests showed which pair of filters performed significantly differently.

Table 5.9 ANOVA table for comparison of chlorine demand removal in full-scale GAC filters

Ho: $\mu_{F1} = \mu_{F2} = \mu_{F3}$

Source	df	SS	MS	$F_{observed}$
Filters	2	134.1	67.0	4.8
Within filter	12	166.5	13.9	
Total	14	300.6		

$F_{2,12,0.05} = 3.89 \quad \rightarrow \quad F_{obs} > F_{tabulated}$

Since the observed F is greater than the tabulated value of F, the null hypothesis can be rejected which confirms that there were significant differences between the performances of these filters in regard to chlorine demand removal at a 95% confidence level. Then each pair of full-scale GAC filters was compared using three different statistical tests.

Ho: $\mu_{F1} = \mu_{F2}$

	F1	F2
Ave	25.8	24.9
STDEV	3.9	4.3
S^2 (Variance)	15.4	18.6

$S^2p = 17.01 \rightarrow Sp = 4.12$ and $T_{obs} = 0.33$

From t-Table:

$T_{0.025,8} = 2.31 \rightarrow$ T obs$< T_{0.025,8} \rightarrow$ Ho is accepted

The observed T value is less than tabulated values which means there was no significant difference between F1 and F2 in regard to chlorine demand removal at a 95% confidence level. Performing the independent t-test (using the following data) to compare the performance of F1 with F3 shows that the F1 performance is significantly different from that of F3 in regard to chlorine demand removal at a 95% confidence level. This was also true for F2 and F3.

Ho: $\mu_{F1} = \mu_{F3}$

	F1	F3
Ave	25.8	19.1
STDEV	3.9	2.8
S^2 Variance	15.4	7.6

$S^2p = 11.5 \rightarrow Sp = 3.4$ and $T_{obs} = 3.14$

From t-Table:

$T_{0.025,8} = 2.31 \rightarrow$ T obs$>T_{0.025,8} \rightarrow$ Ho is rejected

Ho: $\mu_{F1} = \mu_{F2}$

	F2	F3
Ave	24.9	19.1
STDEV	4.3	2.8
S^2 Variance	18.6	7.6

$S^2p = 13.1 \rightarrow Sp = 3.6$ and $T_{obs} = 2.57$

From t-Table:

$T_{0.025,8} = 2.31 \rightarrow$ T obs$>T_{0.025,8} \rightarrow$ Ho is rejected

The LSD method and paired t-test were also performed. They both supported the above t-test results, and confirm that although the two older GAC filters were performing similarly, the filter with the newer GAC did not remove chlorine demand as well. While this was likely because of the age of the media, as described previously, it may have also been influenced by differences in the performances of upstream treatment unit processes (beyond the scope of this study).

5.2 UV254 absorbance Variation During the FS/PS Experiments

As was done for the experiments concerning flow rate effects described in Chapter 4, UV254 absorbance was measured (1 cm path length) when comparing full-scale and pilot-scale filter performance as an indicator of the active parts of organic disinfection by-product (DBP) precursor molecules, which are correlated to the disinfection by-product formation potential. Unfortunately, due to problems with analytical equipment there are only two sets of UV254 absorbance data (Table 5.10 and Figure 5.6) for FS/PS experiments. Nevertheless, the UV absorbance trends confirm the general trends in the DBPs that were measured (to be described in Sections 5.3, 5.4 and 5.5). The data showed that there was a greater UV254 absorbance associated with the influent water samples than with samples of filter effluents. The data also showed that the anthracite filters (full-scale and pilot-scale) performed less well than full-scale and pilot-scale GAC filters in regard toUV254 absorbance removal.

Table 5.10 UV254 absorbance values during the FS/PS experiments

Sampling date / Sample name	Aug 7/07	Aug 13/07
Influent 1	0.030	0.028
Influent 2	0.028	0.036
F.S. Filter 1	0.016	0.013
F.S. Filter 2	0.017	0.011
F.S. Filter 3	0.014	0.010
F.S. Filter 4	0.020	0.016
P.S. Filter 1	0.015	0.007
P.S. Filter 2	0.018	0.016
P.S. Filter 3	0.025	0.018
P.S. Filter 4	0.027	0.018

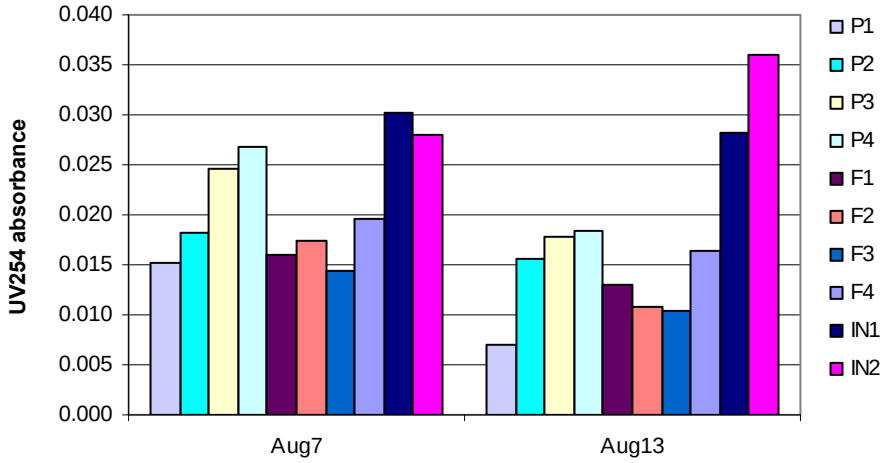

Figure 5.6 UV254 absorbance variation during the FS/PS experiments

5.3 Trihalomethane Variations During FS/PS Experiments

Figure 5.7 illustrates THM species variations in chlorinated pilot filter #2 effluent as a typical filter. THM data for the other filters are given in Appendix A.

During this part of the research, trihalomethane species concentrations ranged from 10 to 30 μg/L in the different full-scale and pilot-scale filter effluents (which were all above the trihalomethane method detection limits that are reported in Appendix C). Higher concentrations of $CHCl_2Br$ and $CHCBr_2$ relative to the other species were observed due to the moderately high level of bromide in Grand River water and a rapid reaction between bromide and organic compounds in the presence of chlorine.

Also TTHM concentration ranged from 55 to 99 μg/L in all filter effluents, which is lower than the current regulated limits. TTHM levels of finished water would be expected to decrease even more before it enters the drinking water distribution system because treatment plant finished water is mixed with ground water prior to distribution.

TTHM concentrations in all full-scale and pilot-scale filter effluents and influents are presented in Figure 5.8. Generally, the figure suggests that there were higher concentrations of TTHM in the chlorinated pilot filter effluents than in the chlorinated full-scale filter effluents in all sampling events. However, differences between the filters in their performance to achieve TTHM precursor removal will be evaluated statistically in subsequent sections.

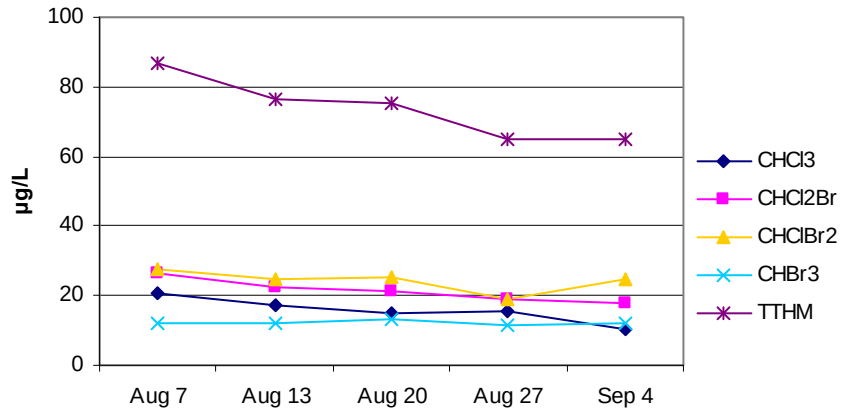

Figure 5.7 THM concentrations in chlorinated pilot filter #2 effluent during the FS/PS experiments

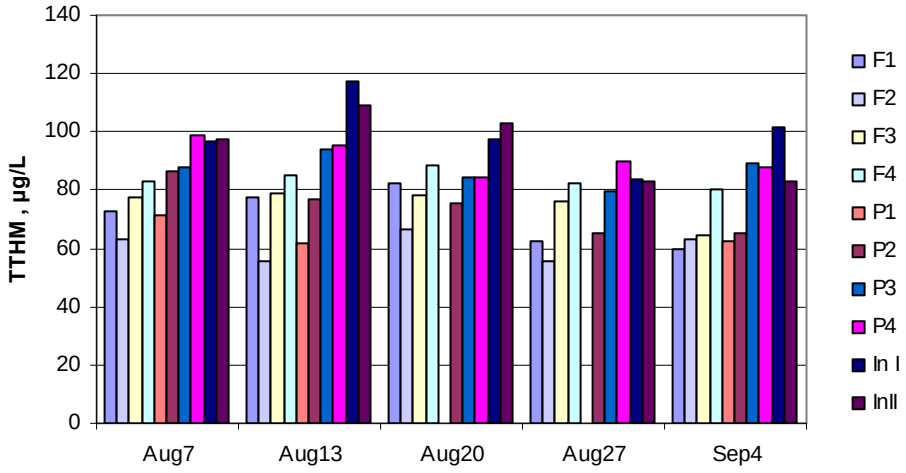

Figure 5.8 Comparing TTHM concentrations in chlorinated FS and PS filter effluents

5.3.1 TTHM Precursor Removal Comparisons for Pilot-Scale Filters

In the first set of comparisons, the behavior of the pilot filters in reducing TTHM formation was compared using five sampling run results. TTHM data were normalized to eliminate influent variations, and Table 5.11 and Figure 5.9 summarize the TTHM percentage reductions in the pilot filters. The better performance for the GAC filters in regard to trihaomethane precursors removal (with an average of 30% reduction) compared to the anthracite filters (with an average of 12% reduction) is shown in Figure 5.9. However, the differences between the performance of the pilot filters must be evaluated statistically.

Table 5.11 TTHM %reduction results in chlorinated pilot filter effluents

	P1	P2	P3	P4
Aug 7	28.6	11.2	9.8	6.5
Aug 13	43.4	30.0	13.8	13.1
Aug 20	-	26.8	17.8	17.7
Aug 27	-	27.5	11.3	1.1
Sep 4	37.9	35.1	15.4	15.4

- : filter #1 was plugged and no sample was taken

In order to confirm that the above performance differences were statistically significant, an F-test was performed using the ANOVA Table. The normality of data distribution was checked prior to performing ANOVA to compare TTHM precursor removals observed in the different pilot filters, and the normal probability plot is shown in Appendix D.

From the following ANOVA Table (Table 5.12) and the greater value of F_{obs} relative to tabulated value of F, it is concluded that there were significant differences between the

performances of pilot filters at a 95% confidence level in regard to TTHM precursor removal.

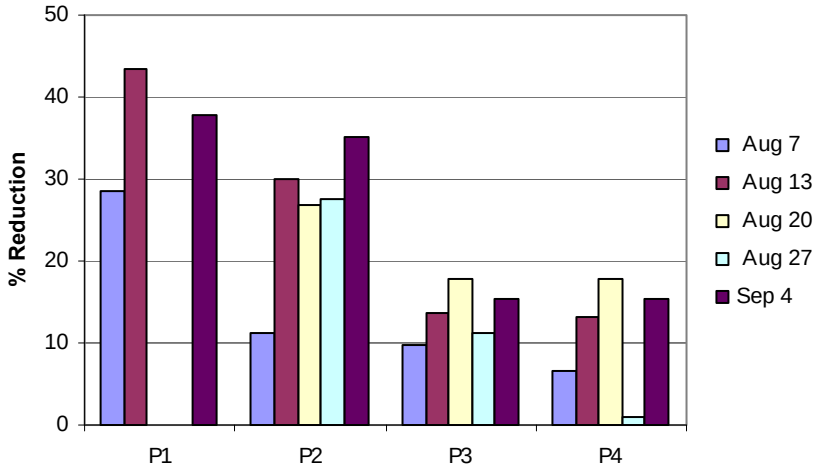

Figure 5.9 TTHM % reductions in chlorinated pilot filter effluents

Table 5.12 ANOVA table for comparison of TTHM precursor removal in the pilot filters

Ho: $\mu_{P1} = \mu_{P2} = \mu_{P3} = \mu_{P4}$

Source	df	SS	MS	$F_{observed}$
Filters	3	1648.5	549.5	11.7
Within filter	14	660.1	47.1	
Total	17	2308.6		

$F_{3,\ 14,0.05} = 3.35 \rightarrow F_{obs} > F_{tabulated}$

Subsequently, similar to the procedures outlined in Section 5.1.1, t-tests were carried out to determine if the pilot filters were different in their performance to achieve TTHM removal.

For the P1 and P2 comparison, the observed T (1.69) was compared with the tabulated value (2.45). Since $T_{obs} < T_{tabulated}$, Ho: $\mu_{P1} = \mu_{P2}$ is not rejected and no significant difference was distinguished between the performance of P1 and P2 (pilot GAC filters) performance in regard to TTHM precursor removal at a 95% confidence level. The paired t-test also confirmed the similarity between the performances of these two filters while the LSD method did not. The differences detected here are likely due to the smaller number of samples obtained from the P1 effluent relative to the other effluents.

The independent and paired t-tests and also the LSD method were performed and no significant difference was observed between the performance of P3 and P4 (pilot-scale anthracite filters) in regard to TTHM precursor removal at a 95% confidence level.

Finally, as expected, two different kinds of t-tests results, obtained from the comparison between the GAC pilot filters and the anthracite pilot filters, showed $T_{obs} > T_{tabulated}$. This means there is a significant difference between these two different types of filter media in regard to TTHM precursor removal at a 95% confidence level.

5.3.2 TTHM Precursor Removal Comparisons for FS/PS GAC Filters

The two pilot scale filter columns that contained GAC (P1 and P2) were compared with F3 in regard to their ability to affect trihalomethane precursor concentrations. F3 was chosen for the comparison instead of F1 and F2 because F3 receives the same influent water as P1 and P2. Table 5.13 and Figure 5.10 represent TTHM percentage reduction results for these GAC filters from in five rounds of sampling, which were used in this set of comparisons.

Table 5.13 TTHM %reduction results in chlorinated GAC filter effluents

	P1	P2	F3
Aug 7	28.6	11.2	20.8
Aug 13	43.4	30.0	27.9
Aug 20	-	26.9	29.7
Aug 27	-	27.5	14.6
Sep 4	37.9	35.1	36.0

- : filter #1 was plugged and no sample was taken

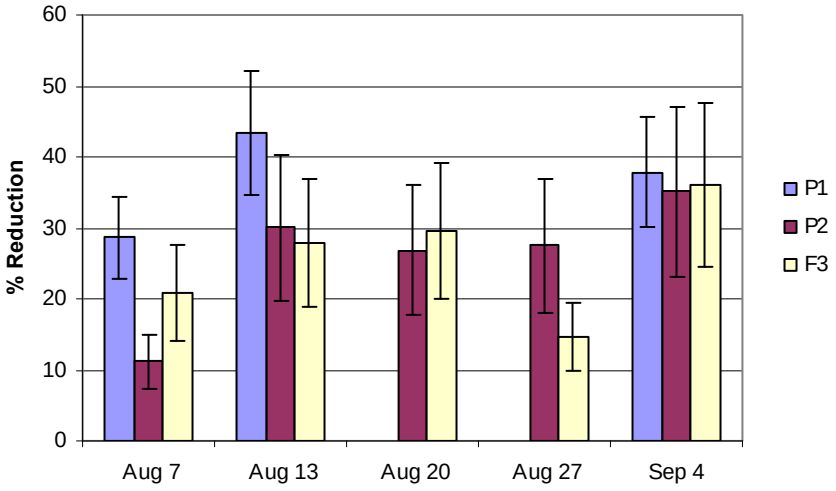

Figure 5.10 TTHM %reductions in chlorinated GAC filter effluents (error bars are % standard deviation calculated from replicate samples)

To confirm that above performance differences were statistically significant, ANOVA was first performed on the data. The above results were used to make an ANOVA table (Table 5.14).

Table 5.14 ANOVA table for comparison of TTHM precursor removal in GAC filters

Ho: $\mu_{P1} = \mu_{P2} = \mu_{F3}$

Source	df	SS	MS	$F_{observed}$
Filters	2	261.7	130.8	1.8
Within filter	10	714.5	71.5	
Total	12	976.2		

$F_{2,10,0.05} = 4.10 \quad \rightarrow \quad F_{obs} < F_{tabulated}$

Since $F_{obs} > F_{tabulated}$, the null hypothesis is accepted and it is concluded that there was no significant difference between the performance of the different GAC filters in regard to TTHM removal at a 95% confidence level.

The independent t-test, paired t-test and LSD tests again were conducted to compare the performance of P1 with F3 and also to compare P2 and F3, and all these tests resulted in the acceptance of the two null hypotheses $\mu_{P1} = \mu_{F3}$ and $\mu_{P2} = \mu_{F3}$. These results confirm that there were not any considerable differences between the performance of the GAC filters at a 95% confidence level in regard to THM precursor removal.

5.3.3 TTHM Precursor Removal Comparisons for FS/PS Anthracite Filters

The full-scale and pilot-scale anthracite filters were also compared. TTHM results for these filter effluents are given in Table 5.15 and Figure 5.11.

Table 5.15 TTHM %reduction in chlorinated anthracite filter effluents

	P3	P4	F4
Aug 7	9.8	6.5	15.3
Aug 13	13.8	13.1	22.2
Aug 20	17.8	17.7	14.0
Aug 27	11.3	1.1	7.8
Sep 4	15.4	15.4	20.1

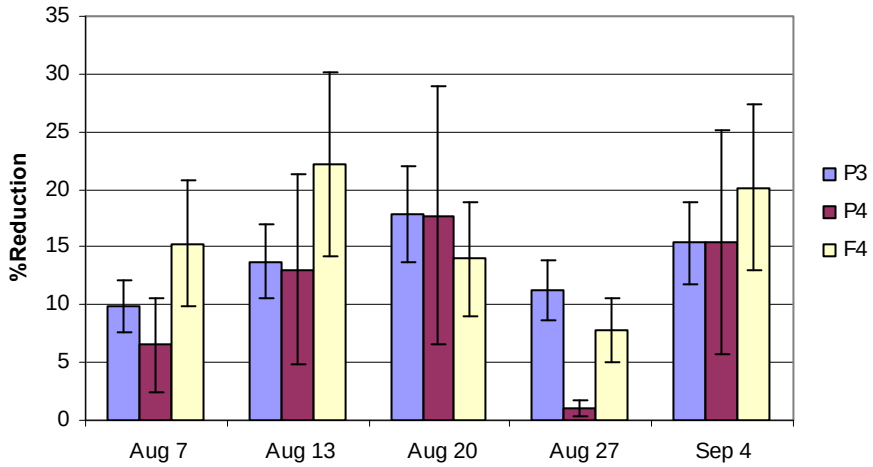

Figure 5.11 TTHM %reduction in chlorinated anthracite filter effluents (error bars are % standard deviation calculated from replicate samples)

To confirm that above performance differences were statistically significant, ANOVA was first performed on the data. It was concluded from the ANOVA table (Table 5.16) that no significant differences were evident between the anthracite filter performances in regard to TTHM removal at a 95% confidence level.

Table 5.16 ANOVA table for comparison of TTHM precursor removal in anthracite filters

Ho: $\mu_{p3} = \mu_{P4} = \mu_{F4}$

Source	df	SS	MS	$F_{observed}$
Filters	2.0	65.7	32.9	1.1
Within filter	12.0	356.3	29.7	
Total	14.0	422.0		

$F_{2,12,0.05} = 3.89 \quad \rightarrow \quad F_{obs} < F_{tabulated}$

The independent t-test, paired t-test and LSD tests were conducted for the P3 and F4 pair comparison and also for the P4 and F4 pair comparison and all confirmed that the anthracite filters performed similarly at a 95% confidence level in regard to TTHM precursor removal regardless of the slightly different physical characteristics of the media.

5.3.4 TTHM Precursor Removal Comparisons for Full-Scale GAC Filters

The performance of the full-scale GAC filters for removing TTHM precursor was also compared, since the GAC media in F3 was fresher relative to the GAC media in F1 and F2. TTHM results are given in Table 5.17 and Figure 5.12.

To confirm that above performance differences were statistically significant, ANOVA was first performed on the data. The null hypothesis of $\mu_{F1} = \mu_{F2} = \mu_{F3}$ was tested by means of an ANOVA table (Table 5.18).

Table 5.17 TTHM %reduction in chlorinated full-scale GAC filter effluents

	F1	F2	F3
Aug 7	25.0	34.7	20.8
Aug 13	33.9	42.5	27.9
Aug 20	15.1	31.3	29.7
Aug 27	25.7	33.8	14.6
Sep 4	41.0	37.5	36.0

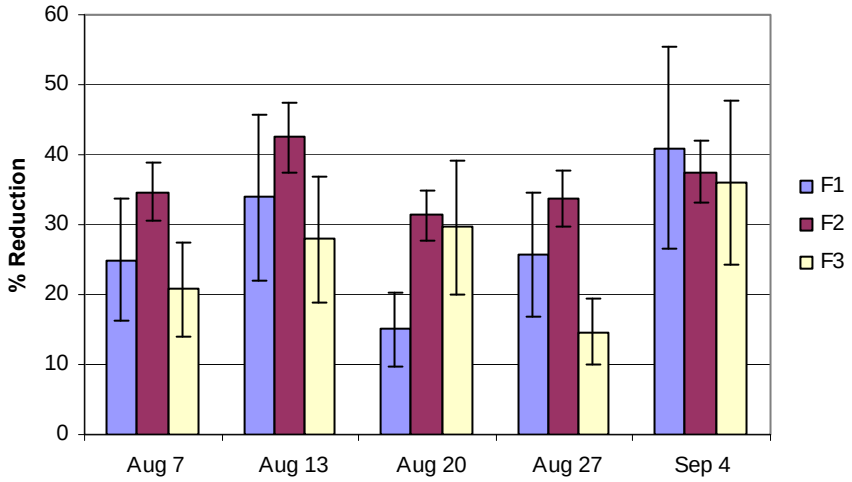

Figure 5.12 TTHM %reduction in chlorinated full-scale GAC filter effluents (error bars are % standard deviation calculated from replicate samples)

Table 5.18 ANOVA table for comparison of TTHM precursor removal in full-scale GAC filters

Ho: $\mu_{F1} = \mu_{F2} = \mu_{F3}$

Source	df	SS	MS	$F_{observed}$
Filters	2	281.4	140.7	2.3
Within filter	12	729.8	60.8	
Total	14	1011.3		

$F_{2,12,0.05} = 3.89 \quad \rightarrow \quad F_{obs} < F_{tabulated}$

Since the observed value of F is less than the tabulated value, the ANOVA analysis does not show any significant difference between these filters in their performance to achieve TTHM removal at a 95% confidence level. Independent and paired t-tests and also the LSD test did not show any considerable difference neither between the performance of similar GAC media in F1 and F2 nor between the performance of different GAC media in F1 and F3. However, F2 and F3 showed different performance in regard to TTHM precursor removal when independent and paired t-tests were used for comparison. This difference can be seen also by looking at Figure 5.12, in which there are fewer overlaps of the error bars for F2 and F3.

5.4 Haloacetic Acid Variations During the PS/FS Experiments

Six of the nine possible haloacetic acids (HAAs) were measured (to be comparable with DWSP) in the chlorinated influents and the effluents of the full-scale and pilot-scale filters. Individual HAA species were detected at very low concentrations and (less than current regulated limits). They varied from 0.45 to 4.7 μg/L in the filter effluents in five rounds of sampling, except for chloroacetic acid and bromoacetic acid which were not detected in any

filter effluent sample. Figure 5.13 represents HAA species concentrations in chlorinated pilot filter #2 effluent, selected as a typical filter in this study. HAA data for the other filters are given in Appendix A.

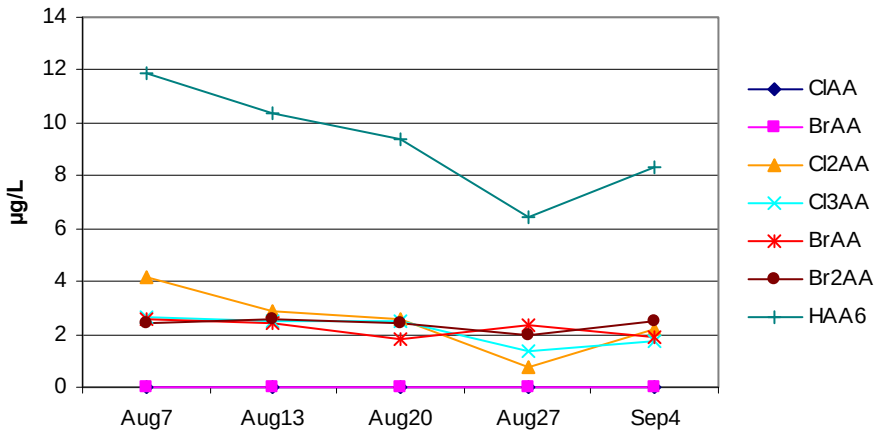

Figure 5.13 HAA6 concentrations in chlorinated pilot filter #2 effluent during the FS/PS experiments

HAA6 concentrations in the chlorinated influents and full-scale and pilot-scale filter effluents are compared in Figure 5.14. From Figure 5.14 it would appear that the pilot-scale filter effluents showed lower concentrations of HAA precursors than the full-scale filter effluents, which means they performed better in reducing HAA6 concentrations in general (same as their performance in regards to TTHM precursor removal). Statistical comparisons of the filters are studied in subsequent sections.

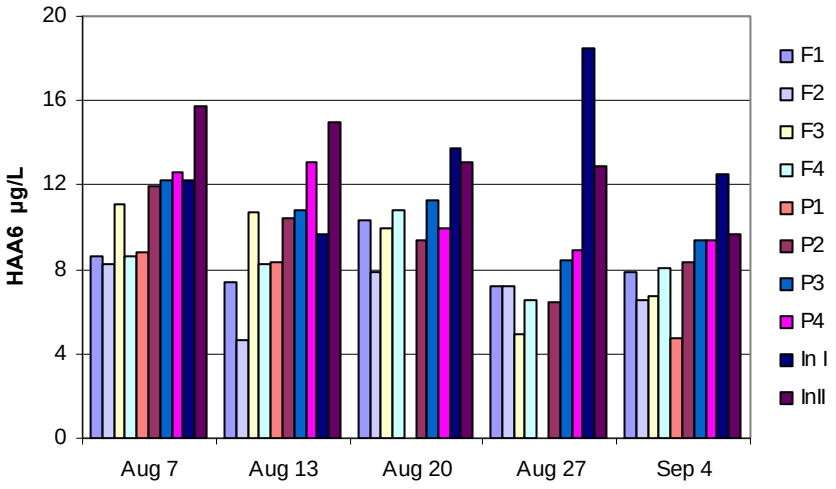

Figure 5.14 Comparing HAA6 concentrations in chlorinated FS and PS filter effluents

5.4.1 HAA6 Precursor Removal Comparisons for Pilot-Scale Filters

In this section, HAA6 data were normalized relative to filter influent values, and HAA6 percentage reductions in the pilot filters were compared using the five filter run results (Table 5.19 and Figure 5.15).

