EPA/600/R-02/068
September 2002

The Occurrence of Disinfection By-Products (DBPs) of Health Concern in Drinking Water: Results of a Nationwide DBP Occurrence Study

Howard S. Weinberg
The Department of Environmental Sciences and Engineering
University of North Carolina at Chapel Hill
Chapel Hill, NC

Stuart W. Krasner
Metropolitan Water District of Southern California
La Verne, CA

Susan D. Richardson and Alfred D. Thruston, Jr.
Ecosystems Research Division
National Exposure Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Athens, GA

National Exposure Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Athens, GA

DISCLAIMER

The United States Environmental Protection Agency (EPA) through its Office of Research and Development partially funded and collaborated in the research described here. The information in this document has been partially funded under Cooperative Agreement No. 826697. It has been peer reviewed by the EPA and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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ACKNOWLEDGMENTS

The authors would like to acknowledge the following people who contributed to this project.

University of North Carolina

Gretchen D. Onstad	Ramiah Sangaiah	Vanessa Pereira
Gary L. Glish	Karupiah Jayaraj	Katrina Jamison
Christine N. Dalton	Lindsay Dubbs	Zhengqi Ye
Philip C. Singer	Petra Strunk	

Metropolitan Water District of Southern California

Alicia Gonzalez	Lely Suhady	Hsiao-Chiu Wang
Salvador Pastor	Jacob Nikonchuk	Ching Kuo
Russell Chinn	Leslie Bender	Suzanne Teague
Michael J. Sclimenti	Vaheh Martyr	Robert Alvarez
Sylvia Barrett	Tim Albrecht	