Table 5.19 HAA6 %reduction in chlorinated pilot filter effluents

	P1	P2	P3	P4
Aug 7	44.1	24.4	22.5	20.0
Aug 13	44.7	38.3	27.7	13.0
Aug 20	-	28.6	14.1	23.7
Aug 27	-	50.5	35.1	30.9
Sep 4	50.0	11.2	3.1	3.6

- : filter #1 was plugged and no sample was taken

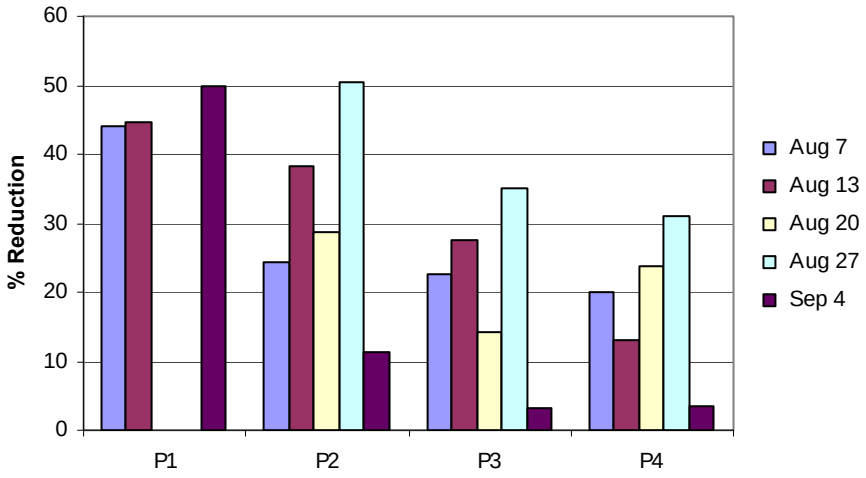

Figure 5.15 HAA6 %reduction in chlorinated pilot filter effluents

Despite the observed variations in HAA6 results due to low HAA concentrations, from the results it is evident that overall HAA6 precursor removal is higher in the GAC filters (with average of 38.4% reduction) than in the anthracite filters (with average of 19.4% reduction). In addition, results show that pilot filters performed better in regards to HAA precursor removal than THM precursor removal by an average of 31.3% for the GAC filters and 12.1% for the anthracite filters.

In order to check if there were significant differences between the performance of the pilot filters for removing HAA6 precursors, the above results were assembled into an ANOVA table (Table 5.20). Normality of data distribution was checked prior to performing ANOVA table for HAA6 precursor removal comparison in pilot filters and normal probability plot was shown in Appendix D.

Table 5.20 ANOVA table for comparison of HAA6 precursor removal in the pilot filters

Ho: $\mu_{P1} = \mu_{P2} = \mu_{P3} = \mu_{P4}$

Source	df	SS	MS	$F_{observed}$
Filters	3	13801.9	4600.6	33.2
Within filter	14	1942.8	138.8	
Total	17	15744.8		

$F_{3, 14, 0.05} = 3.35 \rightarrow F_{obs} > F_{tabulated}$

Since $F_{obs} > F_{tabulated}$, there were significant differences between the pilot filters in their performance to achieve HAA6 removal at a 95% confidence level. In addition, the independent t-test, paired t-test, and LSD test were carried out to distinguish if the pilot-scale filters (with either the same or different types of media) performed differently in terms of their HAA6 removal. Comparison results obtained from above mentioned tests at a 95% confidence level supported each other and are summarized in Table 5.21.

Table 5.21 Results of comparisons for HAA6 precursor %reduction in the pilot filters

	P2	**P4**	**GAC Filters**
P1	No significant difference		
P3		No significant difference	
Anthracite Filters			Significant difference

5.4.2 HAA6 Precursor Removal Comparisons for FS/PS GAC Filters

Table 5.22 and Figure 5.16 show data related to HAA% reductions in the three GAC filters. To confirm that above performance differences were statistically significant, ANOVA (Table 5.23) was first performed on the data.

Table 5.22 HAA6 %reduction in chlorinated GAC filter effluents

	P1	P2	F3
Aug 7	44.1	24.4	29.8
Aug 13	44.7	38.3	28.7
Aug 20	-	28.6	23.7
Aug 27	-	50.5	61.7
Sep 4	51.5	13.9	30.4

- : filter #1 was plugged and no sample was taken

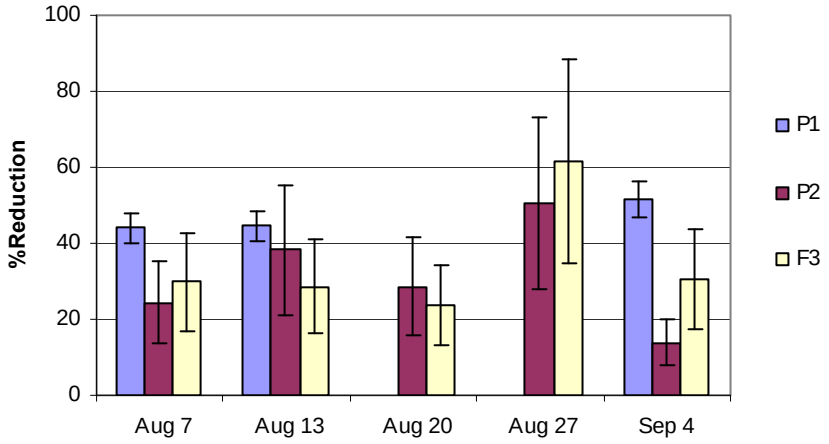

Figure 5.16 HAA6 %reductions in chlorinated GAC filters (error bars are % standard deviations calculated from replicate samples)

Table 5.23 ANOVA table for comparison of HAA precursor removal in GAC filters

Ho: $\mu_{P1} = \mu_{P2} = \mu_{F3}$

Source	df	SS	MS	$F_{observed}$
Filters	2	471.3	235.7	1.4
Within filter	10	1740.2	174.0	
Total	12	2211.5		

$F_{2,10,0.05} = 4.10 \quad \rightarrow \quad F_{obs} < F_{tabulated}$

According to the ANOVA table, since $F_{obs} < F_{tabulated}$ there were no significant differences between any of the GAC filter performances in regard to HAA removal. Independent t-test and LSD results also showed no significant differences between the performance of P1 and F3 while a paired t-test, using the differences between paired data to make a more accurate comparison, was able to identify differences between their performance in regard to HAA6 precursor removal at a 95% confidence level. It should be noted that low HAA concentrations can affect the statistical test results. Regardless, these statistical tests showed no significant difference between the performance of P2 and F3 performance for removing HAA6 precursor at a 95% confidence level, and all of these results are summarized in Table 5.24

Table 5.24 Results of comparison for HAA6 precursor %reduction in GAC filters

	P1	P2
F3	Significant difference	No significant difference
P2	No significant difference	

5.4.3 HAA6 Removal Comparisons for FS/PS Anthracite Filters

In this set of comparison, HAA % reduction in the anthracite filters (given in Table 5.25 and Figure 5.17) are compared.

Table 5.25 HAA6 %reduction in chlorinated anthracite filter effluents

	P3	P4	F4
Aug 7	22.5	20.0	45.4
Aug 13	27.7	13.0	45.0
Aug 20	14.1	23.7	17.6
Aug 27	35.1	30.9	49.4
Sep 4	3.1	3.6	17.0

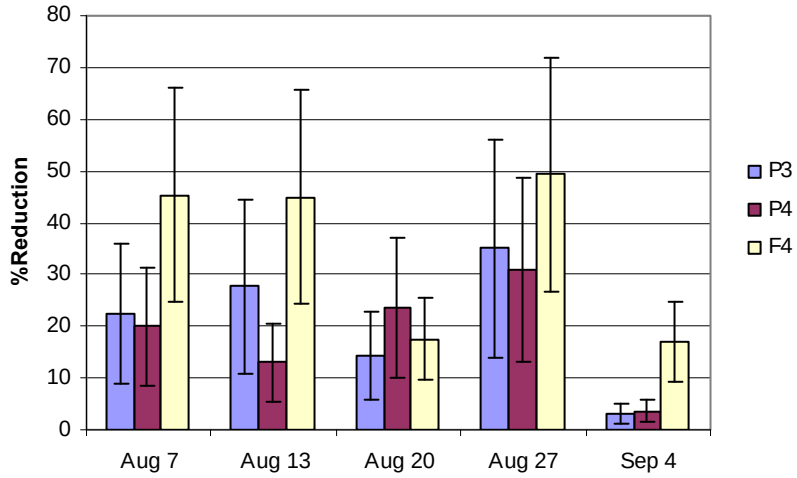

Figure 5.17 HAA6 %reduction in chlorinated anthracite filter effluents (error bars are % standard deviation calculated from replicate samples)

To confirm that above performance differences were statistically significant, ANOVA was first performed on the data. It is observed from the following ANOVA table (Table 5.26) that there is no significant difference between the performance of the anthracite filters at a 95% confidence level in regard to HAA precursor reduction.

Table 5.26 ANOVA table for comparison of HAA6 precursor removal in anthracite filters

Ho: $\mu_{P3} = \mu_{P4} = \mu_{F4}$

Source	df	SS	MS	$F_{observed}$
Filters	2	813.5	406.8	2.3
Within filter	12	2087.9	174.0	
Total	14	2901.4		

$F_{2,12,0.05} = 3.89 \quad \rightarrow \quad F_{obs} < F_{tabulated}$

The independent t-test and the LSD test showed no significant difference between any pair of these anthracite filters in regard to HAA6 precursor removal at a 95% confidence level. However, paired t-tests did not support above comparison results. Paired t-tests showed differences between the performance of P3 and F4 for HAA6 removal, and since for the P4 and F4 paired t-test the observed value of T is smaller but very close to tabulated value of T, there is a possibility of being differences between the performance of P4 and F4 in regard to HAA6 precursor removal. Table 5.27 summarizes comparison results.

Table 5.27 Results of comparison for HAA6 precursor %reduction in anthracite filters

	P3	P4
F4	Significant difference	No Significant difference
P4	No significant difference	

5.4.4 HAA6 Precursor Removal Comparisons for Full-Scale GAC Filters

The performance of the full-scale GAC filters was also compared in regard to removal of HAA6 precursors. Table 5.28 and Figure 5.18 show the HAA6 % reduction results for this set of filters.

Table 5.28 HAA6 %reduction in chlorinated full-scale GAC filter effluents

	F1	F2	F3
Aug 7	29.5	32.4	29.8
Aug 13	23.7	42.1	28.7
Aug 20	24.7	42.5	23.7
Aug 27	60.7	61.0	61.7
Sep 4	37.1	47.8	30.4

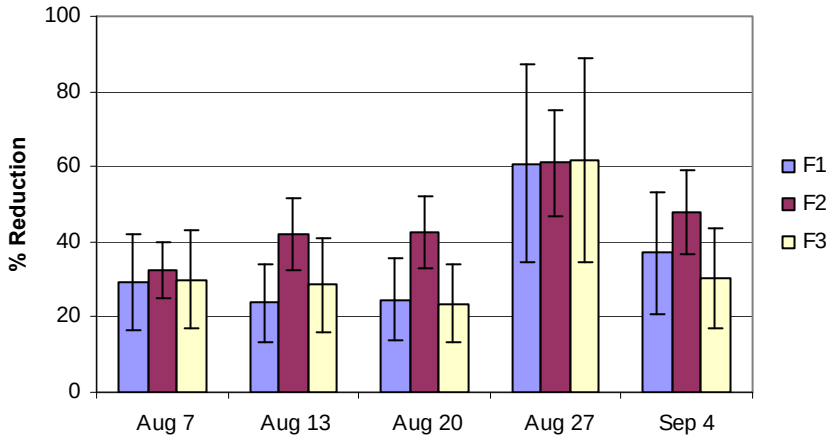

Figure 5.18 HAA6 %reduction in chlorinated full-scale GAC filter effluents (error bars are % standard deviation calculated from replicate samples)

To confirm that above performance differences were statistically significant, ANOVA was first performed on the data. Although from the Figure 5.18 illustrates that some variations were apparent, the ANOVA table analysis (Table 5.29) determined that there was no significant difference (because $F_{obs} < F_{tabulated}$) between the performance of the different media in the full-scale GAC filters in regard to HAA6 precursor removal at a 95% confidence level.

The t-test and LSD method results confirmed that this set of filters performed similarly in regard to HAA6 precursor removal at a 95% confidence level. The paired t-test identified no difference between F1 and F3. Smaller observed and tabulated T values (but very close) in the paired t-tests for F1, F2 and F2, F3 comparisons showed that there might be differences between these full-scale GAC filters (Table 5.30).

Table 5.29 ANOVA table for comparison of HAA6 precursor removal in full-scale GAC filters

Ho: $\mu_{F1} = \mu_{F2} = \mu_{F3}$

Source	df	SS	MS	$F_{observed}$
Filters	2	343.7	171.9	0.9
Within filter	12	2295.7	191.3	
Total	14	2639.4		

$F_{2,12,0.05} = 3.89 \quad \rightarrow \quad F_{obs} < F_{tabulated}$

Table 5.30 Results of comparison for HAA6 precursor %reduction in full-scale GAC filters

	F2	F3
F1	No Significant difference	No significant difference
F2		No Significant difference

5.5 Nitrosamines Variations During the PS/FS Experiments

Nitrosamines were the last group of disinfection by-products that were measured and studied in the chloraminated influents and full-scale and pilot-scale filter effluents. Nitrosamine variations in chloraminated pilot filter #2 effluent (selected as a typical filter) are shown in Figure 5.19. Three nitrosamines (NDMA, NMEA, and NMOR) were consistently detected in samples during these experiments. NDMA had the highest concentration among the nitrosamines estimated from 2.5 to 3.7 ng/L and which was lower than the regulated value of 9 ng/L. All of the nitrosamine concentrations were with in an order of magnitude of their detection limit, leading to increase levels of analytical error relative to the measurement of the other DBPs in this study and making the interpretation of subsequent statistical analyses less definite.

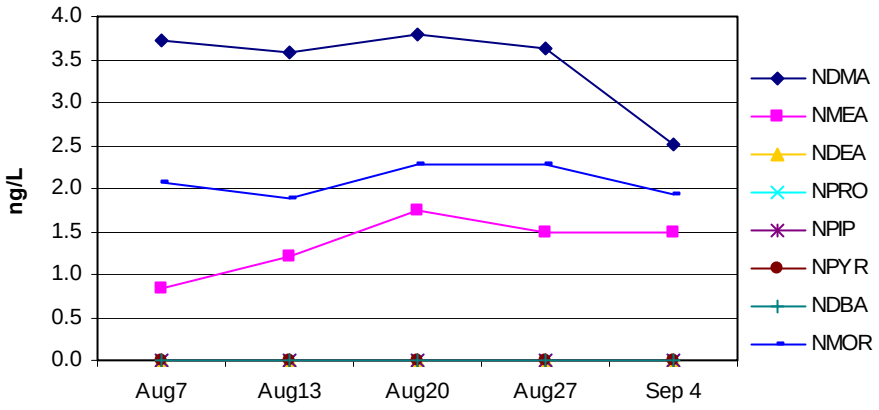

Figure 5.19 Nitrosamine concentrations in chloraminated pilot filter #2 effluent in FS/PS experiments

Since NDMA had the highest level among the nitrosamines and it is the only nitrosamine which has been regulated in Canada, the filter performances were compared statistically in regard to NDMA precursor removal. Figure 5.20 shows NDMA levels in the chloraminated influents and the full-scale and pilot-scale filter effluents.

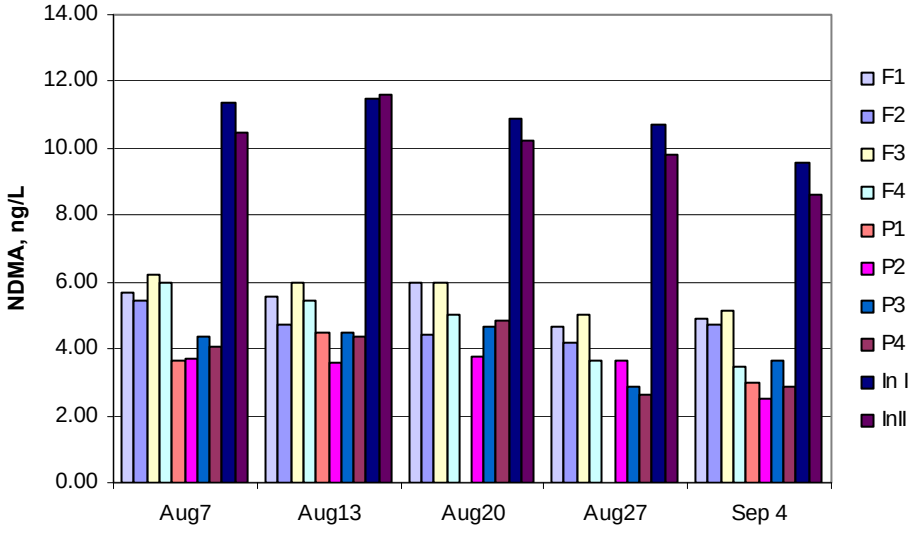

Figure 5.20 Comparing NDMA concentrations in chloraminated FS and PS filter effluents

The above figure suggests that, in general, NDMA had lower concentrations in the pilot filter effluents than the full-scale filter effluents, and different sets of statistical comparisons that were carried out and will be discussed in subsequent sections, show if different filters performed significantly different in regard to NDMA precursor removal. Regardless, high levels in chlorinated influents and good NDMA precursor removal in all filters were observed.

5.5.1 NDMA Precursor Removal Comparisons for Pilot-Scale Filters

Considering the variation in influent NDMA data, NDMA concentrations in the chloraminated filter effluents were normalized to account for variations in the influent water over the series of sampling runs. Thus, NDMA percentage reductions in the pilot filter effluents were compared using the analytical results given in Table 5.31 and Figure 5.21. Unfortunately, P1 was not operational for two of the sampling runs. In general, the NDMA precursor percentage reduction in all of the pilot filters appeared to be consistent throughout the tests at approximately 60%, which is higher than percentage reductions for HAA6 and TTHM precursors in pilot filters during FS/PS experiments.

Table 5.31 NDMA %reduction in chloraminated pilot filter effluents

	P1	P2	P3	P4
Aug 7	65.2	64.4	58.0	61.0
Aug 13	61.2	69.2	61.4	62.6
Aug 20	-	63.0	54.4	52.8
Aug 27	-	63.1	71.0	73.1
Sep 4	65.6	70.8	57.6	66.6

- : filter #1 was plugged and no sample was taken

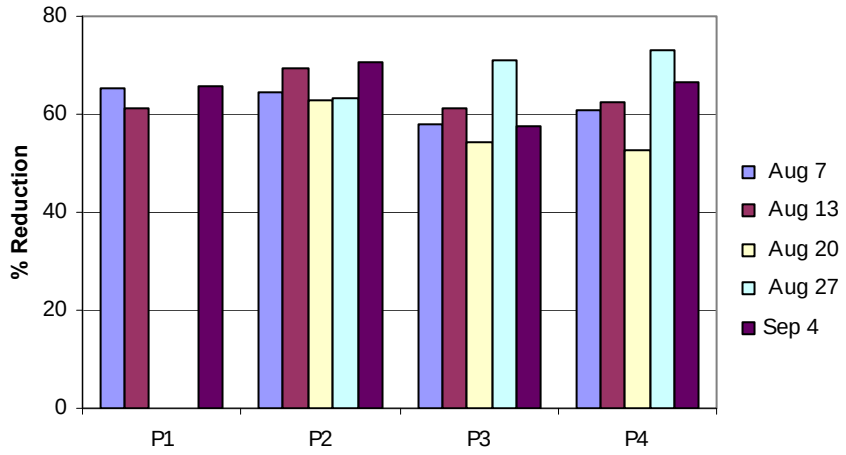

Figure 5.21 NDMA %reduction in chloraminated pilot filter effluents

To confirm that above performance differences were statistically significant, ANOVA was first performed on the above data (Table 5.32). Normality of data distribution was checked prior to performing ANOVA table in regard to NDMA precursor removal comparison in pilot filters and normal probability plot was shown in Appendix D.

Table 5.32 ANOVA table for comparison of NDMA precursor removal in pilot filters

Ho: $\mu_{P1} = \mu_{P2} = \mu_{P3} = \mu_{P4}$

Source	df	SS	MS	$F_{observed}$
Filters	3	80.3	26.8	0.8
Within filter	14	452.1	32.3	
Total	17	532.4		

$F_{3,14,0.05} = 3.35 \rightarrow F_{obs} < F_{tabulated}$

The greater tabulated F value than the observed F value confirms that there was no significant difference between the pilot filter performances at a 95% confidence level.

A summary of the pilot filter comparison results obtained from the different statistical tests is given in Table 5.33. Unlike the other DBPs, no significant difference was observed between the performance of the GAC and the anthracite media in the pilot filters in regard to NDMA precursor removal at a 95% confidence level. This was likely at least partially due to higher levels of analytical error that result from making measurements near the detection limit.

Table 5.33 Results of comparison for NDMA precursor %reduction in the pilot filters

	P2	**P4**	**GAC Filters**
P1	No significant difference		
P3		No significant difference	
Anthracite Filters			No significant difference

5.5.2 NDMA Precursor Removal Comparisons for FS/PS GAC Filters

NDMA percentage reduction data for chlorinated GAC filter effluents (Table 5.34 and Figure 5.22) were used to compare GAC filter performance in regard to NDMA precursor removal.

Table 5.34 NDMA % reduction in chloraminated GAC filter effluents

	P1	P2	F3
Aug 7	65.2	64.4	40.6
Aug 13	61.2	69.2	48.7
Aug 20	-	63.0	41.2
Aug 27	-	63.1	48.8
Sep 4	65.6	70.8	40.3

-: filter #1 was plugged and no sample was taken

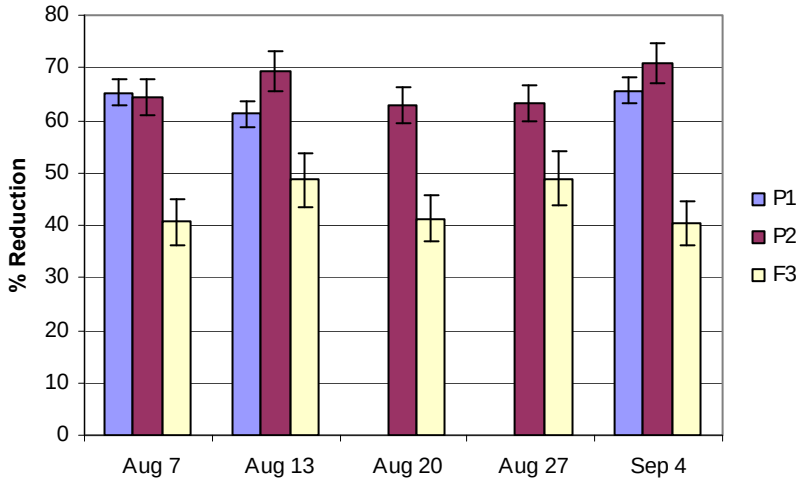

Figure 5.22 NDMA % reduction in chloraminated GAC filter effluents (error bars are % standard deviation calculated from replicate samples)

To confirm that above performance differences were statistically significant, ANOVA was first performed on the data. As the ANOVA table results (Table 5.35) show, there was a significant difference in the performance of GAC filters for removing NDMA precursor removal at a 95% confidence level because $F_{obs} > F_{tabulated}$.

Table 5.35 ANOVA table for comparison of NDMA precursor removal in GAC filters

Ho: $\mu_{P1} = \mu_{P2} = \mu_{F3}$

Source	df	SS	MS	$F_{observed}$
Filters	2	1414.3	707.1	49.3
Within filter	10	143.4	14.3	
Total	12	1557.7		

$F_{2,10,0.05} = 4.10 \rightarrow F_{obs} > F_{tabulated}$

Independent t-test, paired t-test and the LSD test results (summarized in Table 5.36) confirmed the similar performance of the two pilot-scale GAC filters (P1 and P2) which performed significantly differently and more efficiently than the full-scale GAC filter (F3) (by an average of 65% for P1 and P2 and 44% for F3) in regard to NDMA precursor removal at a 95% confidence level. Again, it should be noted that the lack of data from two sampling runs for P1, and the very low detected NDMA concentrations in the samples throughout these experiments, could affect the statistical analysis comparing possible differences between the performance of FS/PS GAC filters in regard to NDMA precursor removal.

Table 5.36 Results of comparison for NDMA precursor %reduction in GAC filters

	P1	P2
F3	Significant difference	Significant difference
P2	No significant difference	

5.5.3 NDMA Precursor Removal Comparisons for FS/PS Anthracite Filters

NDMA percentage reduction results for chloraminated effluent from the anthracite filters that are given in Table 5.37 and Figure 5.23 used to compare NDMA precursor removal in the anthracite filters.

Table 5.37 NDMA % reduction in chloraminated anthracite filter effluents

	P3	P4	F4
Aug 7	58.0	61.0	42.5
Aug 13	61.4	62.6	53.3
Aug 20	54.4	52.8	50.7
Aug 27	71.0	73.1	62.6
Sep 4	57.6	66.6	59.5

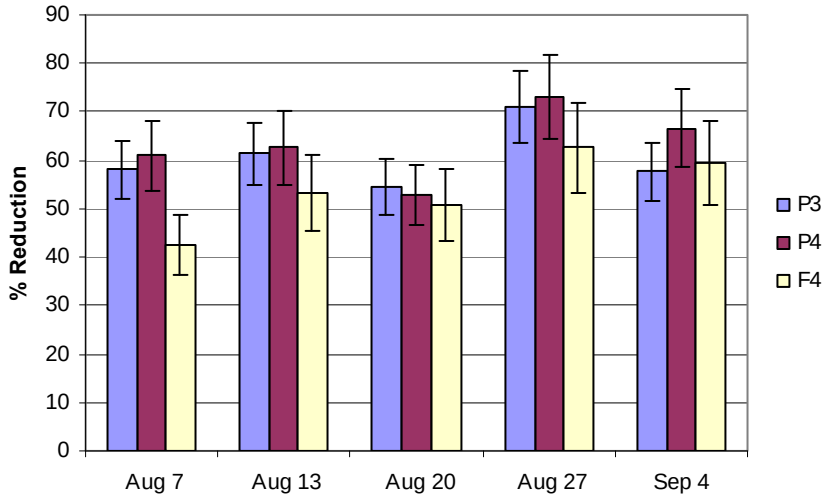

Figure 5.23 NDMA % reduction in chloraminated anthracite filter effluents (error bars are % standard deviation calculated from replicate samples)

To confirm that above performance differences were statistically significant, ANOVA was first performed on the data. The ANOVA table results (Table 5.38) determines that there were no considerable differences between the performances of the anthracite filters in regard to NDMA precursor removal at a 95% confidence level because $F_{obs}<F_{tabulated}$.

Table 5.38 ANOVA table for comparison of NDMA removal in anthracite filters

Ho: $\mu_{P3} = \mu_{P4} = \mu_{F4}$

Source	df	SS	MS	$F_{observed}$
Filters	2	238.6	119.3	2.3
Within filter	12	635.1	52.9	
Total	14	873.7		

$F_{2,12,0.05} = 3.89 \rightarrow F_{obs} < F_{tabulated}$

The ANOVA table results were supported by further statistical tests (independent and paired t-tests and LSD method), except that the paired t-test showed a significant difference between the performance of P4 and F4 for NDMA precursor removal at a 95% confidence level. Table 5.39 summarizes the comparison results.

Table 5.39 Results of comparison for NDMA precursor %reduction in anthracite filters

	P3	P4
F4	No significant difference	Significant difference
P4	No significant difference	

5.5.4 NDMA Precursor Removal Comparisons for Full-Scale GAC Filters

Table 5.40 and Figure 5.24 show the NDMA removal results in chloraminated full-scale GAC filter effluents. NDMA percentage reduction values were calculated to be between 40-60% in these filters.

Table 5.40 NDMA %reduction in chloraminated full-scale GAC filter effluents

	F1	F2	F3
Aug 7	50.1	58.8	40.6
Aug 13	51.3	58.8	48.7
Aug 20	45.1	59.4	41.2
Aug 27	56.8	50.6	48.8
Sep 4	48.9	50.6	40.3

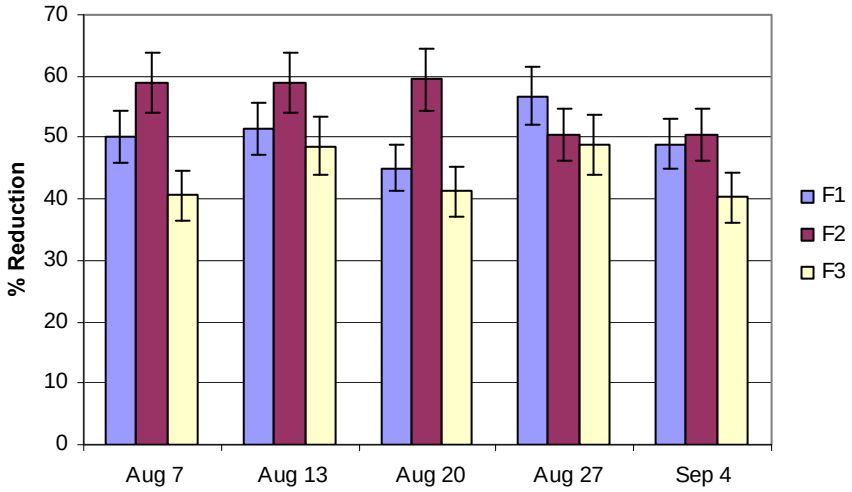

Figure 5.24 NDMA %reduction in chlorinated full-scale GAC filter effluents (error bars are % standard deviation calculated from replicate samples

From the above results it would appear that full-scale GAC filters with older age media (F1, F2) performed more efficiently than the filter with fresh GAC (F3) in regard to NDMA precursor removal. To confirm that above performance differences were statistically significant, ANOVA was first performed on the data. From the corresponding ANOVA table (Table 5.41) it is evident that a significant difference existed between the performance of the

full-scale GAC filters in regard NDMA removal at a 95% confidence level. Statistical tests confirmed that F1 and F2 did not significantly differently from each other, but they performed significantly differently from F3 in regard to NDMA precursor removal (Table 5.42). The effect of GAC age was not too surprising. Even though the newer GAC had been in service for several months, it is likely that it was still not able to biologically remove NDMA precursors as well as F1 and F2.

Table 5.41 ANOVA table for comparison of NDMA precursor removal in full-scale GAC filters

Ho: $\mu_{F1}=\mu_{F2}=\mu_{F3}$

Source	df	SS	MS	$F_{observed}$
Filters	2	344.0	172.0	8.8
Within filter	12	235.3	19.6	
Total	14	579.3		

$F_{2,12,0.05}=3.89 \rightarrow F_{obs} > F_{tabulated}$

Table 5.42 Results of comparison for NDMA precursor %reduction in full-scale GAC filters

	F2	F3
F1	No significant difference	Significant difference
F2		Significant difference

Chapter 6 Conclusions and Recommendations

6.1 Full-Scale and Pilot-Scale Comparisons

One of the main objectives of this research was to assess if pilot-scale filters at the Mannheim Water Treatment Plant represent full-scale filter performance with respect to DBP formation when they are operated under approximately the same conditions as the full-scale filters (filter loading rate and backwashing regime). Experiments on the pilot-scale and full-scale filter effluents were conducted with an effort to follow full-scale chlorination and ammoniation procedures to simulate DBP formation in the plant effluent and distribution system. Statistical analyses were carried out on the DBP concentrations obtained from these experiments to help identify significant differences between the performances of the different filters. Some conclusions resulting from this research are described as follows.

Significant differences at the 95%confidence level were found in the performance of the pilot filters containing different general media types (GAC vs. anthracite) in regard to HAA6 and TTHM precursor and chorine demand removal. HAA6 and TTHM removal and chlorine demand removal by GAC surpassed that of anthracite because GAC, in addition to having some residual adsorptive capacity, provides better attachment sites for bacteria to grow than anthracite does. In contrast, NDMA precursor removal seemed to be not significantly affected by the type of media in the pilot filters. NDMA precursors were removed by both types of filter media to a high percentage (approximately 60%) and even more efficiently than removals observed for HAA6 precursors (with average of 36.5% and 19.4% for GAC

and anthracite, respectively) and TTHM precursors (with average of 30.1% and 12.2% for GAC and anthracite, respectively).

In comparing the performance of different types of GAC filters, no significant difference was demonstrated (a) between the two pilot GAC filters P1 and P2 in terms of chlorine demand and DBP precursor removal, (b) between P1 and F3 (full-scale fresh GAC) in regards to THM precursor and chlorine demand, and (c) between P2 and F3 in regards to chlorine demand, THM and HAA precursor removal when evaluated with paired T-test results. However, the paired T-test showed significant differences between P1 and F3 in regards to HAA precursor removal in that P1 (which is older media with more established biomass), performed better than F3 for HAA precursor removal. Fewer data points were available for P1 due to operational problems.

NDMA formation following the GAC filters appeared to be both affected by the age of the GAC media in the filters and differences in media specifications. A significant increase in NDMA removal by P1 and P2 (approximately 60%) over F3 (approximately 40%) was observed in spite of P2's and F3's similar physical characteristics. This suggests that the combination of residual adsorption capabilities and a longer established biofilm in the GAC filters provided additional benefit over the combination of adsorption and a newly established biofilm in terms of NDMA precursor removal. The same behavior for NDMA removal was seen when old full-scale GAC filter media (F1 and F2) was compared with new full-scale filter media (F3), even though F3 media had a different effective size and uniformity coefficient, supporting the above mentioned suggestion. However, the fact that upstream

treatment process trains for F1 and F2 can perform differently from that for F3 perhaps also should be taken in account.

Anthracite pilot filters (P3 and P4) showed similar performance in regard to DBP and chlorine demand removal in spite of their subtle media specification differences. No significant difference was shown between full-scale anthracite filters with fresh media (F4) and any of anthracite pilot filters in terms of TTHM removal. These results can be justified by the fact that regardless of media age, anthracite is not a good biosupporter, and as a result the anthracite pilot filters (P3 and P4) represented F4 in regards to TTHM removal. Paired t-tests, however, identified some differences between the performance of full-scale and pilot-scale anthracite filters in terms of HAA6 and NDMA precursor removal and chlorine demand removal. These differences may be partially due to the low concentrations of HAA and NDMA in samples (near their detection limit) and partially because of variations in F4 operating conditions (e.g. full-scale filter backwashing schedules), which were out of our control and which could cause an imperfect simulation).

In general, however, similar performance of pilot and full-scale filters was observed (especially in terms of TTHM precursor removal and chlorine demand removal) and confirmed that the pilot-scale filters provided a good estimate of the DBP formation potential removal in the full-scale filters.

6.2 Pilot-Scale Filters Flow Rate Experiments

The second objective of this research was to study the impact of flow rate or loading rate on DBP formation following the pilot filters at the Mannheim Water Treatment Plant. The results were discussed in Chapter 4 and the following conclusions can be drawn.

The chlorine demand of influent and effluent samples was measured at different flow rates as a rough a parameter to suggest the potential for samples to form DBPs. However, it was observed chlorine demand variations were almost independent of changes in flow-rate, and chlorine demand was less affected by flow rate than was DBP formation. This shows that the fraction of organic matter which contained DBP precursors was affected by flow rate. It was also found that the chlorine demand of the effluent from the anthracite filters was higher than that of the GAC filters, likely due to the coarser surface GAC provides for bacteria to grow and the higher residual adsorptive capacity of GAC relative to anthracite.

UV254 absorbance was measured in all filter influent and effluent samples at different filter flow rate conditions, as an indicator of the THMFP of the water. Changes in the UV254 absorbance of the filter effluents were determined to be directly influenced by flow rate. Absorbance values increased as flow rate increased and, therefore, the percentage reduction of UV absorbance decreased by increasing the flow rate. As well, the difference between the performance of GAC and anthracite filters for UV254 absorbance removal was greater for flow rates below 7L/m (loading rates below 13 m/h). This poorer performance of filters in regard to UV254 absorbance removal at high flow rates (which was also observed for chlorine demand, TTHM, and HAA6) was likely due to the of shorter contact time of water with filter media at higher flow rates, which does not allow enough time for organic

precursors to be removed from water. Similar to chlorine demand, UV254 absorbance removal levels were shown to be less in anthracite filters than in GAC filters, consistently and at all flow rates. As well, the difference between the performance of GAC and anthracite filters for UV254 absorbance removal was greater for flow rates below 7L/m (loading rates below 13 m/h).

THM species concentrations (and TTHM) in chlorinated pilot filter effluents also showed an increasing trend as flow rates were increased in all of the pilot filters. This was observed regardless of the type of filter media employed, which also supported the trends observed for chlorine demand and UV absorbance removal. Chloroform was the trihalomethane species with the lowest measured concentrations and the highest removal efficiencies in all of the effluent samples. $CHCl_2Br$ and $CHClBr_2$ were present at the highest levels, due to a moderately high bromide concentration in Grand River water. TTHM concentrations that were formed under high flow rate conditions sometimes were measured at levels near or slightly higher than those allowed by current regulations, however, the full-scale treatment plant does not operate filters at such high flow rates and finished water from this water treatment planr\t is always mixed with groundwater before it enters the distribution system. Negative percentage removals (i.e. overall percentage increases) of UV absorbance, TTHM and also HAA6 that were observed at higher flow rates were likely due to sloughing off the organic matter from the filter media to the effluent, adding to the contribution of those DBP precursors that might already be present.

GAC filters performed more efficiently than anthracite filters in terms of TTHM removal and, similar to the UV 254 absorbance data, media-specific differences in THM precursor

removals were exaggerated at flow rates less than approximately 7 L/m (loading rates below 13 m/h). This is because at high flow rates organic matter passed through the filters too quickly for the different removal mechanisms to occur to an extent that enables their differences to be evident

The HAA6 concentrations in the different chlorinated filter effluents varied from approximately 6µg/L to approximately 19µg/L and their percentage removals ranged from approximately -18% (i.e. 18% increase relative to the influent) to approximately 70% during the flow rate experiments. Flow rate was determined as a factor affecting HAA removal in the different pilot filters. HAA6 removal rates decreased as flow rates increased. However, HAA species and HAA6 precursor removal appeared less affected by loading rate than were the trihalomethanes. Overall, better HAA6 precursor removal was observed in GAC filters than in anthracite filters; however, an anomaly in one of the anthracite filters (P3) showed its removal to be higher than that in the GAC filters, likely due to the low HAA concentrations identified in samples, which makes it difficult for consistent trendsin HAA6 concentrations to be observed with changes in flow rate.

N-nitrosodimethylamine (NDMA), N-nitrosomethylethylamine (NMEA), and N-nitrosomorpholine (NMOR) were the only nitrosamines detected in the samples and they were present at a maximum level in filter #1 at a flow rate of 8.6 L/m. Results also showed that nitrosamines, compared to other DBPs, were less affected by flow rate. No consistent trend was observed as flow rate increased in any type of filter media. The changes in the concentrations of each of these nitrosamines as flow rate changed was also similar regardless of filter media type, which suggests that filter performance was independent of filter media

(anthracite or GAC. The lack of definite trends may have been due to the low concentrations observed. However, high percentage removals (from 60 to 95%) were observed in all filters for the range of flow rates that were tested. This confirms that good performance was achieved for decreasing NDMA levels in the finished water to below the Ontario interim maximum acceptable concentration of 9 ng/L for all types of filter media and throughout the range of employed flow rates in decreasing

6.3 Recommendations

From the obtained results it is recommended that the pilot-scale filters should be operated at low flow rates (less than 7 L/m or 13 m/h loading rate) for additional runs, to investigate if there is residual adsorption capacity in pilot filters. It will help future researchers and operators better understand biofiltration mechanisms and their affects on the DBP formation following the GAC filters.

Samplings during spring runoff are needed to test the effect of higher organic precursor concentrations in influent water on filter performance in regards to DBPFP. Also, since nitrosamine concentrations were low, even in chloraminated influent samples, adding model nitrosamine precursors to the filter influent (if allowable) may help to understand the media effects on nitrosamine precursor removal.

In future experiments, DOC data is recommended to be measured to allow for the calculation of SUVA and provide additional confirmation of the DBPFP results.

Also, additional replicate runs for both the flow rate and full-scale/pilot-scale comparison experiments may assist in reducing probable errors, increasing the confidence in data interpretation, and obtaining more consistent results from different statistical tests.

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Appendix A: DBPs Results

Table A.1 THM species and TTHM concentrations (µg/L) in chlorinated pilot filter #2 effluent during flow rate experiment

Flow Rate (L/m)	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	TTHM
1	9.3	18.0	23.7	13.7	64.6
5	7.6	22.0	32.5	18.4	80.5
7.7	19.7	33.9	39.9	15.5	109.0
8	21.3	36.4	47.4	16.9	121.9

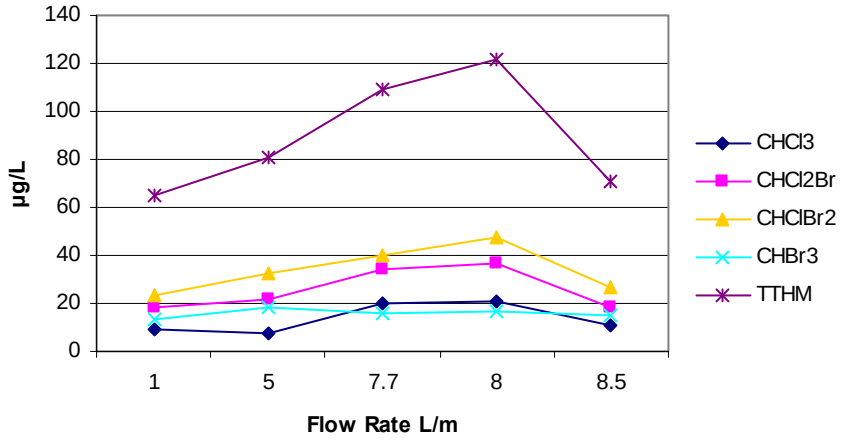


Figure A.1THM concentrations in chlorinated pilot filter #2 effluent at different flow rates

Table A.2 THM species and TTHM concentrations (µg/L) in chlorinated pilot filter #3 effluent during flow rate experiment

Flow Rate (L/m)	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	TTHM
1	14.3	23.7	24.9	12.6	75.4
5	15.7	28.2	36.4	19.6	99.9
9	20.8	31.3	33.7	14.5	100.2
12.8	27.2	39.7	44.6	17.6	129.1

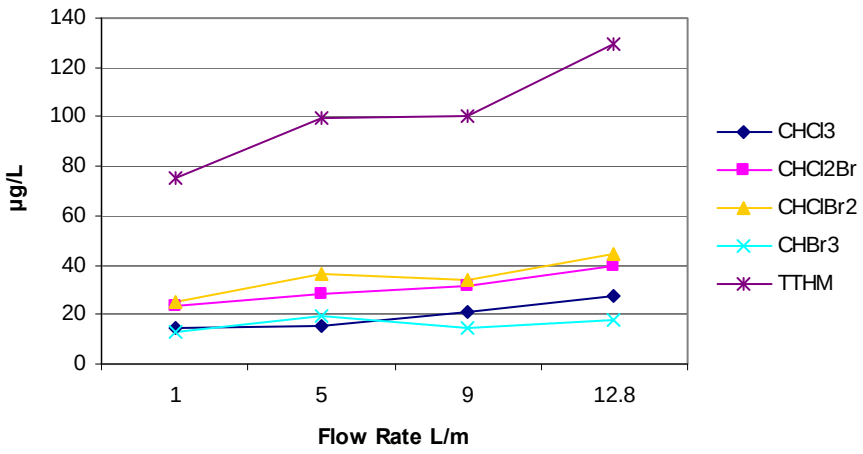


Figure A.2 THM concentrations in chlorinated pilot filter #3 effluent at different flow rates

Table A.3 THM species and TTHM concentrations (µg/L) in chlorinated pilot filter #4 effluent during flow rate experiment

Flow Rate (L/m)	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	TTHM
1.85	10.8	14.8	21.4	14.0	60.9
4.3	11.0	22.1	34.2	18.1	85.4
7.5	26.5	38.6	40.1	16.0	121.1
11.2	31.3	40.6	45.7	17.0	134.4

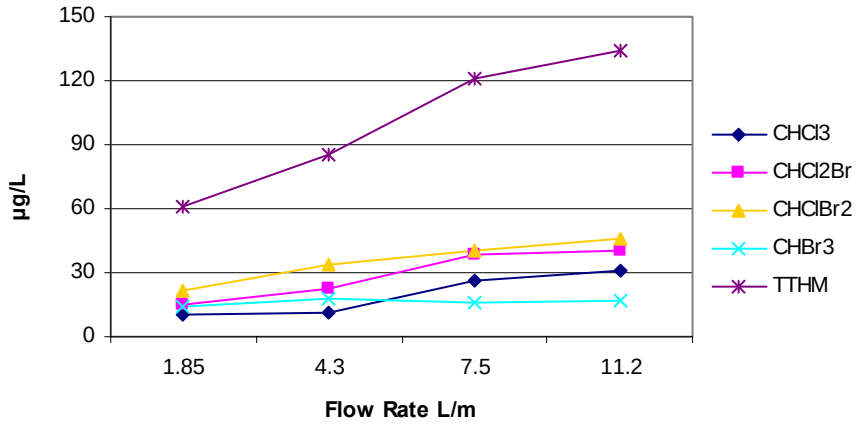


Figure A.3 THM concentrations in chlorinated pilot filter #4 effluent at different flow rates

Table A.4 THM %reduction in chlorinated pilot filter #2 effluent during flow rate experiment

Flow Rate(L/m)	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	TTHM
1	65.0	40.4	17.0	1.8	34.8
5	46.5	4.8	-7.6	-29.6	1.5
7.7	12.8	-22.4	-50.0	-13.1	-20.3
8	-33.6	-24.1	-20.3	9.4	-18.1

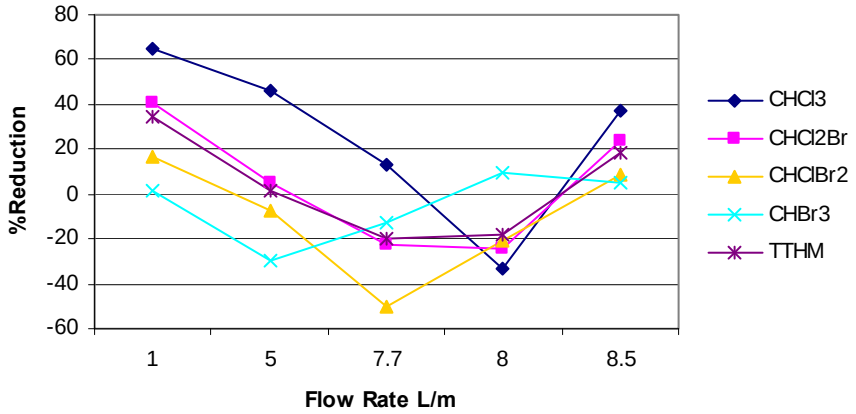


Figure A.4 THM %reduction in chlorinated pilot filter #2 at different flow rate

Table A.5 THM %reduction in chlorinated pilot filter #3 effluent during flow rate experiment

Flow Rate(L/m)	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	TTHM
1	46.1	21.3	13.0	10.0	23.9
5	-10.6	-22.1	-20.5	-38.0	-22.3
9	8.2	-12.8	-26.7	-5.5	-10.5
12.8	-71.1	-35.3	-13.3	5.4	-25.1

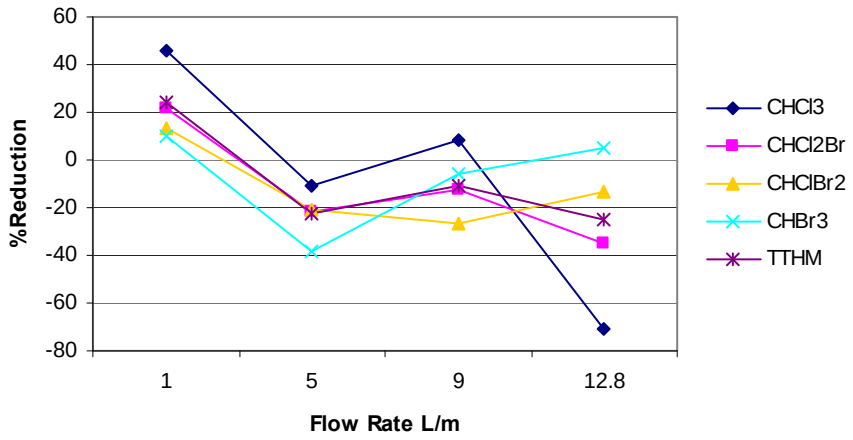


Figure A.5 THM %reduction in chlorinated pilot filter #3 at different flow rate

Table A.6 THM %reduction in chlorinated pilot filter #4 effluent during flow rate experiment

Flow Rate (L/m)	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	TTHM
1.85	51.1	40.8	31.6	7.0	34.7
4.3	22.5	4.3	-13.2	-27.5	-4.5
7.5	-17.0	-39.2	-50.6	-16.8	-33.6
11.2	-96.5	-38.2	-16.0	8.9	-30.2

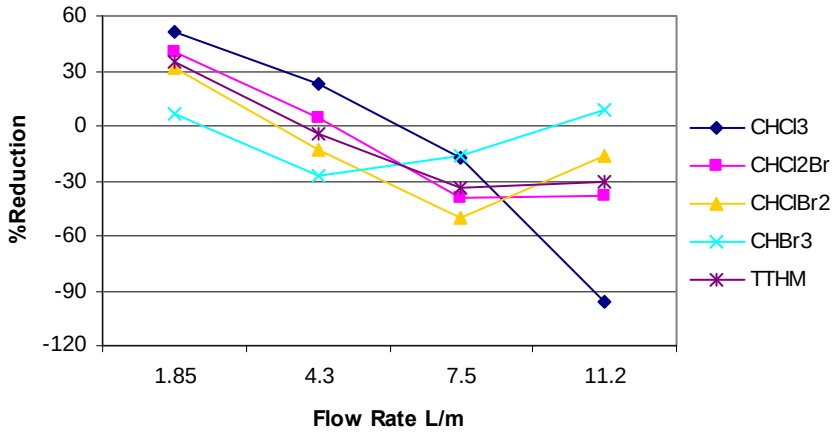


Figure A.6 THM %reduction in chlorinated pilot filter #4 at different flow rate

Table A.7 HAA concentrations (µg/L) in chlorinated pilot filter #2 effluent during flow rate experiment

Flow Rate(L/m)	ClAA	BrAA	Cl_2AA	Cl_3AA	BrClAA	Br_2AA	HAA6
1	0.0	0.0	3.9	2.0	3.6	3.5	12.8
5	0.0	0.0	2.2	1.7	3.0	3.7	10.6
7.7	0.0	0.0	3.4	2.7	3.1	2.8	11.9
8	0.0	0.0	4.0	1.7	3.8	3.6	13.0

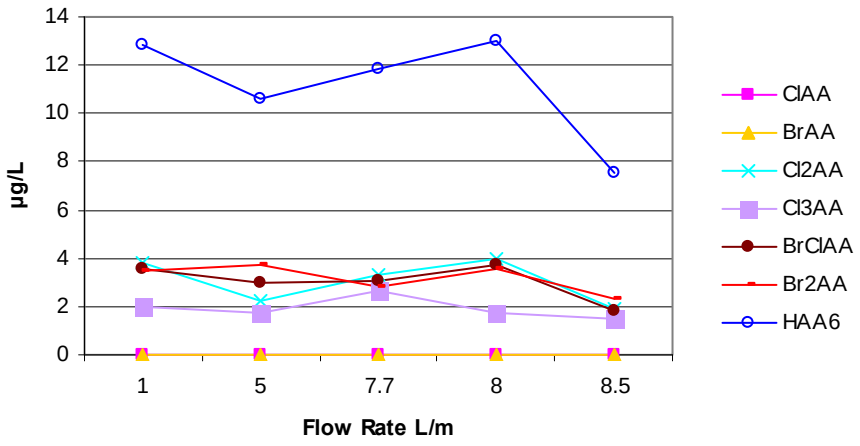


Figure A.7 HAA concentrations in chlorinated pilot filter #2 at different flow rates

Table A.8 HAA concentrations (µg/L) in chlorinated pilot filter #3 effluent during flow rate experiment

Flow Rate(L/m)	ClAA	BrAA	Cl_2AA	Cl_3AA	BrClAA	Br_2AA	HAA6
1	0.0	0.0	2.5	3.2	2.3	1.7	9.6
5	0.0	0.0	2.2	2.3	3.0	2.8	10.3
9	0.0	0.0	2.3	2.2	3.2	3.1	10.8
12.8	0.0	0.0	4.3	2.1	3.4	3.2	12.9

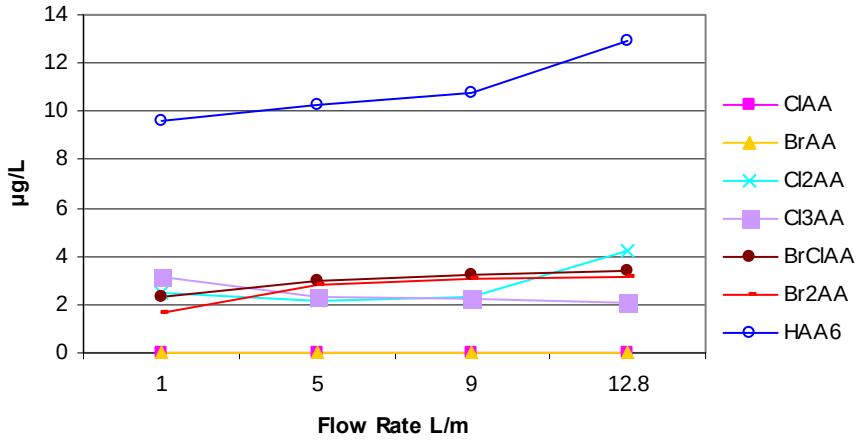


Figure A.8 HAA concentrations in chlorinated pilot filter #3 at different flow rates

Table A.9 HAA concentrations (µg/L) in chlorinated pilot filter #4 effluent during flow rate experiment

Flow Rate(L/m)	ClAA	BrAA	Cl_2AA	Cl_3AA	BrClAA	Br_2AA	HAA6
1.85	0.0	0.0	1.6	1.8	2.1	1.4	6.9
4.3	0.0	0.0	3.2	2.0	3.1	3.5	11.8
7.5	0.0	0.0	4.8	3.5	5.1	3.5	16.8
11.2	0.0	0.0	6.0	4.0	4.7	4.1	18.7

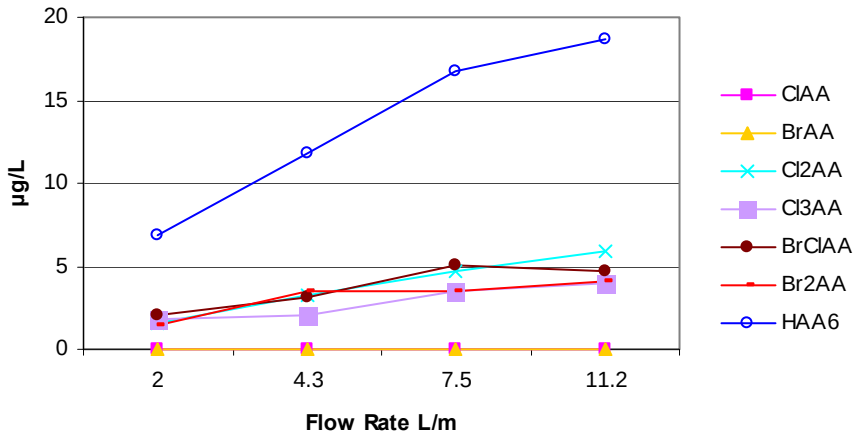


Figure A.9 HAA concentrations in chlorinated pilot filter #4 at different flow rates

Table A.10 HAA %reduction in chlorinated pilot filter # 2 effluent during flow rate experiment

Flow Rate(L/m)	ClAA	BrAA	Cl_2AA	Cl_3AA	BrClAA	Br_2AA	HAA_6
1	0.0	0.0	57.5	80.6	50.0	1.4	54.2
5	0.0	0.0	55.6	66.7	39.4	8.6	44.4
7.7	0.0	0.0	28.7	14.5	44.5	3.4	26.9
8	0.0	0.0	44.0	60.0	-1.7	-25.7	28.5

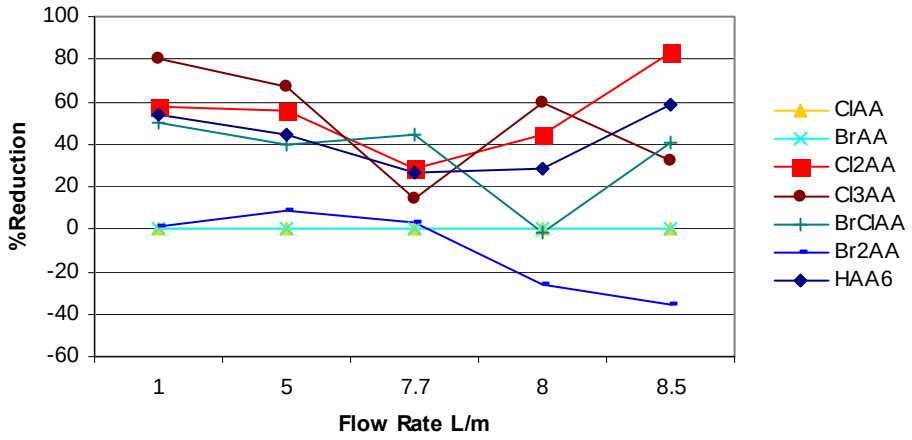


Figure A.10 HAA %reduction in chlorinated pilot filter #2 effluent at different flow rates

Table A.11 HAA %reduction in chlorinated pilot filter # 3 effluent during flow rate experiment

Flow Rate(L/m)	ClAA	BrAA	Cl_2AA	Cl_3AA	BrClAA	Br_2AA	HAA_6
1	0.0	0.0	72.4	64.0	67.6	52.9	43.5
5	0.0	0.0	56.6	54.9	39.4	30.9	42.8
9	0.0	0.0	51.1	29.0	41.8	-6.9	33.3
12.8	0.0	0.0	26.7	50.6	8.1	-16.7	21.6

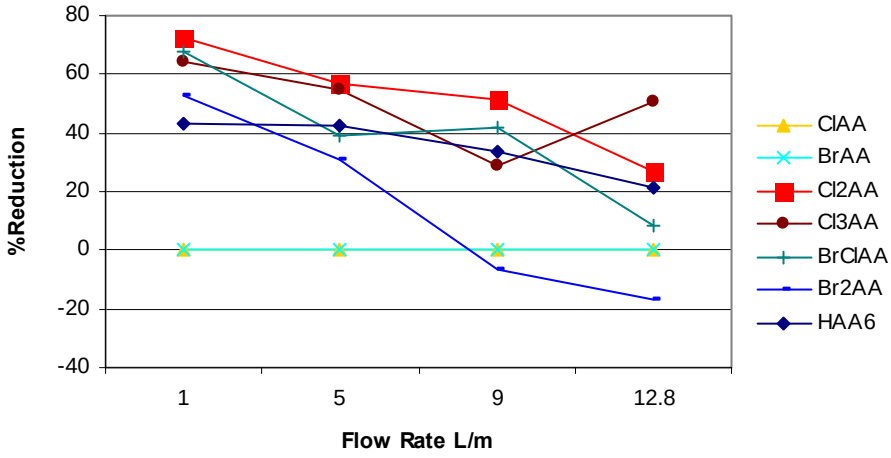


Figure A.11 HAA %reduction in chlorinated pilot filter #3 effluent at different flow rates

Table A.12 HAA %reduction in chlorinated pilot filter # 4 effluent during flow rate experiment

Flow Rate(L/m)	ClAA	BrAA	Cl_2AA	Cl_3AA	BrClAA	Br_2AA	HAA_6
1.85	0.0	0.0	20.0	37.9	16.0	54.8	34.3
4.3	0.0	0.0	35.4	60.8	37.4	13.6	38.1
7.5	0.0	0.0	-1.1	-12.9	7.3	-19.0	-3.7
11.2	0.0	0.0	-2.6	5.9	-25.7	-51.9	-13.7

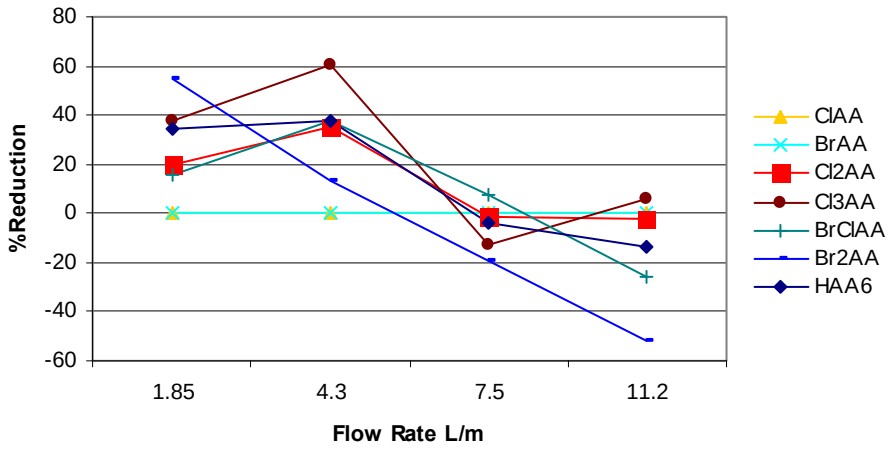


Figure A.12 HAA %reduction in chlorinated pilot filter #4 effluent at different flow rates

Table A.13 Nitrosamine concentrations (ng/L) in chlorinated pilot filter #2 effluent during flow rate experiments

Flow Rate(L/m)	NDMA	NMEA	NDEA	NPRO	NPIP	NPYR	NDBA	NMOR
1	1.8	0.6	0.0	0.0	0.0	0.0	0.0	0.9
5	1.0	0.7	0.0	0.0	0.0	0.0	0.0	1.6
7.7	2.0	0.8	0.0	0.0	0.0	0.0	0.0	1.6
8	1.6	0.9	0.0	0.0	0.0	0.0	0.0	1.0

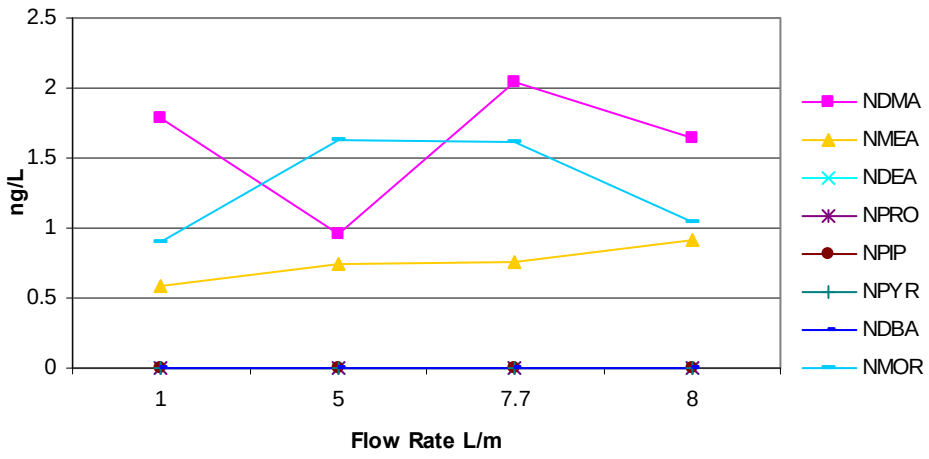


Figure A.13 Nitrosamine concentrations in chlorinated pilot filter #2 effluent at different flow rates

Table A.14 Nitrosamine concentrations (ng/L) in chlorinated pilot filter #3 effluent during flow rate experiments

Flow Rate(L/m)	NDMA	NMEA	NDEA	NPRO	NPIP	NPYR	NDBA	NMOR
1	2.1	1.4	0.0	0.0	0.0	0.0	0.0	1.6
5	1.1	1.1	0.0	0.0	0.0	0.0	0.0	2.1
9	3.5	1.9	0.0	0.0	0.0	0.0	0.0	1.4
12.8	1.7	1.7	0.0	0.0	0.0	0.0	0.0	1.8

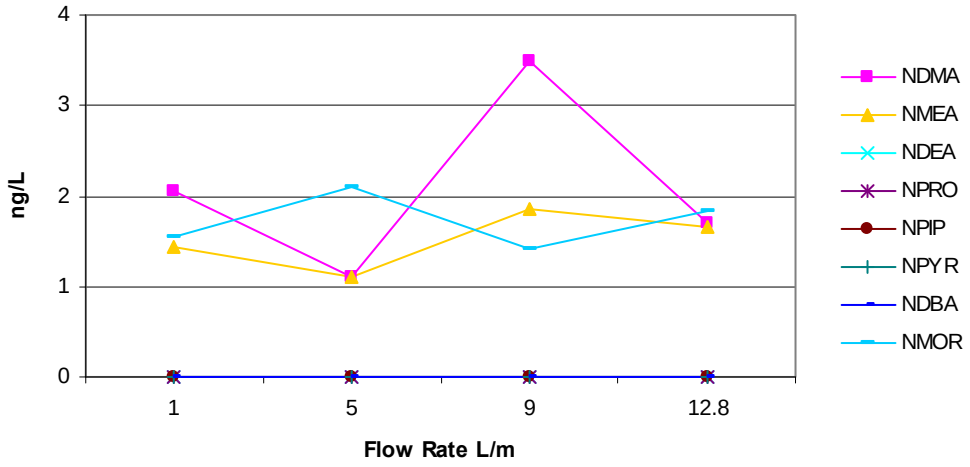


Figure A.14 Nitrosamine concentrations in chlorinated pilot filter #3 effluent at different flow rates

Table A.15 Nitrosamine concentrations (ng/L) in chlorinated pilot filter #4 effluent during flow rate experiments

Flow Rate(L/m)	NDMA	NMEA	NDEA	NPRO	NPIP	NPYR	NDBA	NMOR
1.85	2.1	1.5	0.0	0.0	0.0	0.0	0.0	1.7
4.3	1.9	1.9	0.0	0.0	0.0	0.0	0.0	2.1
7.5	2.7	0.5	0.0	0.0	0.0	0.0	0.0	2.1
11.2	0.8	2.1	0.0	0.0	0.0	0.0	0.0	1.6

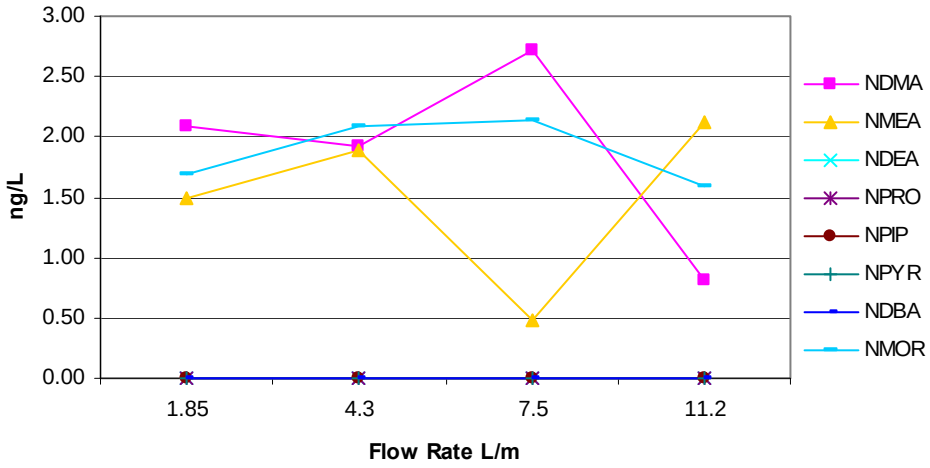


Figure A.15 Nitrosamine concentrations in chlorinated pilot filter #4 effluent at different flow rates

Table A.16 Nitrosamines %reduction in chlorinated pilot filter #2 effluent during flow rate experiment

Flow Rate(L/m)	NDMA	NMEA	NDEA	NPRO	NPIP	NPYR	NDBA	NMOR
1	85.0	89.5	100.0	0.0	0.0	0.0	0.0	89.2
5	79.8	75.4	100.0	0.0	0.0	0.0	0.0	71.2
7.7	84.6	86.4	100.0	0.0	0.0	0.0	0.0	81.2
8	86.4	88.1	100.0	0.0	0.0	0.0	0.0	89.3

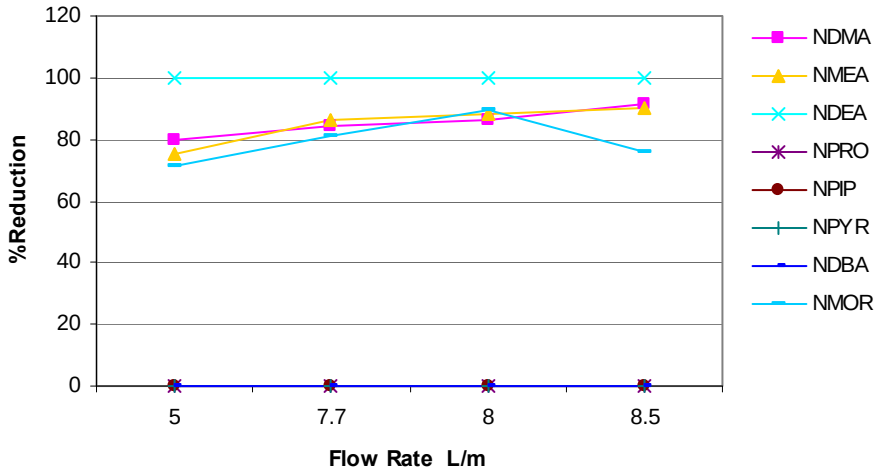


Figure A.16 Nitrosamines% reduction in chlorinated pilot filter #2 effluent at different flow rates

Table A.17 Nitrosamines %reduction in chlorinated pilot filter #3 effluent during flow rate experiment

Flow Rate(L/m)	NDMA	NMEA	NDEA	NPRO	NPIP	NPYR	NDBA	NMOR
1	82.7	74.3	100.0	0.0	0.0	0.0	0.0	81.5
5	76.4	63.8	100.0	0.0	0.0	0.0	0.0	63.0
9	73.6	66.6	100.0	0.0	0.0	0.0	0.0	83.5
12.8	86.0	78.2	100.0	0.0	0.0	0.0	0.0	81.3

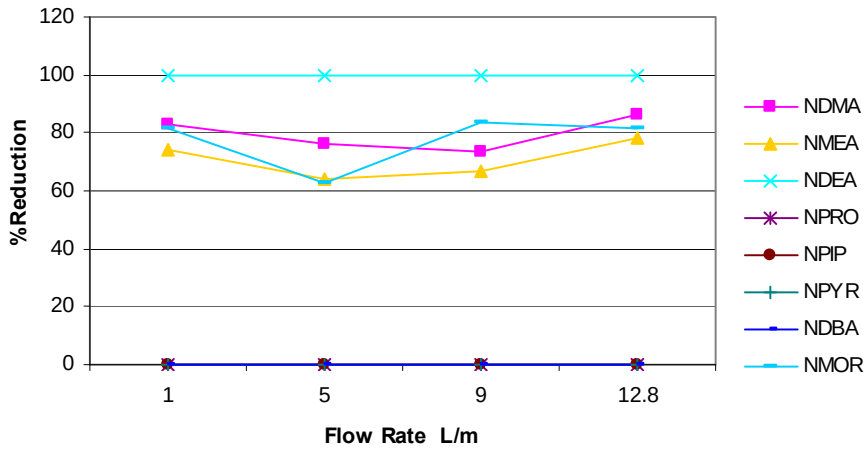


Figure A.17 Nitrosamines% reduction in chlorinated pilot filter #3 effluent at different flow rates

Table A.18 Nitrosamines %reduction in chlorinated pilot filter #4 effluent during flow rate experiment

Flow Rate(L/m)	NDMA	NMEA	NDEA	NPRO	NPIP	NPYR	NDBA	NMOR
1	82.7	74.3	100.0	0.0	0.0	0.0	0.0	81.5
5	76.4	63.8	100.0	0.0	0.0	0.0	0.0	63.0
9	73.6	66.6	100.0	0.0	0.0	0.0	0.0	83.5
12.8	86.0	78.2	100.0	0.0	0.0	0.0	0.0	81.3

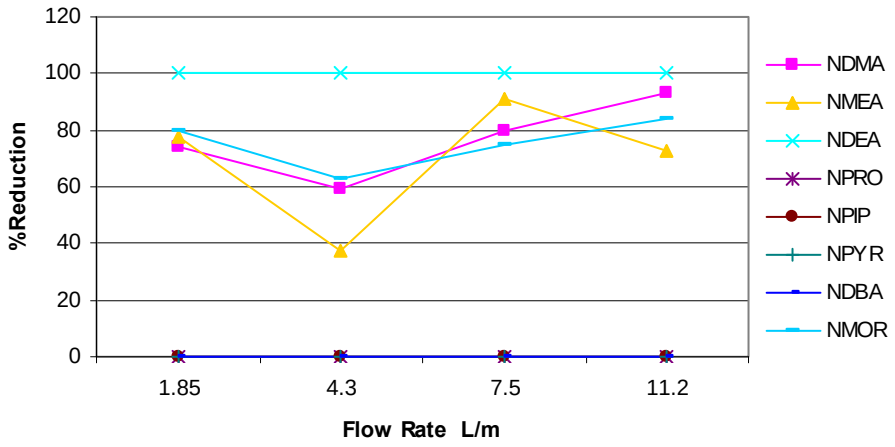


Figure A.18 Nitrosamines% reduction in chlorinated pilot filter #4 effluent at different flow rates

Table A.19 THM concentrations in chlorinated pilot filter #1 effluent in FS/PS experiments

Sampling Date	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	TTHM
Aug7	14.7	20.8	23.8	12.4	71.6
Aug13	13.0	17.5	20.3	11.3	62.0
Sep4	9.2	15.7	23.8	13.9	62.5

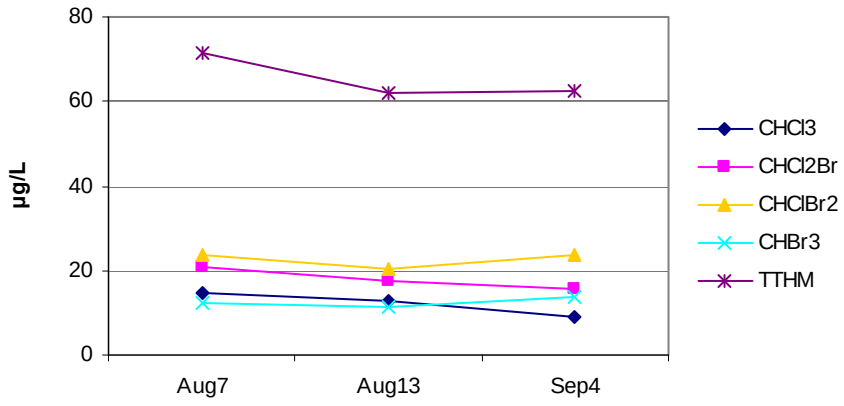


Figure A.19 THM concentrations in chlorinated pilot filter #1 effluent in FS/PS experiments

Table A.20 THM concentrations in chlorinated pilot filter #3 effluent in FS/PS experiments

Sampling Date	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	TTHM
Aug7	24.3	25.8	25.5	12.5	88.1
Aug13	26.3	29.1	27.1	12.0	94.4
Aug20	18.3	24.4	27.2	14.8	84.6
Aug27	24.7	23.1	20.4	11.4	79.5
Sep 4	16.8	25.8	32.3	14.5	89.4

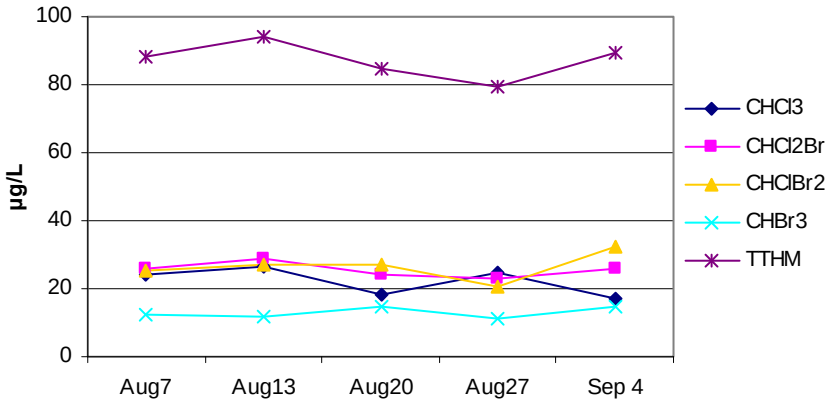


Figure A.20 THM concentrations in chlorinated pilot filter #3 effluent in FS/PS experiments

Table A.21 THM concentrations in chlorinated pilot filter #4 effluent in FS/PS experiments

Sampling Date	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	TTHM
Aug7	29.3	30.3	27.6	11.9	99.0
Aug13	28.7	28.7	26.2	11.6	95.1
Aug20	19.8	25.0	26.6	13.3	84.6
Aug27	30.3	26.1	22.1	11.6	90.0
Sep4	18.0	26.2	34.2	9.3	87.6

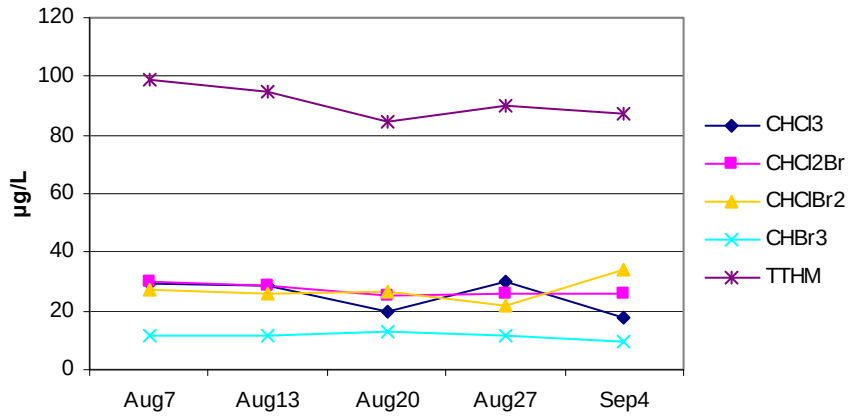


Figure A.21 THM concentrations in chlorinated pilot filter #4 effluent in FS/PS experiments

Table A.22 THM concentrations in chlorinated full-scale filter #1 effluent in FS/PS experiments

Sampling Date	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	TTHM
Aug7	15.7	20.4	24.4	12.3	72.6
Aug13	17.0	21.7	26.3	12.6	77.4
Aug20	17.8	23.5	27.6	13.6	82.5
Aug27	15.8	17.5	17.8	11.3	62.3
Sep4	8.8	15.5	22.8	12.8	59.8

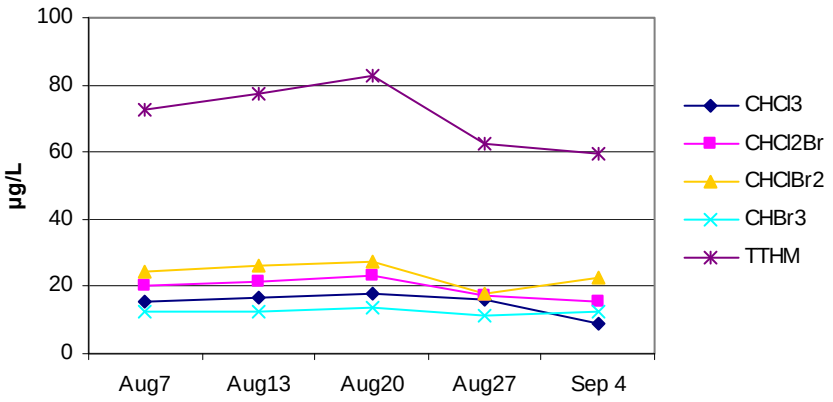


Figure A.22 THM concentrations in chlorinated full-scale filter #1 effluent in FS/PS experiments

Table A.23 THM concentrations in chlorinated full-scale filter #2 effluent in FS/PS experiments

Sampling Date	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	TTHM
Aug7	14.9	17.2	20.0	11.3	63.2
Aug13	10.4	13.6	19.6	12.1	55.7
Aug20	12.9	18.6	23.1	12.2	66.8
Aug27	14.6	14.2	15.3	11.5	55.5
Sep 4	9.6	15.8	24.1	13.9	63.3

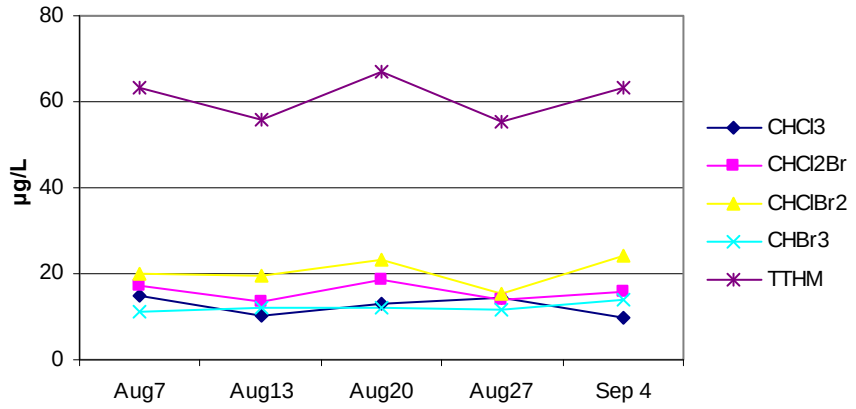
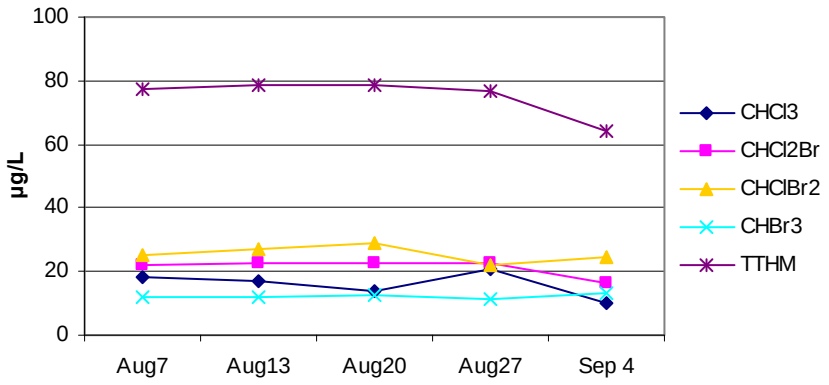


Figure A.23 THM concentrations in chlorinated full-scale filter #2 effluent in FS/PS experiment

Table A.24 THM concentrations in chlorinated full-scale filter #3 effluent in FS/PS experiments

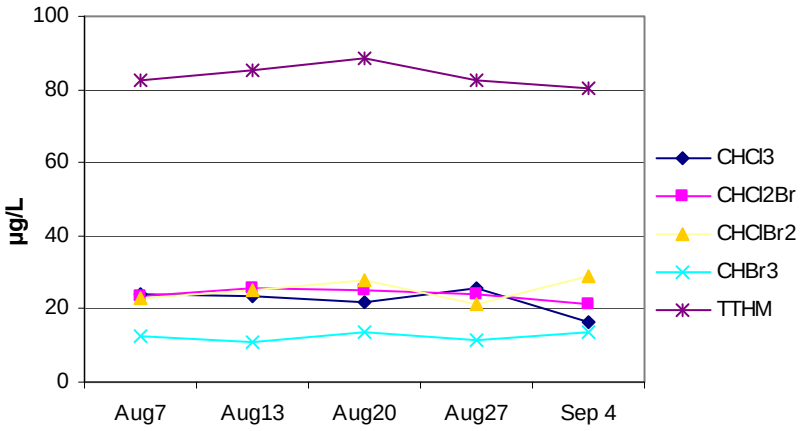
Sampling Date	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	TTHM
Aug7	18.1	21.8	25.2	12.2	77.3
Aug13	17.2	22.9	26.9	12.0	78.9
Aug20	13.9	23.0	28.8	12.8	78.5
Aug27	20.5	22.6	22.2	11.3	76.5
Sep 4	9.9	16.5	24.8	13.2	64.3



FigureA.24 THM concentrations in chlorinated full-scale filter #3 effluent in FS/PS experiments

Table A.25 THM concentrations in chlorinated full-scale filter #4 effluent in FS/PS experiments

Sampling Date	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	TTHM
Aug7	24.0	23.4	23.1	12.3	82.8
Aug13	23.5	25.8	25.2	10.8	85.1
Aug20	22.0	25.1	27.7	13.8	88.5
Aug27	25.5	24.2	21.5	11.5	82.6
Sep 4	16.3	21.5	29.0	13.5	80.3



FigureA.25 THM concentrations in chlorinated full-scale filter #4 effluent in FS/PS experiments

Table A.26 THM %reduction in chlorinated full-scale filter #1 effluent in FS/PS experiments

Sampling Date	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	TTHM
Aug7	52.3	27.7	-0.2	-6.5	25.0
Aug13	61.7	37.2	4.4	-14.1	33.9
Aug20	40.6	19.2	-6.2	-12.0	15.1
Aug27	50.0	25.1	-1.7	1.7	25.7
Sep 4	62.8	47.6	31.1	15.6	41.0

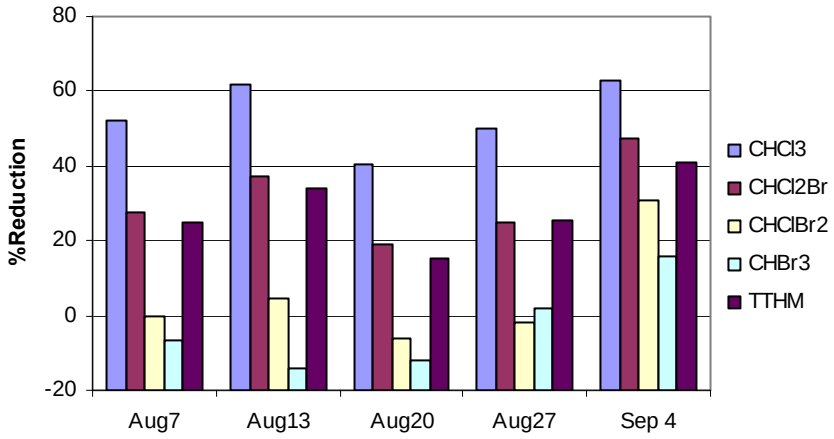


Figure A.26 THM %reduction in chlorinated full-scale filter #1 effluent in FS/PS experiments

Table A.27 THM %reduction in chlorinated full-scale filter #2 effluent in FS/PS experiments

Sampling Date	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	TTHM
Aug7	54.7	39.1	17.9	2.2	34.7
Aug13	76.5	60.5	28.6	-10.0	52.5
Aug20	57.1	36.1	11.2	-0.8	31.3
Aug27	53.8	39.3	12.6	0.0	33.8
Sep 4	59.6	46.4	27.0	8.3	37.5

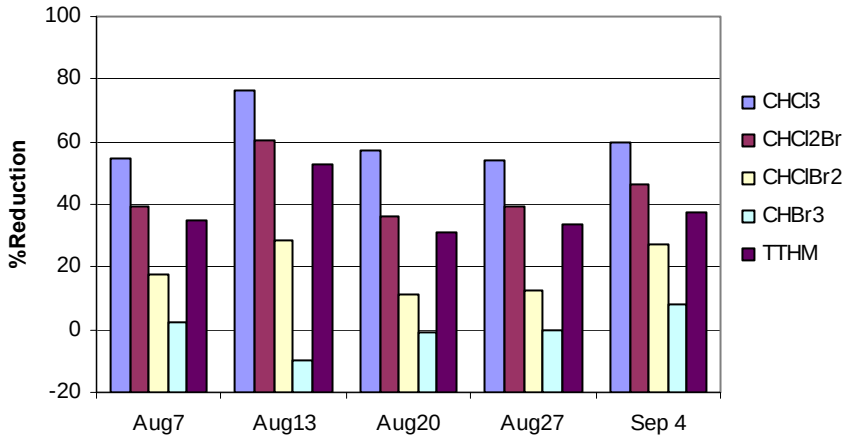


Figure A.27 THM %reduction in chlorinated full-scale filter #2 effluent in FS/PS experiments

Table A.28 THM %reduction in chlorinated full-scale filter #3 effluent in FS/PS experiments

Sampling Date	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	TTHM
Aug7	43.1	24.4	0.6	-4.7	20.8
Aug13	57.3	27.2	-3.7	-0.8	27.9
Aug20	52.9	24.5	1.2	7.2	29.7
Aug27	31.0	17.4	-3.0	-1.8	14.6
Sep 4	61.1	42.1	22.8	9.3	36.0

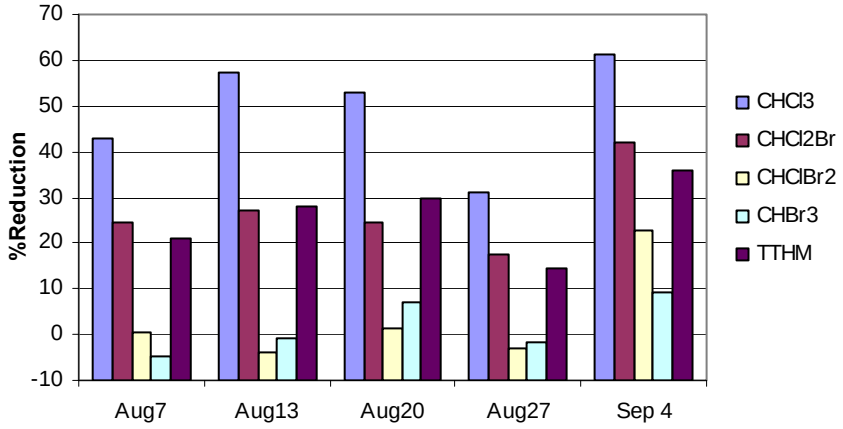


Figure A.28 THM %reduction in chlorinated full-scale filter #3 effluent in FS/PS experiments

Table A.29 THM %reduction in chlorinated full-scale filter #4 effluent in FS/PS experiments

Sampling Date	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	TTHM
Aug7	24.5	18.9	9.1	-5.6	15.3
Aug13	41.6	18.1	2.9	9.7	22.2
Aug20	25.6	17.6	5.0	0.0	14.0
Aug27	14.1	11.5	0.2	-4.1	7.8
Sep 4	36.0	24.7	9.5	6.9	20.1

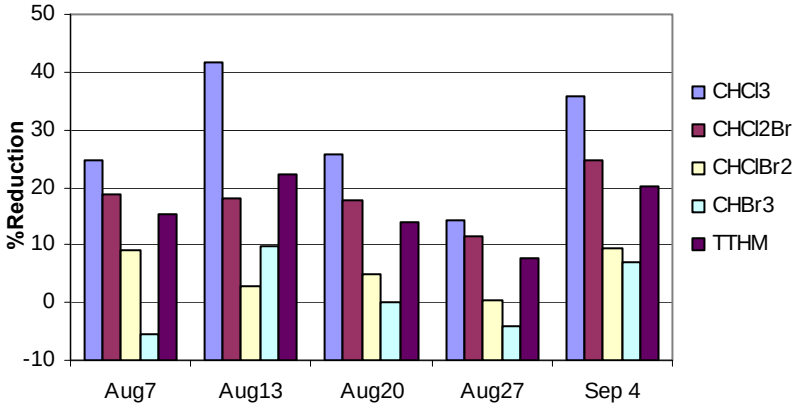


Figure A.29 THM %reduction in chlorinated full-scale filter #4 effluent in FS/PS experiments

Table A.30 THM %reduction in chlorinated pilot filter #1 effluent in FS/PS experiments

Sampling Date	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	TTHM
Aug7	53.8	34.5	6.3	-6.0	28.6
Aug13	67.7	44.4	21.8	5.5	43.4
Sep 4	64.0	45.1	25.9	4.1	37.9

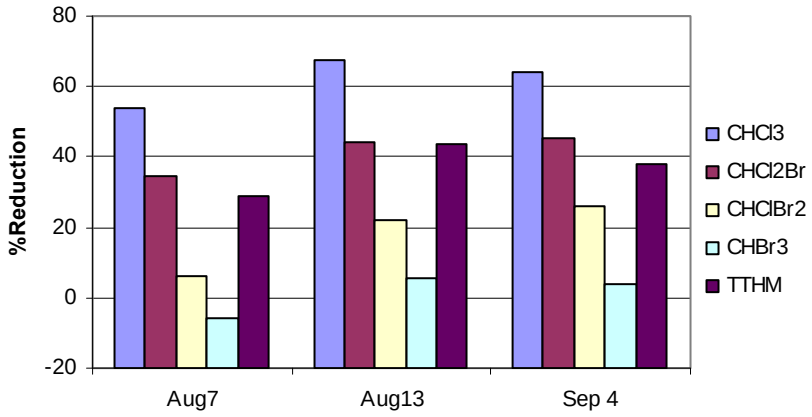


Figure A.30 THM %reduction in chlorinated pilot filter #1 effluent in FS/PS experiments

Table A.31 THM %reduction in chlorinated pilot filter #3 effluent in FS/PS experiments

Sampling Date	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	TTHM
Aug7	23.7	10.6	-0.6	-7.3	9.8
Aug13	34.6	7.5	-4.4	-0.4	13.8
Aug20	38.1	19.9	6.7	-6.9	17.8
Aug27	17.0	15.4	5.3	-2.7	11.3
Sep 4	29.3	8.2	1.2	36.2	15.4

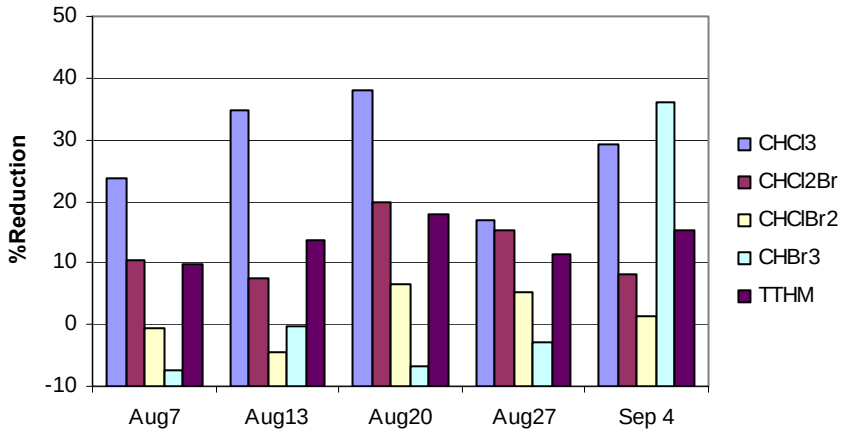


Figure A.31 THM %reduction in chlorinated pilot filter #3 effluent in FS/PS experiments

Table A.32 THM %reduction in chlorinated pilot filter #3 effluent in FS/PS experiments

Sampling Date	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	TTHM
Aug7	8.0	9.2	5.3	-1.7	6.5
Aug13	28.5	8.7	-1.0	2.9	13.1
Aug20	32.9	17.8	8.9	4.0	17.7
Aug27	-1.9	9.5	-2.6	-5.0	1.1
Sep 4	29.3	8.2	1.2	36.2	15.4

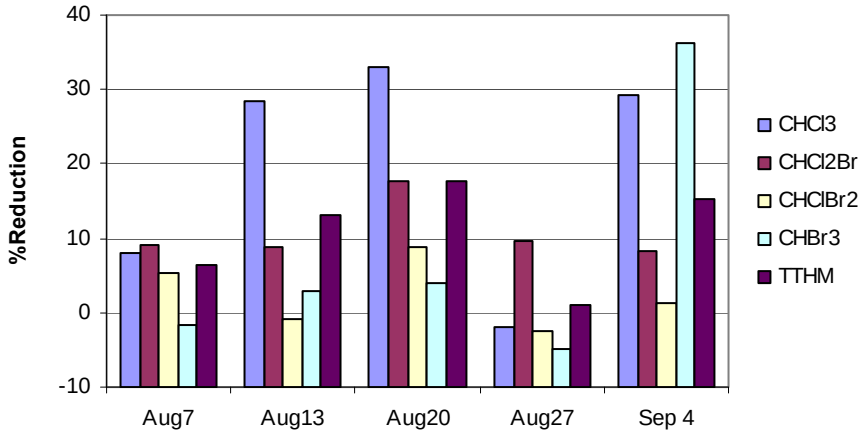


Figure A.32 THM %reduction in chlorinated pilot filter #3 effluent in FS/PS experiments

Table A.33 HAA concentrations in chlorinated full-scale filter #1 effluent in FS/PS experiments

Sampling Date	ClAA	BrAA	Cl_2AA	Cl_3AA	BrClAA	Br_2AA	HAA6
Aug7	0.0	0.0	2.2	2.2	2.1	2.2	8.6
Aug13	0.0	0.0	1.8	1.8	2.0	1.8	7.4
Aug20	0.0	0.0	2.6	2.6	2.7	2.6	10.4
Aug27	0.0	0.0	1.8	2.0	1.8	1.8	7.3
Sep4	0.0	0.0	1.7	2.0	2.1	2.2	7.9

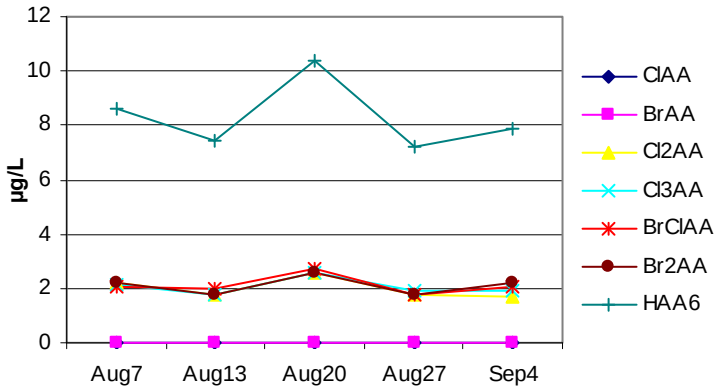


Figure A.33 HAA concentrations in chlorinated full-scale filter #1 effluent in FS/PS experiments

Table A.34 HAA concentrations in chlorinated full-scale filter #2 effluent in FS/PS experiments

Sampling Date	ClAA	BrAA	Cl_2AA	Cl_3AA	BrClAA	Br_2AA	HAA6
Aug7	0.0	0.0	2.0	2.6	1.9	1.8	8.3
Aug13	0.0	0.0	1.0	1.1	1.3	1.3	4.7
Aug20	0.0	0.0	2.1	2.0	2.0	2.0	7.9
Aug27	0.0	0.0	1.8	2.0	1.6	1.9	7.2
Sep4	0.0	0.0	1.4	2.0	1.5	1.8	6.6

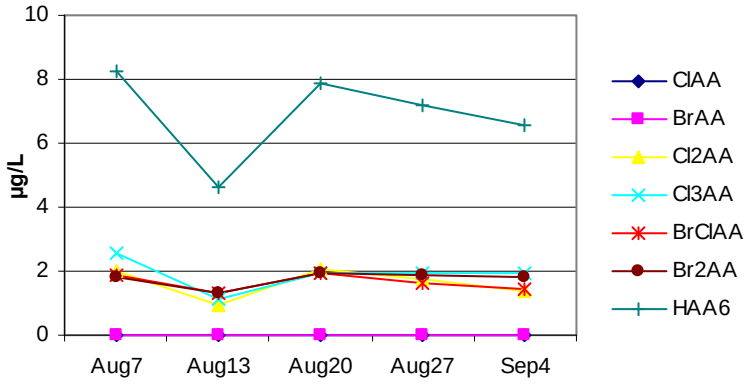


Figure A.34 HAA concentrations in chlorinated full-scale filter #2 effluent in FS/PS experiments

Table A.35 HAA concentrations in chlorinated full-scale filter #3 effluent in FS/PS experiments

Sampling Date	ClAA	BrAA	Cl_2AA	Cl_3AA	BrClAA	Br_2AA	HAA6
Aug7	0.0	0.0	2.8	3.0	3.2	2.1	11.1
Aug13	0.0	0.0	2.9	2.4	2.7	2.8	10.7
Aug20	0.0	0.0	2.4	2.3	2.7	2.7	10.0
Aug27	0.0	0.0	0.5	0.9	1.9	1.8	5.0
Sep4	0.0	0.0	1.3	1.8	1.9	1.8	6.8

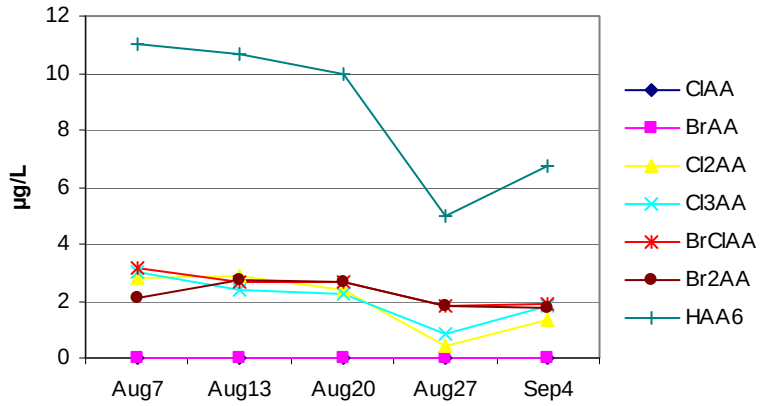


Figure A.35 HAA concentrations in chlorinated full-scale filter #3 effluent in FS/PS experiments

Table A.36 HAA concentrations in chlorinated full-scale filter #4 effluent in FS/PS experiments

Sampling Date	ClAA	BrAA	Cl_2AA	Cl_3AA	BrClAA	Br_2AA	HAA6
Aug7	0.0	0.0	2.4	2.7	2.2	1.4	8.6
Aug13	0.0	0.0	2.1	2.3	2.6	1.3	8.3
Aug20	0.0	0.0	3.0	2.7	2.8	2.5	10.8
Aug27	0.0	0.0	1.2	1.9	1.9	1.7	6.6
Sep4	0.0	0.0	2.1	2.3	1.7	2.0	8.1

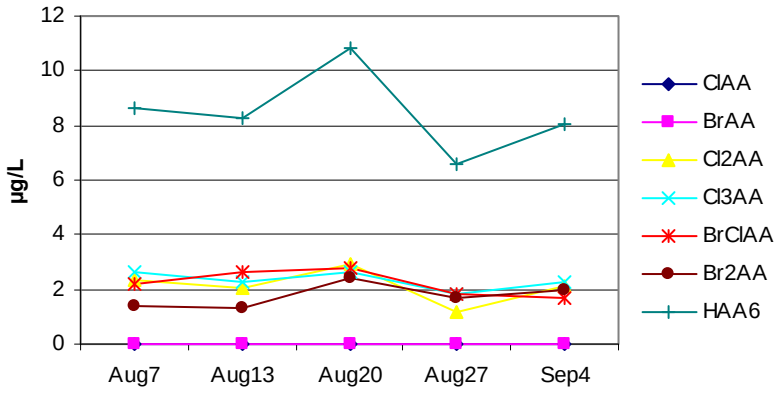


Figure A.36 HAA concentrations in chlorinated full-scale filter #4 effluent in FS/PS experiments

Table A.37 HAA concentrations in chlorinated pilot filter #1 effluent in FS/PS experiments

Sampling Date	ClAA	BrAA	Cl_2AA	Cl_3AA	BrClAA	Br_2AA	HAA6
Aug7	0.0	0.0	2.1	2.5	2.4	1.9	8.8
Aug13	0.0	0.0	2.2	2.6	2.0	1.6	8.3
Sep4	0.0	0.0	1.0	1.2	1.1	1.4	4.7

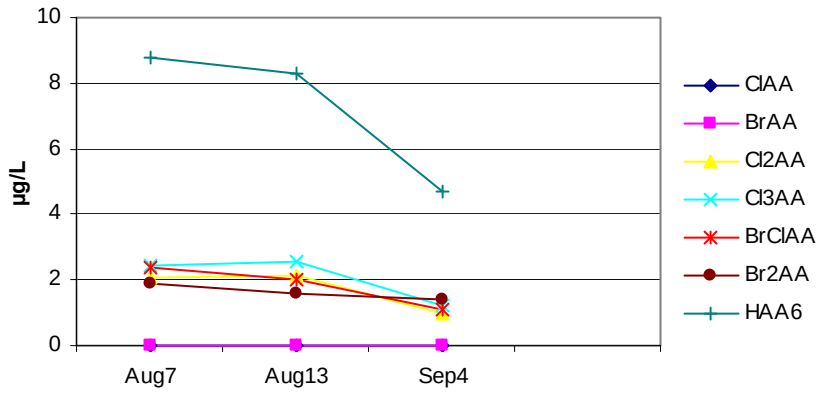


Figure A.37 HAA concentrations in chlorinated pilot filter #1 effluent in FS/PS experiments

Table A.38 HAA concentrations in chlorinated pilot filter #3 effluent in FS/PS experiments

Sampling Date	ClAA	BrAA	Cl_2AA	Cl_3AA	BrClAA	Br_2AA	HAA6
Aug7	0.0	0.0	4.4	3.2	2.6	2.0	12.2
Aug13	0.0	0.0	3.2	3.4	2.2	2.2	10.9
Aug20	0.0	0.0	3.3	2.9	2.6	2.6	11.3
Aug27	0.0	0.0	1.1	1.5	1.9	1.7	8.4
Sep4	0.0	0.0	2.6	2.4	2.3	2.2	9.4

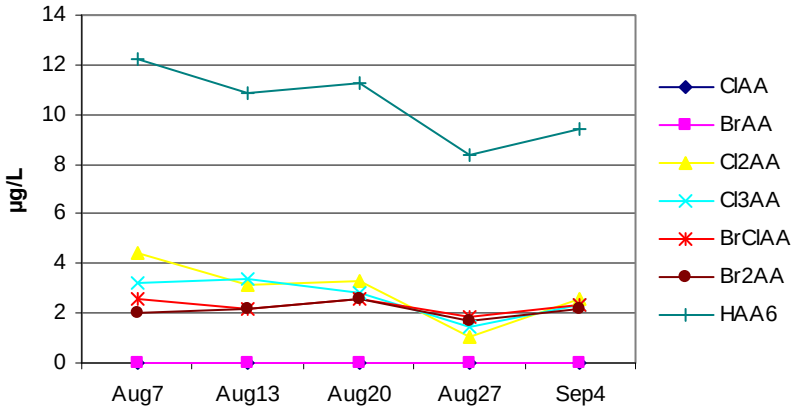


Figure A.38 HAA concentrations in chlorinated pilot filter #3 effluent in FS/PS experiments

Table A.39 HAA concentrations in chlorinated pilot filter #4 effluent in FS/PS experiments

Sampling Date	ClAA	BrAA	Cl_2AA	Cl_3AA	BrClAA	Br_2AA	HAA6
Aug7	0.0	0.0	4.7	3.3	2.5	2.2	12.6
Aug13	0.0	0.0	3.9	3.7	2.8	2.7	13.1
Aug20	0.0	0.0	3.0	2.6	2.2	2.3	10.0
Aug27	0.0	0.0	0.9	1.8	1.9	1.9	8.9
Sep4	0.0	0.0	2.6	2.5	2.3	2.0	9.4

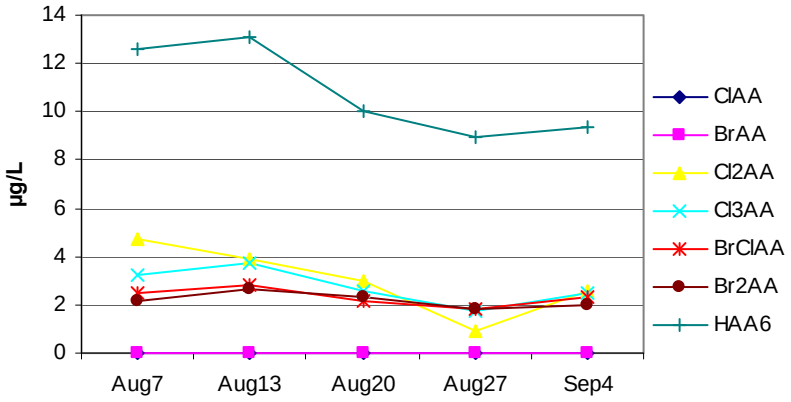


Figure A.39 HAA concentrations in chlorinated pilot filter #4 effluent in FS/PS experiments

Table A.40 HAA %reduction in chlorinated full-scale filter #1 effluent in FS/PS experiments

Sampling Date	ClAA	BrAA	Cl_2AA	Cl_3AA	BrClAA	Br_2AA	HAA6
Aug7	0.0	0.0	38.0	46.9	21.2	-10.0	29.5
Aug13	0.0	0.0	47.8	44.6	-17.6	-38.5	23.7
Aug20	0.0	0.0	42.0	29.2	14.3	1.9	24.7
Aug27	0.0	0.0	71.1	66.7	60.7	14.3	60.7
Sep4	0.0	0.0	47.7	41.8	36.9	18.5	37.1

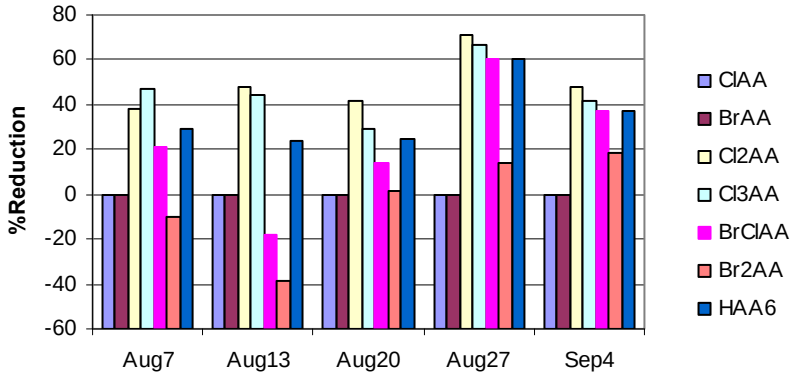


Figure A.40 HAA %reduction in chlorinated full-scale filter #1 effluent in FS/PS experiments

Table A.41 HAA %reduction in chlorinated full-scale filter #2 effluent in FS/PS experiments

Sampling Date	ClAA	BrAA	Cl_2AA	Cl_3AA	BrClAA	Br_2AA	HAA6
Aug7	0.0	0.0	43.7	37.0	26.9	10.0	32.4
Aug13	0.0	0.0	72.5	66.2	23.5	0.0	52.1
Aug20	0.0	0.0	53.4	45.8	38.1	25.0	42.5
Aug27	0.0	0.0	71.1	66.7	64.0	9.5	61.0
Sep4	0.0	0.0	58.5	41.8	55.4	33.3	47.8

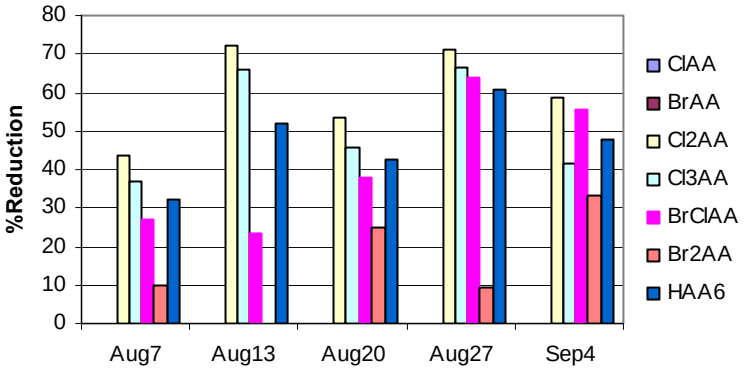


Figure A.41 HAA %reduction in chlorinated full-scale filter #2 effluent in FS/PS experiments

Table A.42 HAA %reduction in chlorinated full-scale filter #3 effluent in FS/PS experiments

Sampling Date	ClAA	BrAA	Cl_2AA	Cl_3AA	BrClAA	Br_2AA	HAA6
Aug7	0.0	0.0	41.7	41.2	20.3	-10.5	29.8
Aug13	0.0	0.0	43.0	55.1	1.8	-44.7	28.7
Aug20	0.0	0.0	39.2	29.7	12.9	7.0	23.7
Aug27	0.0	0.0	89.2	79.8	37.3	-12.5	61.7
Sep4	0.0	0.0	45.8	33.3	22.4	18.6	30.4

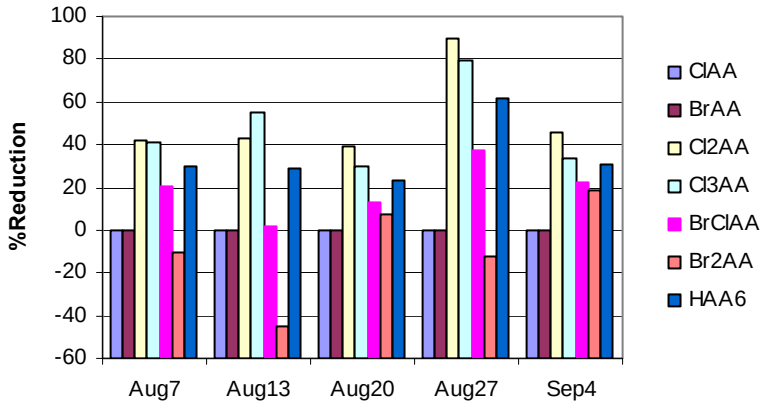


Figure A.42 HAA %reduction in chlorinated full-scale filter #3 effluent in FS/PS experiments

Table A.43 HAA %reduction in chlorinated full-scale filter #4 effluent in FS/PS experiments

Sampling Date	ClAA	BrAA	Cl_2AA	Cl_3AA	BrClAA	Br_2AA	HAA6
Aug7	0.0	0.0	51.0	48.0	44.3	26.3	45.4
Aug13	0.0	0.0	59.0	57.0	5.5	31.6	45.0
Aug20	0.0	0.0	25.3	17.2	11.3	14.0	17.6
Aug27	0.0	0.0	72.5	56.0	37.3	-6.2	49.4
Sep4	0.0	0.0	12.5	14.8	32.7	7.0	17.0

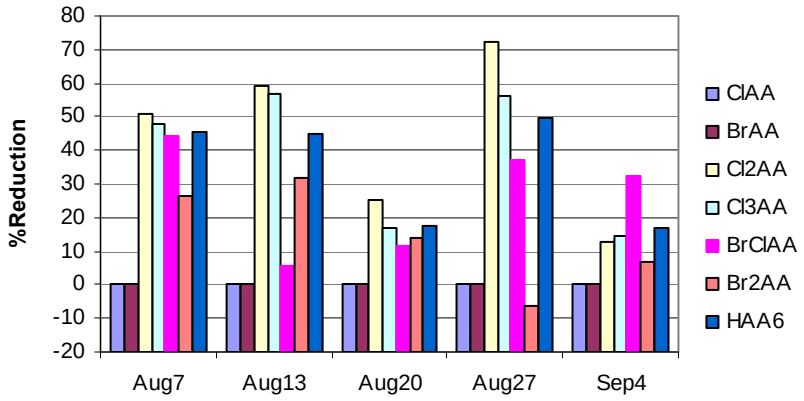


Figure A.43 HAA %reduction in chlorinated full-scale filter #4 effluent in FS/PS experiments

Table A.44 HAA %reduction in chlorinated pilot filter #1 effluent in FS/PS experiments

Sampling Date	ClAA	BrAA	Cl_2AA	Cl_3AA	BrClAA	Br_2AA	HAA6
Aug7	0.0	0.0	57.3	52.0	39.2	0.0	44.1
Aug13	0.0	0.0	57.0	52.3	27.3	15.8	44.7
Aug20	0.0	0.0	58.3	55.6	55.1	34.9	51.5

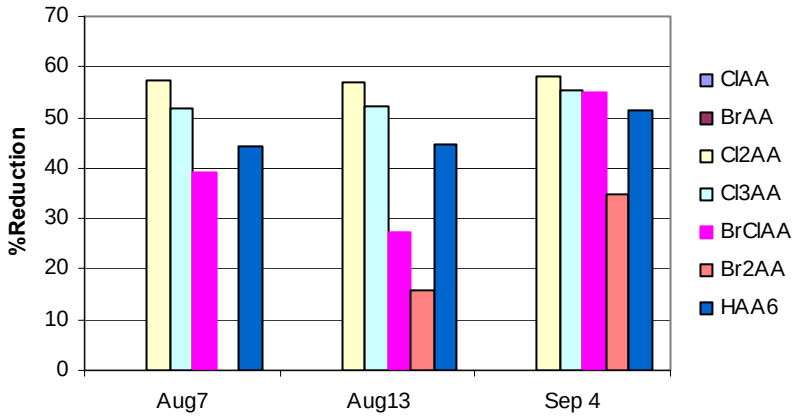


Figure A.44 HAA %reduction in chlorinated pilot filter #1 effluent in FS/PS experiments

Table A.45 HAA %reduction in chlorinated pilot filter #2 effluent in FS/PS experiments

Sampling Date	ClAA	BrAA	Cl_2AA	Cl_3AA	BrClAA	Br_2AA	HAA6
Aug7	0.0	0.0	12.5	48.0	34.2	-28.9	24.4
Aug13	0.0	0.0	42.0	53.3	12.7	-36.8	30.7
Aug20	0.0	0.0	35.4	21.9	40.3	14.0	28.6
Aug27	0.0	0.0	82.1	67.9	20.3	-21.9	50.5
Sep4	0.0	0.0	8.3	35.2	22.4	-16.3	13.9

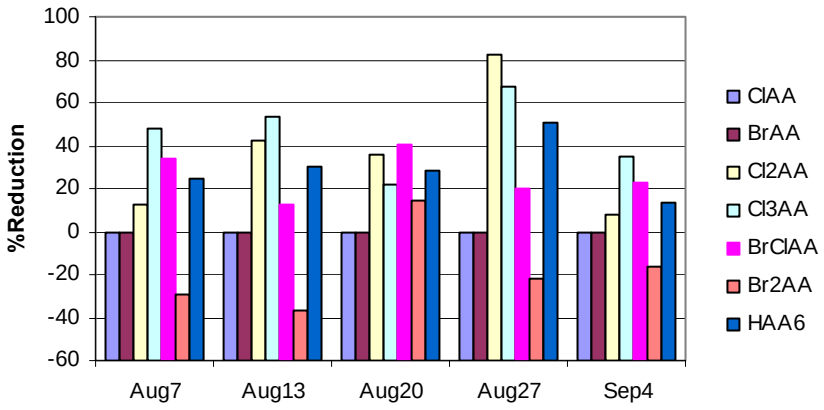


Figure A.45 HAA %reduction in chlorinated pilot filter #2 effluent in FS/PS experiments

Table A.46 HAA %reduction in chlorinated pilot filter #3 effluent in FS/PS experiments

Sampling Date	ClAA	BrAA	Cl_2AA	Cl_3AA	BrClAA	Br_2AA	HAA6
Aug7	0.0	0.0	8.3	37.3	34.2	-5.3	22.5
Aug13	0.0	0.0	37.0	37.4	21.8	-15.8	27.7
Aug20	0.0	0.0	16.5	10.9	17.7	10.5	14.1
Aug27	0.0	0.0	74.9	65.5	37.3	-6.2	35.1
Sep4	0.0	0.0	-6.3	13.0	6.1	-2.3	3.1

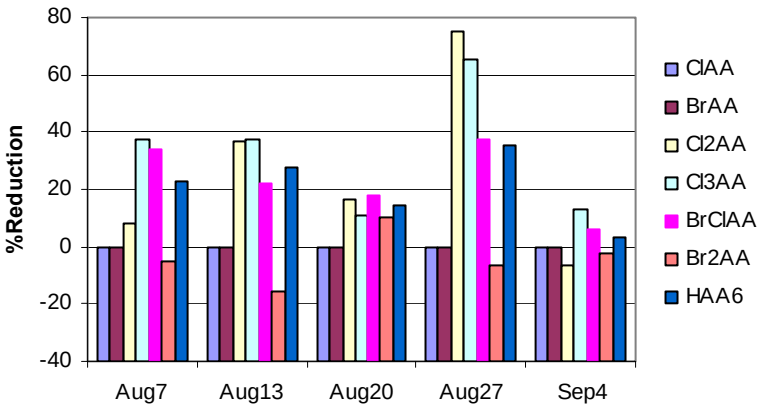


Figure A.46 HAA %reduction in chlorinated pilot filter #3 effluent in FS/PS experiments

Table A.47 HAA %reduction in chlorinated pilot filter #4 effluent in FS/PS experiments

Sampling Date	ClAA	BrAA	Cl_2AA	Cl_3AA	BrClAA	Br_2AA	HAA6
Aug7	0.0	0.0	2.1	36.3	36.7	-13.2	20.0
Aug13	0.0	0.0	22.0	30.8	-1.8	-39.5	13.0
Aug20	0.0	0.0	25.3	18.8	30.6	19.3	23.7
Aug27	0.0	0.0	78.5	58.3	37.3	-15.6	30.9
Sep4	0.0	0.0	-8.3	9.3	6.1	7.0	3.6

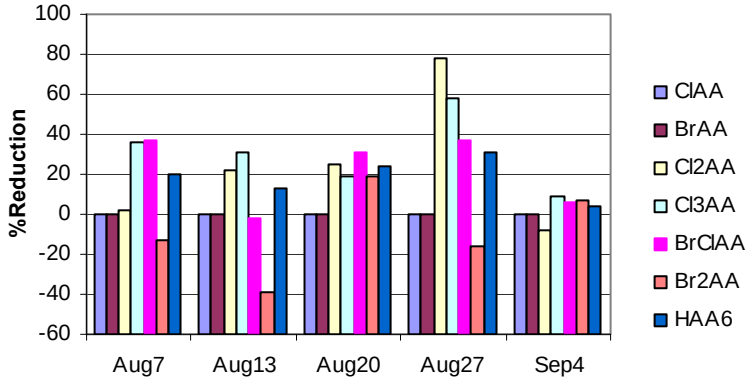


Figure A.47 HAA %reduction in chlorinated pilot filter #4 effluent in FS/PS experiments

Table A.48 Nitrosamine concentrations in full-scale filter #1 effluent in FS/PS experiments

Sampling Date	NDMA	NMEA	NDEA	NPRO	NPIP	NPYR	NDBA	NMOR
Aug7	5.7	1.5	0.0	0.0	0.0	0.0	0.0	5.2
Aug13	5.6	1.4	0.0	0.0	0.0	0.0	0.0	6.1
Aug20	6.0	1.3	0.0	0.0	0.0	0.0	0.0	5.9
Aug27	4.6	1.3	0.0	0.0	0.0	0.0	0.0	3.8
Sep 4	4.9	1.3	0.0	0.0	0.0	0.0	0.0	3.7

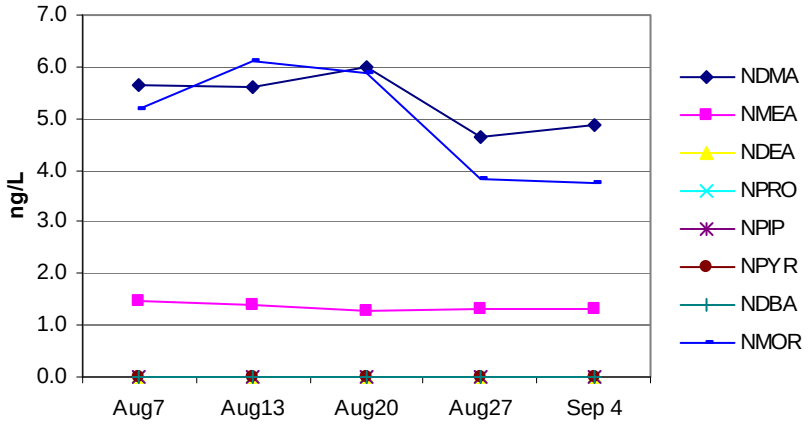


Figure A.48 Nitrosamine concentrations in full-scale filter #1 effluent in FS/PS experiments

Table A.49 Nitrosamine concentrations in chlorinated full-scale filter #2 effluent in FS/PS experiments

Sampling Date	NDMA	NMEA	NDEA	NPRO	NPIP	NPYR	NDBA	NMOR
Aug7	5.4	1.4	0.0	0.0	0.0	0.0	0.0	5.2
Aug13	4.7	1.4	0.0	0.0	0.0	0.0	0.0	3.7
Aug20	4.4	1.5	0.0	0.0	0.0	0.0	0.0	3.6
Aug27	4.2	1.6	0.0	0.0	0.0	0.0	0.0	3.5
Sep 4	4.7	1.6	0.0	0.0	0.0	0.0	0.0	3.5

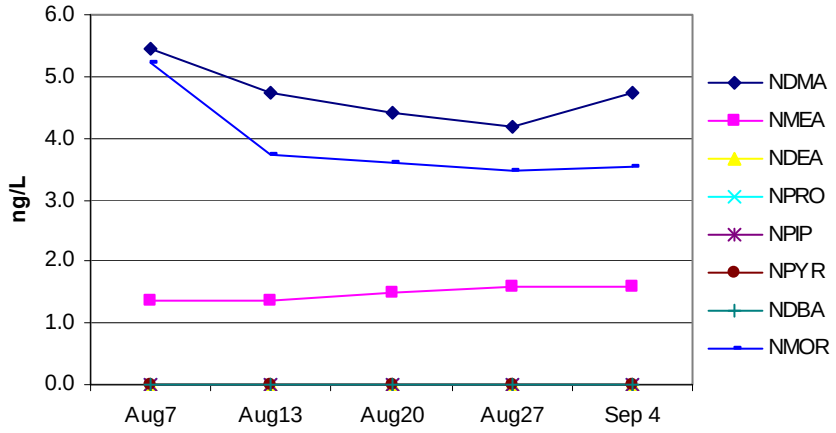


Figure A.49 Nitrosamine concentrations in chlorinated full-scale filter #2 effluent in FS/PS experiments

Table A.50 Nitrosamine concentrations in chlorinated full-scale filter #3 effluent in FS/PS experiments

Sampling Date	NDMA	NMEA	NDEA	NPRO	NPIP	NPYR	NDBA	NMOR
Aug7	6.2	1.0	0.0	0.0	0.0	0.0	0.0	5.3
Aug13	6.0	1.0	0.0	0.0	0.0	0.0	0.0	4.9
Aug20	6.0	1.0	0.0	0.0	0.0	0.0	0.0	4.1
Aug27	5.0	1.3	0.0	0.0	0.0	0.0	0.0	3.3
Sep 4	5.1	1.1	0.0	0.0	0.0	0.0	0.0	3.2

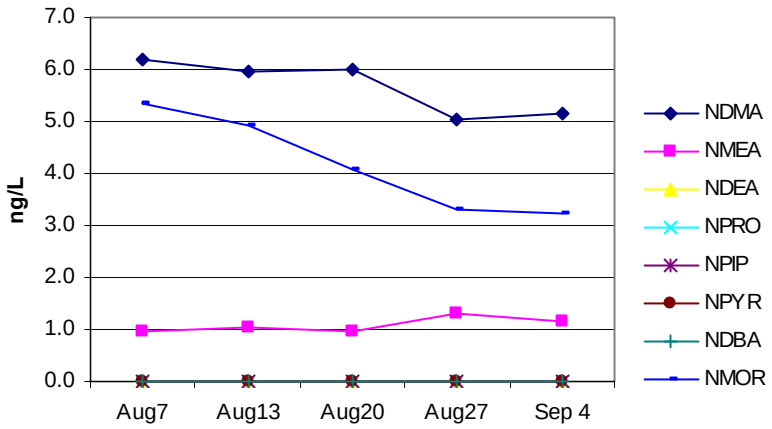


Figure A.50 Nitrosamine concentrations in chlorinated full-scale filter #3 effluent in FS/PS experiments

Table A.51 Nitrosamine concentrations in chlorinated full-scale filter #4 effluent in FS/PS experiments

Sampling Date	NDMA	NMEA	NDEA	NPRO	NPIP	NPYR	NDBA	NMOR
Aug7	6.0	1.1	0.0	0.0	0.0	0.0	0.0	4.1
Aug13	5.4	1.2	0.0	0.0	0.0	0.0	0.0	3.7
Aug20	5.0	1.2	0.0	0.0	0.0	0.0	0.0	3.6
Aug27	3.7	1.3	0.0	0.0	0.0	0.0	0.0	3.3
Sep 4	3.5	1.4	0.0	0.0	0.0	0.0	0.0	3.2

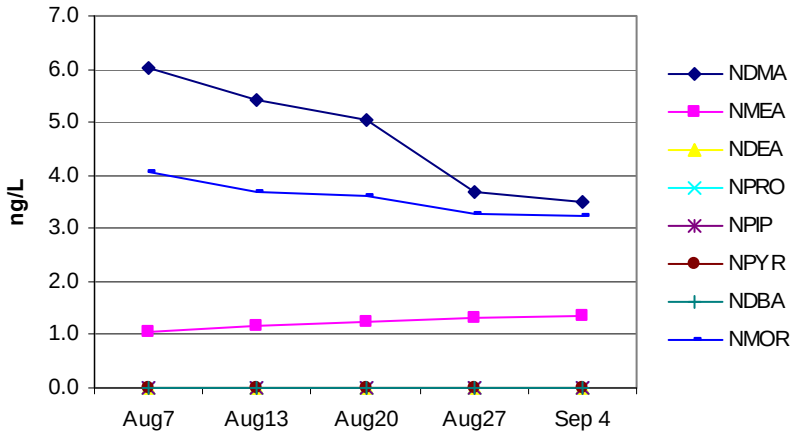


Figure A.51 Nitrosamine concentrations in chlorinated full-scale filter #4 effluent in FS/PS experiments

Table A.52 Nitrosamine concentrations in chlorinated pilot filter #1 effluent in FS/PS experiments

Sampling Date	NDMA	NMEA	NDEA	NPRO	NPIP	NPYR	NDBA	NMOR
Aug7	3.6	1.4	0.0	0.0	0.0	0.0	0.0	2.9
Aug13	4.5	1.9	0.0	0.0	0.0	0.0	0.0	3.1
Aug20	3.0	1.9	0.0	0.0	0.0	0.0	0.0	2.2

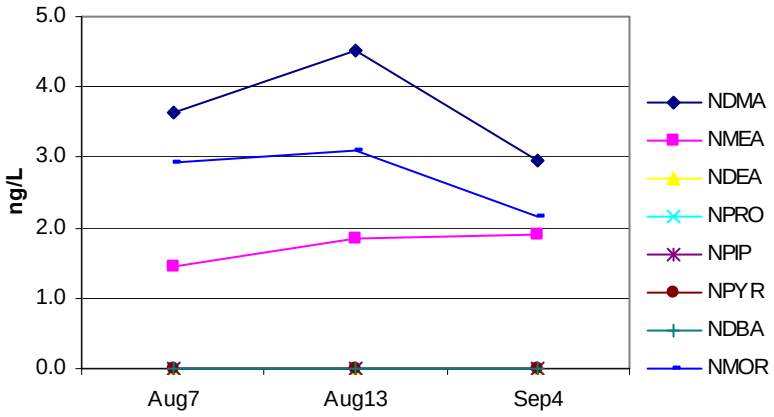


Figure A.52 Nitrosamine concentrations in chlorinated pilot filter #1 effluent in FS/PS experiments

Table A.53 Nitrosamine concentrations in chlorinated pilot filter #3 effluent in FS/PS experiments

Sampling Date	NDMA	NMEA	NDEA	NPRO	NPIP	NPYR	NDBA	NMOR
Aug7	6.0	1.1	0.0	0.0	0.0	0.0	0.0	4.1
Aug13	5.4	1.2	0.0	0.0	0.0	0.0	0.0	3.7
Aug20	5.0	1.2	0.0	0.0	0.0	0.0	0.0	3.6
Aug27	3.7	1.3	0.0	0.0	0.0	0.0	0.0	3.3
Sep 4	3.5	1.4	0.0	0.0	0.0	0.0	0.0	3.2

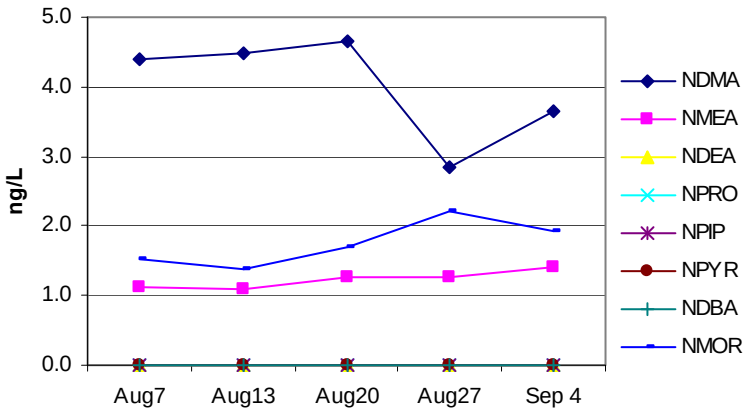


Figure A.53 Nitrosamine concentrations in chlorinated pilot filter #3 effluent in FS/PS experiments

Table A.54 Nitrosamine concentrations in pilot filter #4 effluent in FS/PS experiments

Sampling Date	NDMA	NMEA	NDEA	NPRO	NPIP	NPYR	NDBA	NMOR
Aug7	4.1	0.9	0.0	0.0	0.0	0.0	0.0	1.3
Aug13	4.4	1.1	0.0	0.0	0.0	0.0	0.0	1.4
Aug20	4.8	1.5	0.0	0.0	0.0	0.0	0.0	1.4
Aug27	2.6	1.5	0.0	0.0	0.0	0.0	0.0	1.9
Sep 4	2.9	1.6	0.0	0.0	0.0	0.0	0.0	1.6

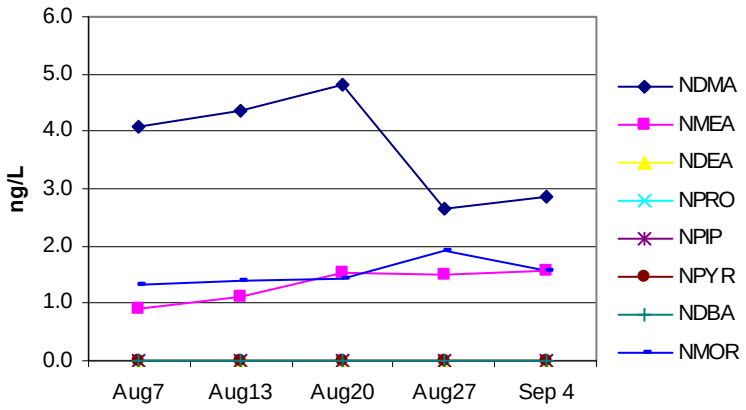


Figure A.54 Nitrosamine concentrations in chlorinated pilot filter #4 effluent in FS/PS experiments

Table A.55 Nitrosamine %reductions in full-scale in chlorinated full-scale filter #1 effluent in FS/PS experiments

Sampling Date	NDMA	NMEA	NDEA	NPRO	NPIP	NPYR	NDBA	NMOR
Aug7	50.1	40.8	100.0	0.0	0.0	0.0	0.0	34.7
Aug13	51.3	52.5	100.0	0.0	0.0	0.0	0.0	36.3
Aug20	45.1	55.4	100.0	0.0	0.0	0.0	0.0	41.4
Aug27	56.8	55.3	100.0	0.0	0.0	0.0	0.0	59.7
Sep 4	48.9	59.0	100.0	0.0	0.0	0.0	0.0	62.8

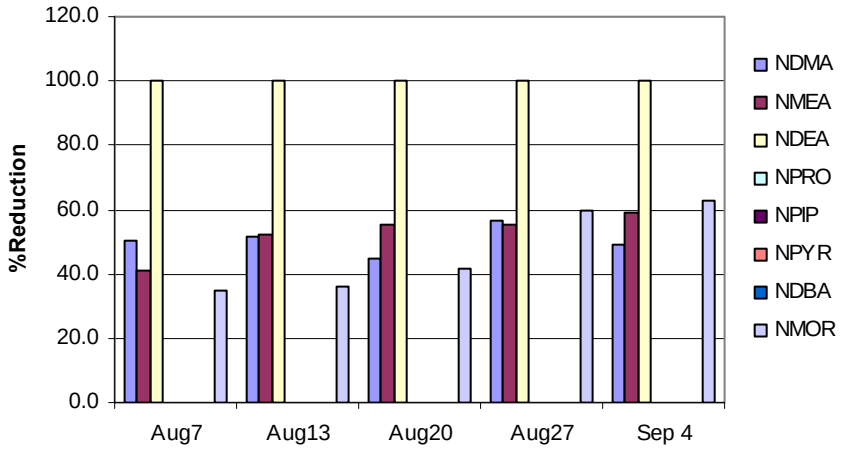


Figure A.55 Nitrosamine %reduction in chlorinated full-scale #1 effluent in FS/PS experiments

Table A.56 Nitrosamine %reductions in chlorinated full-scale filter #2 effluent in FS/PS experiments

Sampling Date	NDMA	NMEA	NDEA	NPRO	NPIP	NPYR	NDBA	NMOR
Aug7	58.8	53.5	100.0	0.0	0.0	0.0	0.0	61.0
Aug13	58.8	53.5	100.0	0.0	0.0	0.0	0.0	61.0
Aug20	59.4	48.4	100.0	0.0	0.0	0.0	0.0	64.2
Aug27	50.6	49.5	100.0	0.0	0.0	0.0	0.0	65.0
Sep 4	50.6	49.5	100.0	0.0	0.0	0.0	0.0	65.0

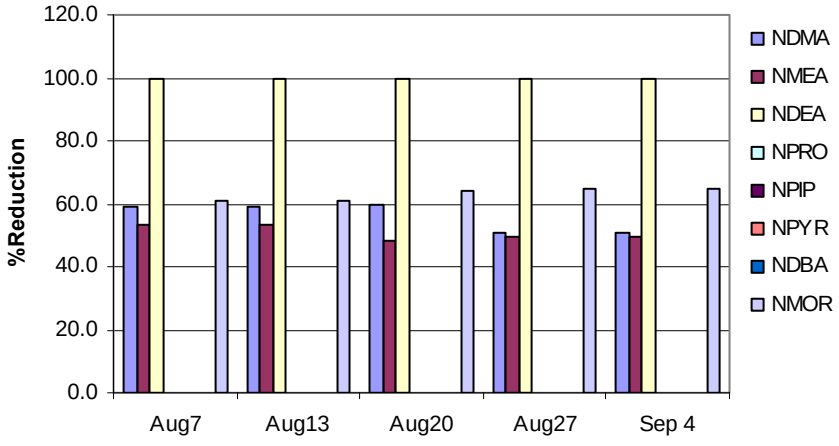


Figure A.56 Nitrosamine %reduction in chlorinated full-scale #2 effluent in FS/PS experiments

Table A.57 Nitrosamine %reductions in chlorinated full-scale filter #3 effluent in FS/PS experiments

Sampling Date	NDMA	NMEA	NDEA	NPRO	NPIP	NPYR	NDBA	NMOR
Aug7	40.6	59.2	100.0	0.0	0.0	0.0	0.0	30.8
Aug13	48.7	64.8	100.0	0.0	0.0	0.0	0.0	50.3
Aug20	41.2	65.3	100.0	0.0	0.0	0.0	0.0	54.7
Aug27	48.8	56.9	100.0	0.0	0.0	0.0	0.0	68.2
Sep 4	40.3	63.3	100.0	0.0	0.0	0.0	0.0	66.2

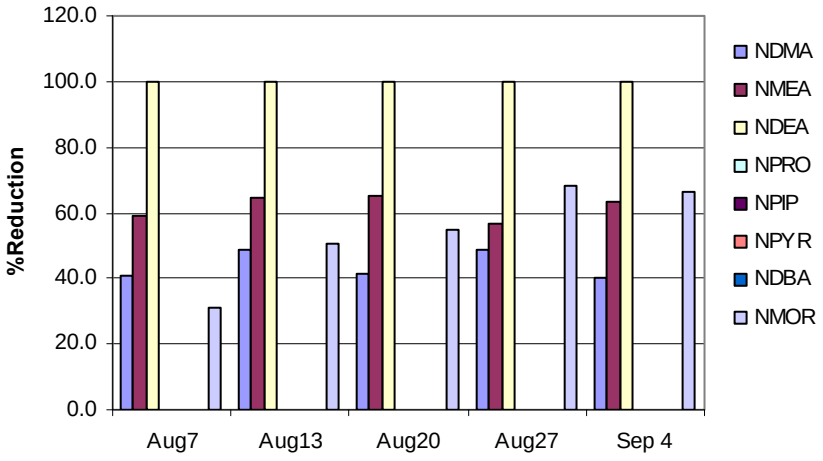


Figure A.57 Nitrosamine %reduction in chlorinated full-scale #3 effluent in FS/PS experiments

Table A.58 Nitrosamine %reductions in chlorinated full-scale filter #4effluent in FS/PS experiments

Sampling Date	NDMA	NMEA	NDEA	NPRO	NPIP	NPYR	NDBA	NMOR
Aug7	42.5	55.1	100.0	0.0	0.0	0.0	0.0	47.6
Aug13	53.3	60.9	100.0	0.0	0.0	0.0	0.0	62.5
Aug20	50.7	56.5	100.0	0.0	0.0	0.0	0.0	59.8
Aug27	62.6	56.7	100.0	0.0	0.0	0.0	0.0	68.3
Sep 4	59.5	56.6	100.0	0.0	0.0	0.0	0.0	66.0

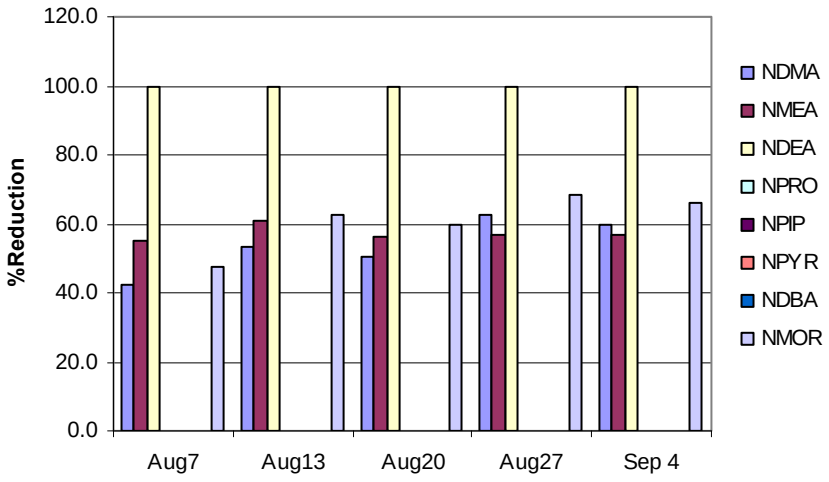


Figure A.58 Nitrosamine %reduction in full-scale #4 effluent in FS/PS experiments

Table A.59 Nitrosamine %reductions in chlorinated pilot filter #1 effluent in FS/PS experiments

Sampling Date	NDMA	NMEA	NDEA	NPRO	NPIP	NPYR	NDBA	NMOR
Aug7	42.5	55.1	100.0	0.0	0.0	0.0	0.0	47.6
Aug13	53.3	60.9	100.0	0.0	0.0	0.0	0.0	62.5
Aug20	50.7	56.5	100.0	0.0	0.0	0.0	0.0	59.8

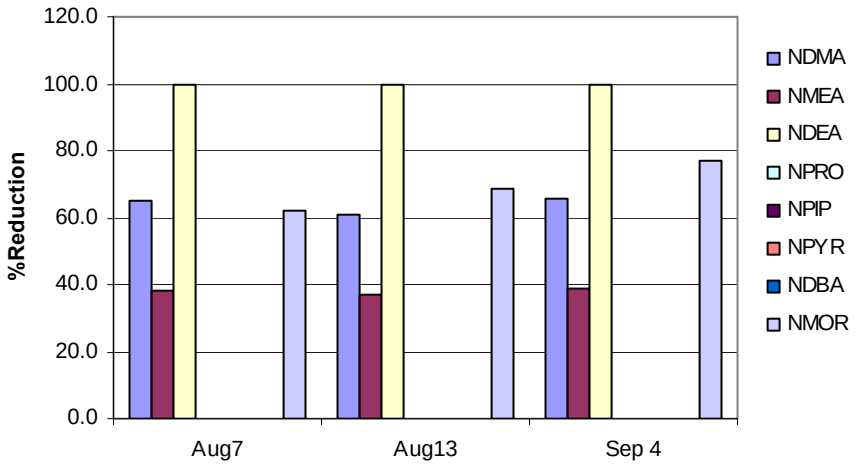


Figure A.59 Nitrosamine %reduction in chlorinated pilot filter #1 effluent in FS/PS experiments

Table A.60 Nitrosamine %reductions in chlorinated pilot filter #2 effluent in FS/PS experiments

Sampling Date	NDMA	NMEA	NDEA	NPRO	NPIP	NPYR	NDBA	NMOR
Aug7	64.4	64.3	100.0	0.0	0.0	0.0	0.0	73.3
Aug13	69.2	58.8	100.0	0.0	0.0	0.0	0.0	80.9
Aug20	63.0	38.3	100.0	0.0	0.0	0.0	0.0	74.7
Aug27	63.1	51.0	100.0	0.0	0.0	0.0	0.0	77.9
Sep 4	70.8	52.5	100.0	0.0	0.0	0.0	0.0	79.7

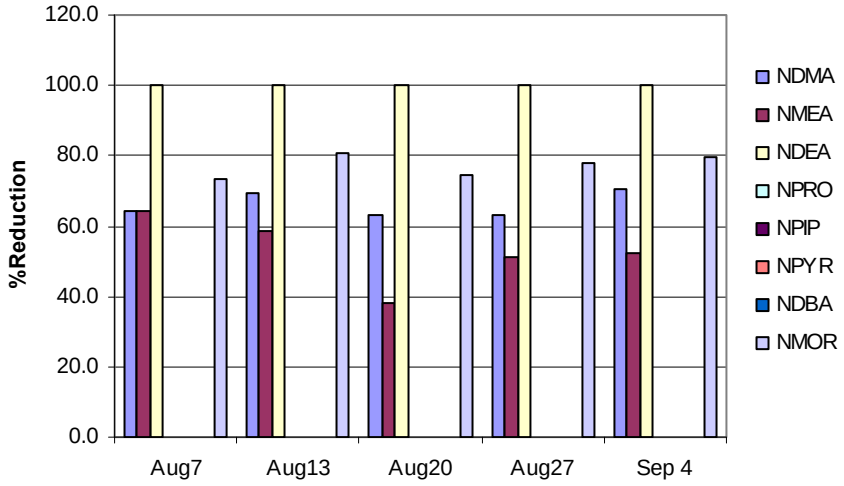


Figure A.60 Nitrosamine %reduction in chlorinated pilot filter #2 effluent in FS/PS experiments

Table A.61 Nitrosamine %reductions in chlorinated pilot filter #3 effluent in FS/PS experiments

Sampling Date	NDMA	NMEA	NDEA	NPRO	NPIP	NPYR	NDBA	NMOR
Aug7	58.0	52.3	100.0	0.0	0.0	0.0	0.0	80.3
Aug13	61.4	63.3	100.0	0.0	0.0	0.0	0.0	85.9
Aug20	54.4	55.4	100.0	0.0	0.0	0.0	0.0	81.0
Aug27	71.0	58.6	100.0	0.0	0.0	0.0	0.0	78.6
Sep 4	57.6	55.4	100.0	0.0	0.0	0.0	0.0	79.7

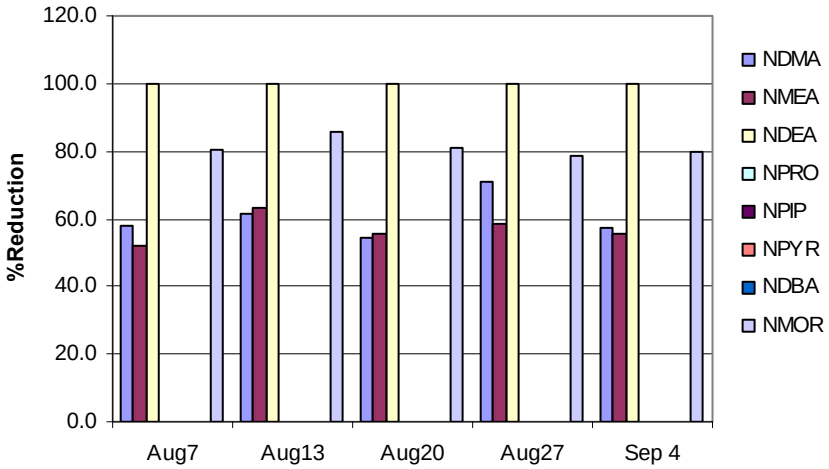


Figure A.61 Nitrosamine %reduction in chlorinated pilot filter #3 effluent in FS/PS experiments

Table A.62 Nitrosamine %reductions in chlorinated pilot filter #4 effluent in FS/PS experiments

Sampling Date	NDMA	NMEA	NDEA	NPRO	NPIP	NPYR	NDBA	NMOR
Aug7	61.0	61.8	100.0	0.0	0.0	0.0	0.0	82.9
Aug13	62.6	62.0	100.0	0.0	0.0	0.0	0.0	85.9
Aug20	52.8	45.3	100.0	0.0	0.0	0.0	0.0	84.2
Aug27	73.1	50.1	100.0	0.0	0.0	0.0	0.0	81.6
Sep 4	66.6	49.5	100.0	0.0	0.0	0.0	0.0	83.4

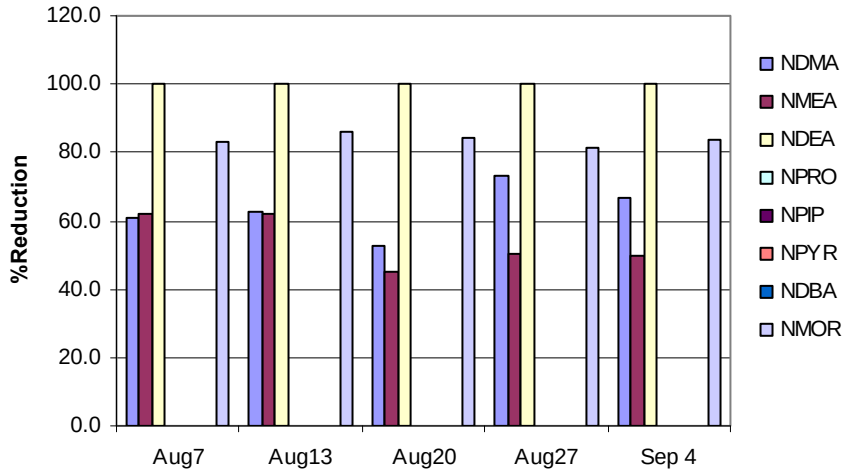
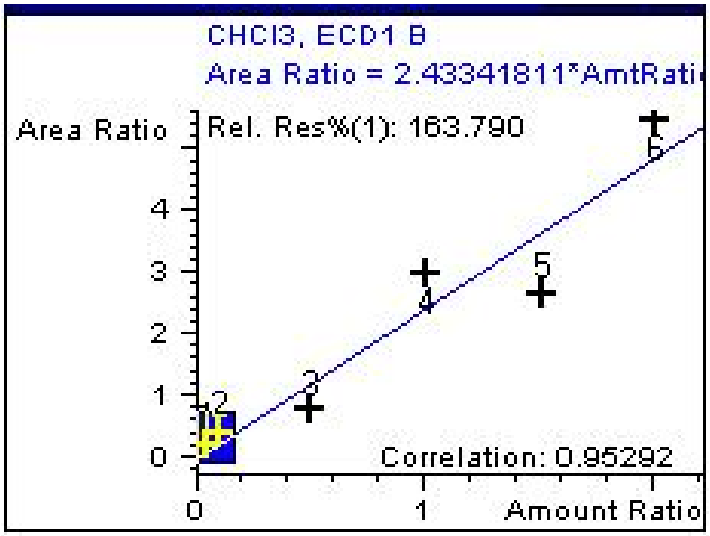


Figure A.62 Nitrosamine %reduction in chlorinated pilot filter #4 effluent in FS/PS experiments

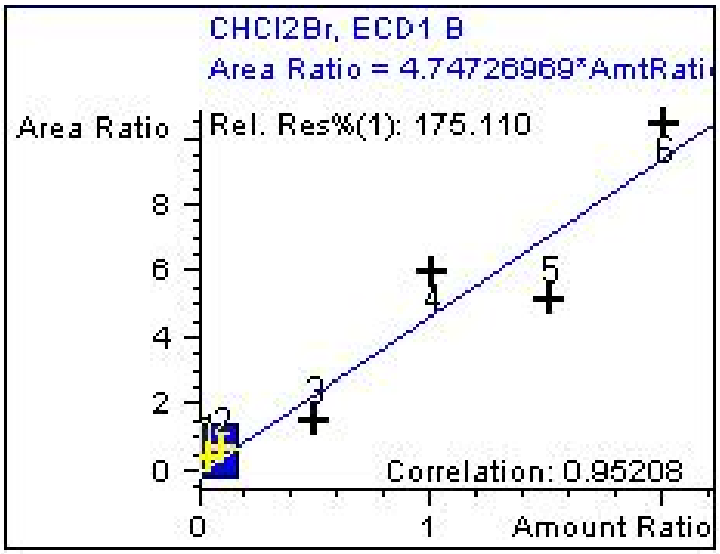
Appendix B1:THM Species, HAA Species, and Nitrosamines Calibration Curves

$CHCl_3$ Calibration Curve



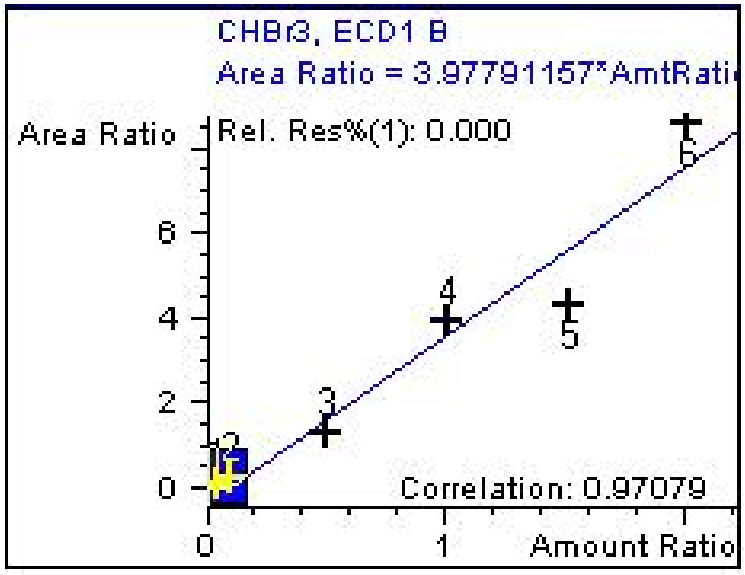
Slop	***2.433***
Intercept	
R^2	***0.95292***

$CHCl_2Br$ Calibration Curve



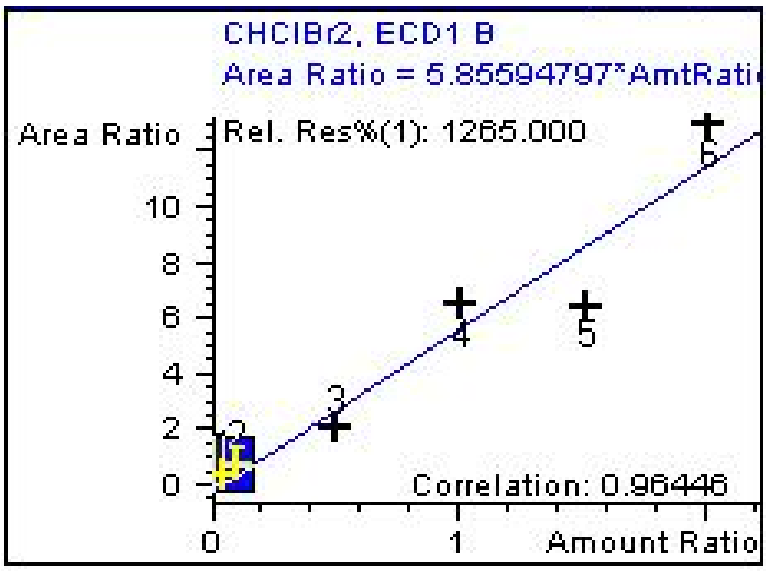
Slop	***4.747***
Intercept	
R^2	***0.95208***

CHB_3 Calibration Curve



Slop	***3.9779***
Intercept	
R^2	***0.97079***

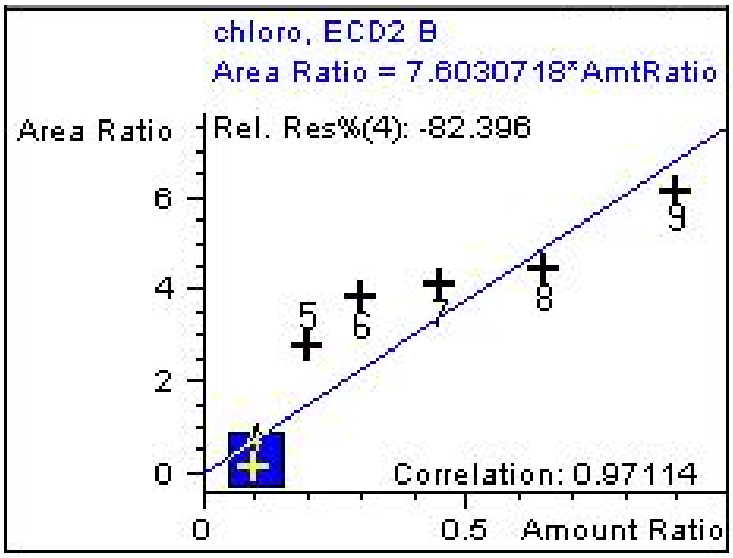
$CHClBr_2$ Calibration Curve



Slop	***5.85594***
Intercept	
R^2	***0.96446***

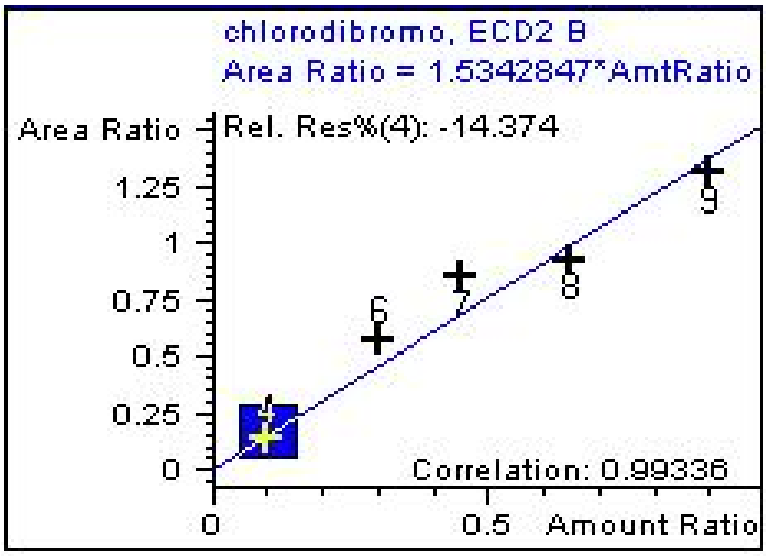
HAA Species Calibration Curves

Chloroacetic acid Calibration Curve



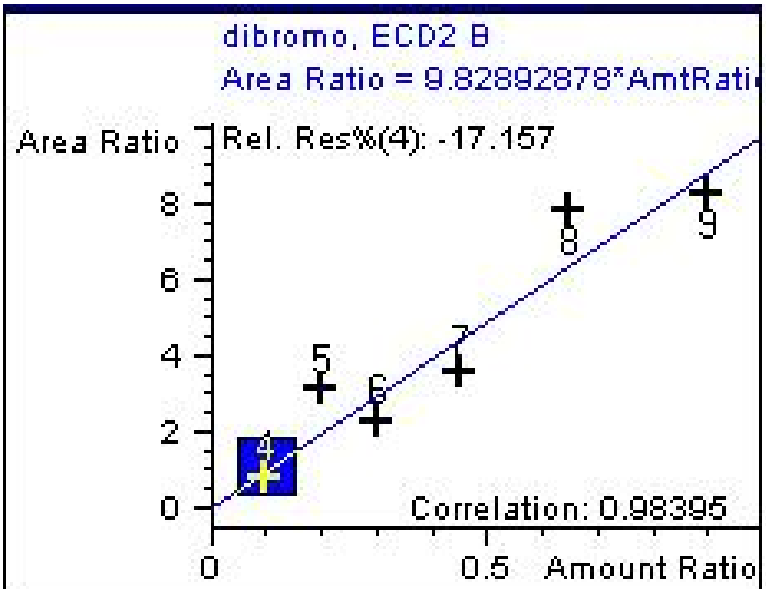
Slop	***7.6030***
Intercept	
R^2	***0.97114***

Chlorodibromoacetic acid Calibration Curve



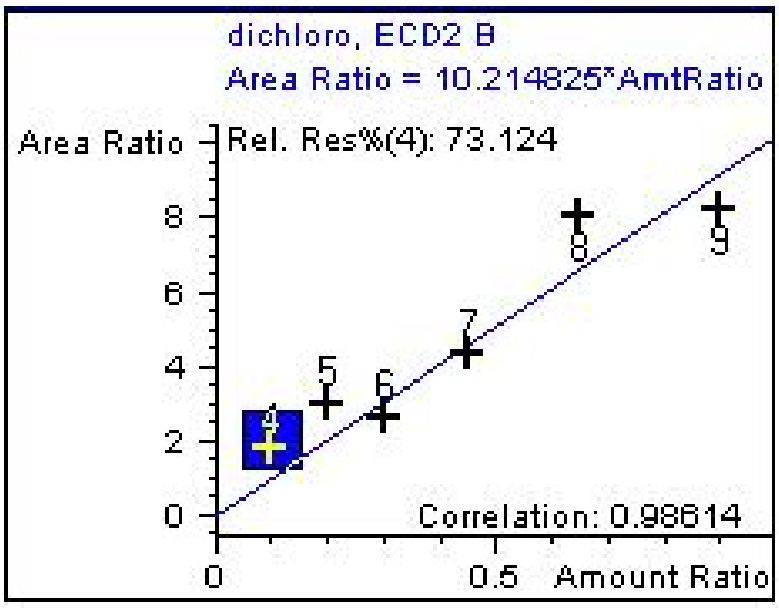
Slop	***1.53428***
Intercept	
R^2	***0.99336***

Dibromoacetic acid Calibration Curve



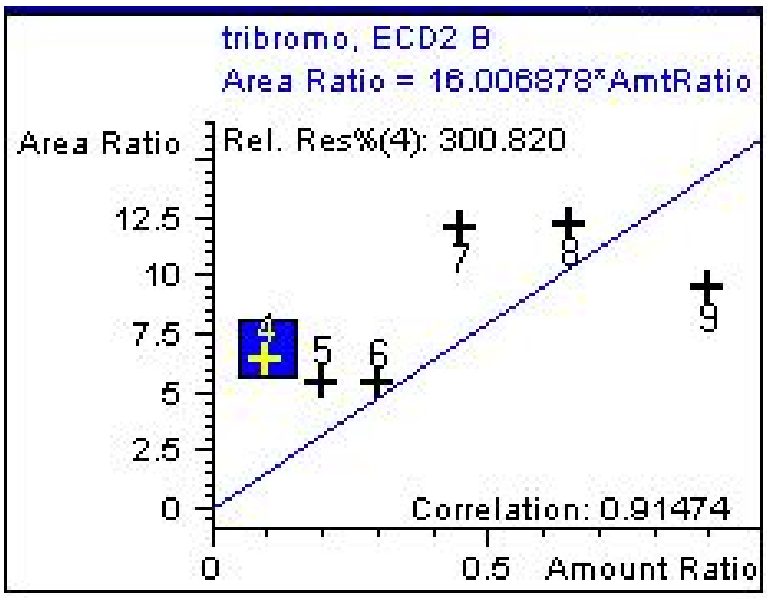
Slop	***9.828928***
Intercept	
R^2	***0.98395***

Dichloroacetic acid Calibration Curve



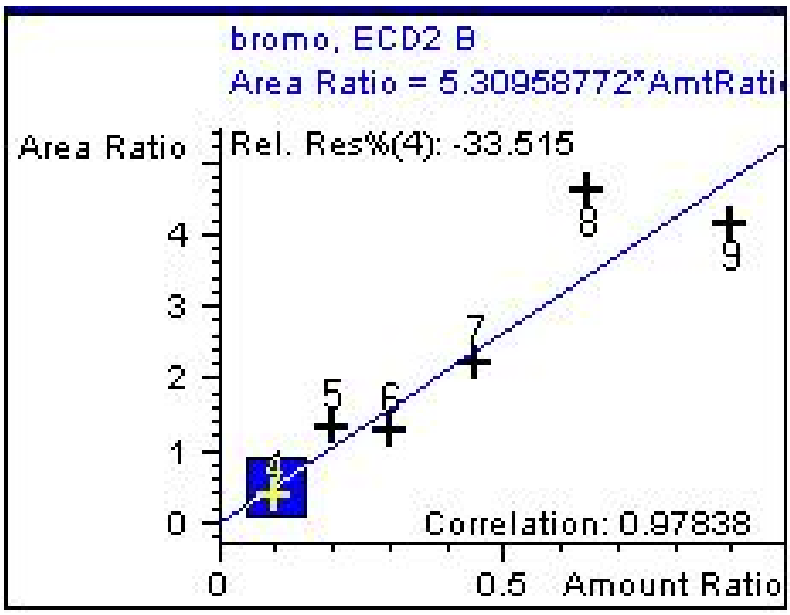
Slop	***10.214825***
Intercept	
R^2	***0.98614***

Tribromoacetic acid Calibration Curve



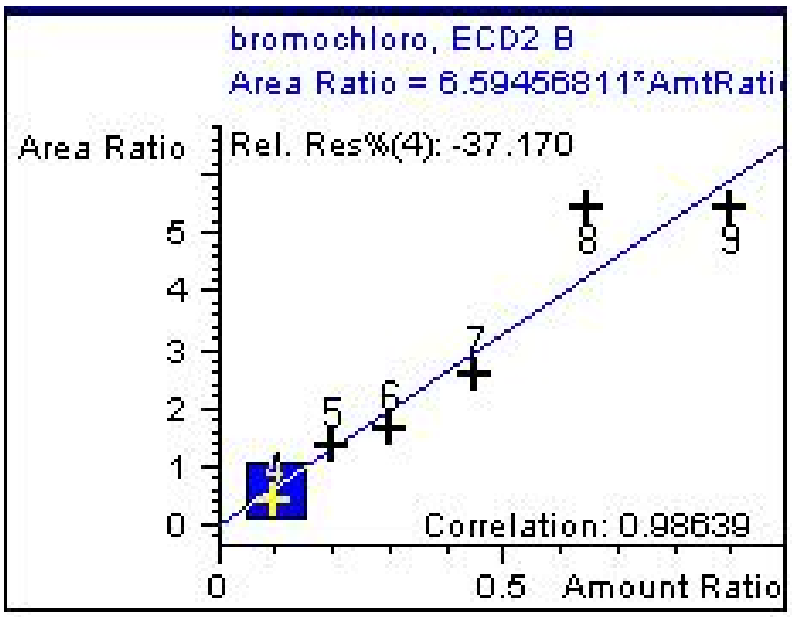
Slop	***16.006878***
Intercept	
R^2	***0.91474***

Bromoacetic acid Calibration Curve



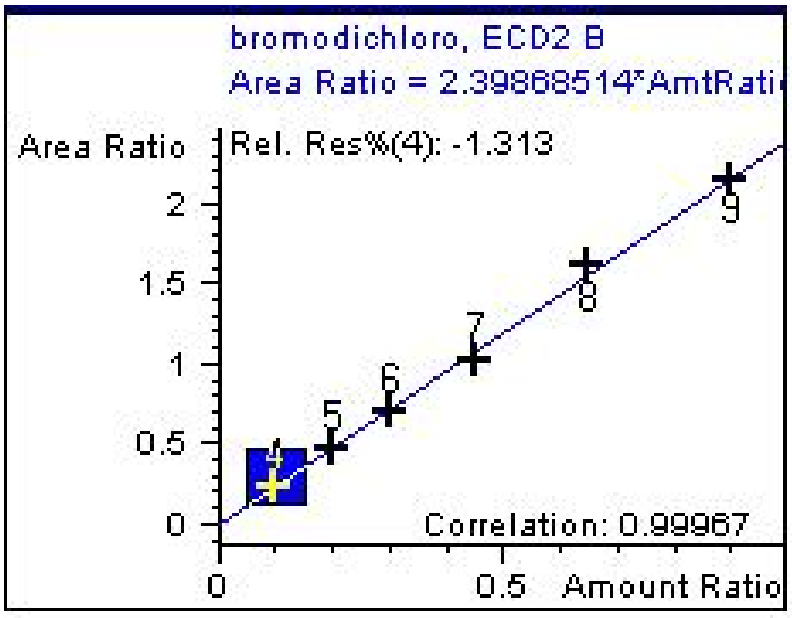
Slop	***5.30958***
Intercept	
R^2	***0.97838***

Bromochloroacetic acid Calibration Curve



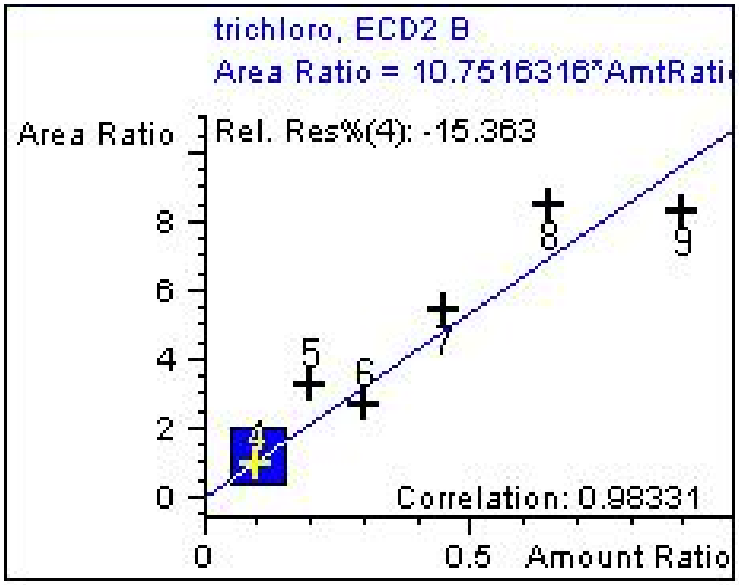
Slop	***6.5945***
Intercept	
R^2	***0.98639***

Bromodichloroacetic acid Calibration Curve



Slop	***2.39868***
Intercept	
R^2	***0.99967***

Trichloroacetic acid Calibration Curve



Slop	***10.75163***
Intercept	
R^2	***0.98331***

Appendix B2: DBPs Analytical Method Detection Limits (MDLs)

Table B2.1 THM species method detection limits

THM Species	CHCl3	CHCl2Br	CHClBr2	CHBr3
MDL (µg/L)	2.59	2.93	3.08	2.97

Table B.2.2 HAA species method detection limits

HAA Species	ClAA	BrAA	Cl_2AA	Cl_3AA	BrClAA	Br_2AA
MDL(µg/L)	1.33	2.84	1.52	2.61	2.09	1.36

Table B.2.3 Nitrosamines method detection limits

Nitrosamine Compound	NDMA	NMEA	NDEA	NPRO	NPIP	NPYR	NDBA	NMOR
MDL (ng/L)	1.79	1.74	1.143	1.81	1.55	1.06	1.27	1.78

Appendix B3: DBPs Methods Control Charts

Figure B.3.1 THMs variation in standard solutions of 25 µg/L

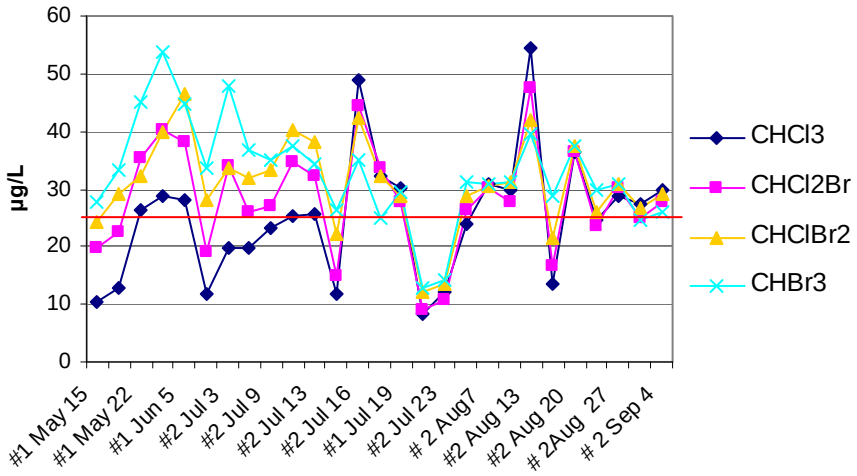


Figure B.3.2 HAAs variation in standard solutions of 25 µg/L

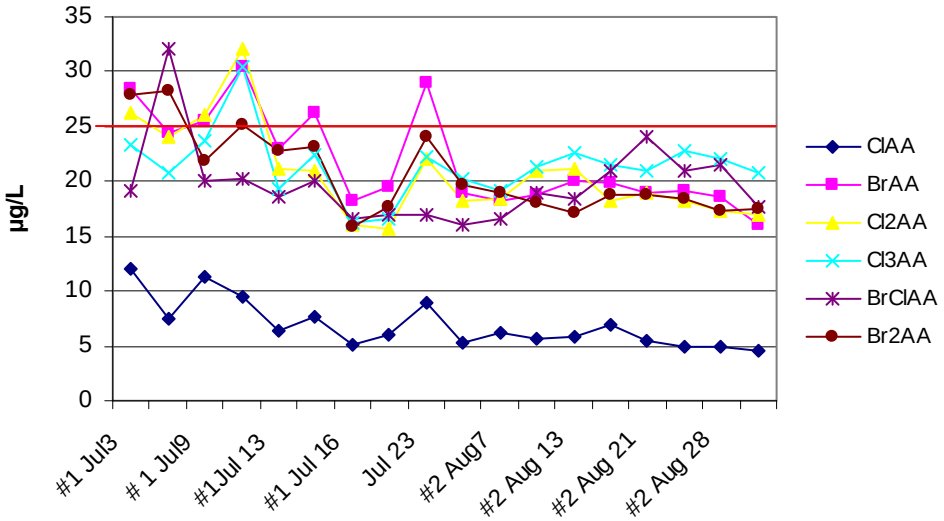
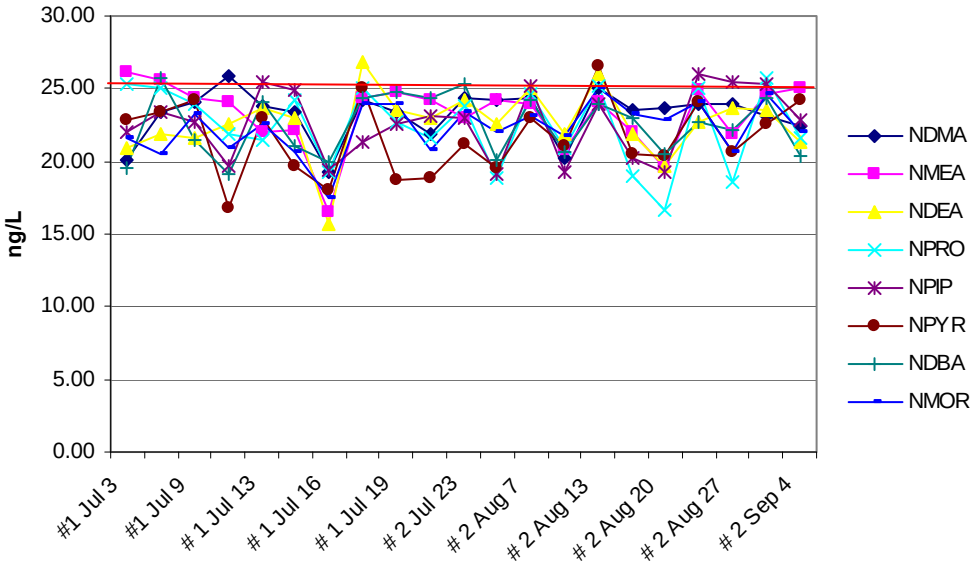


Figure B.3.3 Nitrosamines variation in standard solutions of 25 ng/L



Appendix C: Mannheim Water Treatment Plant Flow Rate and Loading Rate Calculations

Table C.1 Loading rate/flow rate conversion in pilot filters

PILOT-SCALE	flow rate	conversion	conversion	area	conversion	column diameter
LOADING (m/h)	L/min	m^3/1000L	100^2 cm^2/m^2	cm^2	60 min/h	in
1.9	1	0.001	10000	324.1	60	8
3.7	2	"	"	"	"	"
5.6	3	"	"	"	"	"
7.4	4	"	"	"	"	"
9.3	5	"	"	"	"	"
11.1	6	"	"	"	"	"
11.2	6.05	"	"	"	"	"
12.0	6.5	"	"	"	"	"
13.0	7	"	"	"	"	"
14.8	8	"	"	"	"	"
15.0	8.1	"	"	"	"	"
16.7	9	"	"	"	"	"
18.5	10	"	"	"	"	"
20.4	11	"	"	"	"	"
22.2	12	"	"	"	"	"
24.1	13	"	"	"	"	"

Table C.2 Loading rate/flow rate conversion in full-scale filters

						Imperial	
FULL-SCALE	**flow rate(filter)**	**conversion**	**conversion**	**area**	**conversion**	**MGD (Plant)**	**L/s (Plant)**
LOADING (m/h)	L/s	$m^3/1000L$	3.2808^2 ft^2/m^2	ft^2	3600 s/h		
5.9	110	0.001	10.76	726	3600	8.4	440
6.4	120	"	"	"	"	9.1	480
6.9	130	"	"	"	"	9.9	520
7.5	140	"	"	"	"	10.6	560
8.0	150	"	"	"	"	11.4	600
8.5	160	"	"	"	"	12.2	640
9.1	170	"	"	"	"	12.9	680
9.6	180	"	"	"	"	13.7	720
10.1	190	"	"	"	"	14.4	760
10.7	200	"	"	"	"	15.2	800
11.2	210	"	"	"	"	16.0	840
11.7	220	"	"	"	"	16.7	880
12.0	225	"	"	"	"	17.1	900
12.3	230	"	"	"	"	17.5	920

Note: Calculations provided by M.B. Emelko.

Appendix D: Normal Probability Plots

Zi= Expected normal value from standard Normal Distribution Table

Xi= Observed value (percent reduction of DBP precursor in the filter)

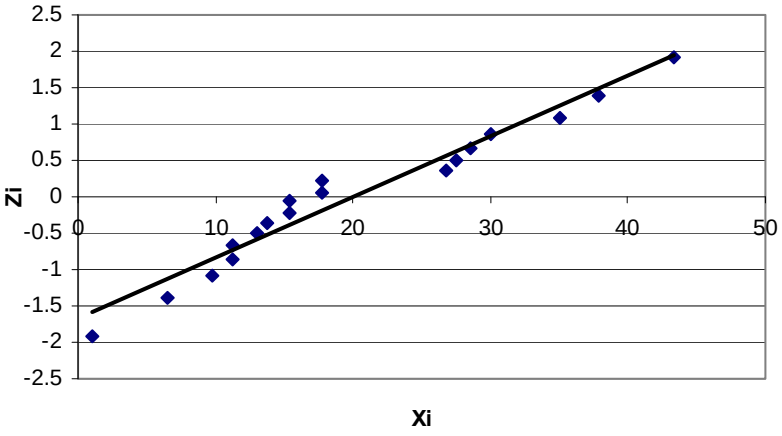


Figure D.1 Normal probability plot of TTHM percent removal data from pilot filters

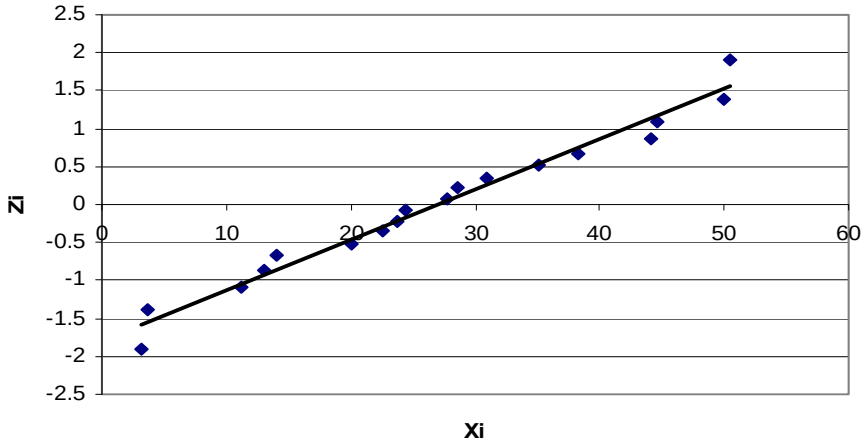


Figure D.2 Normal probability plot for HAA6 percent removal data from pilot filters

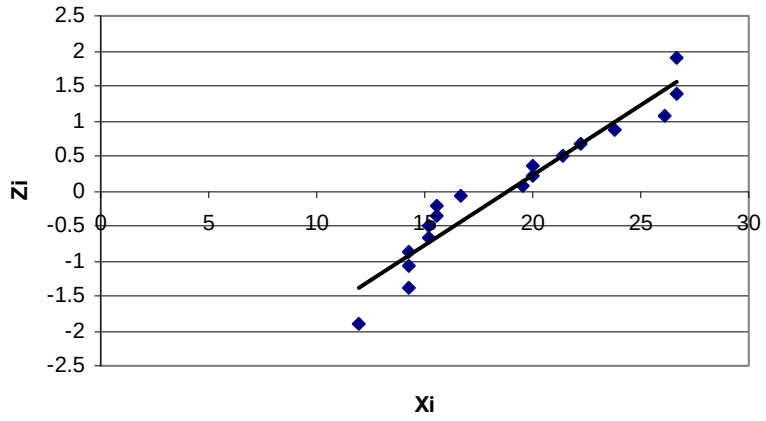


Figure D.3 Normal probability plot of chlorine demand percent removal data from pilot filters

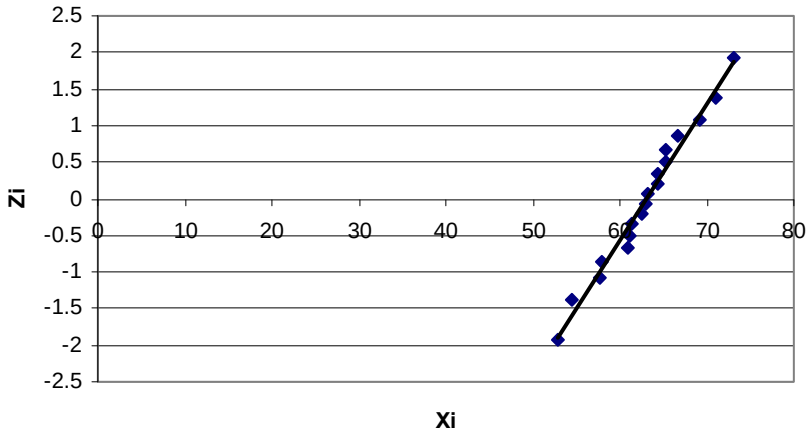


Figure D.4 Normal probability plot of NDMA percent removal data from pilot filters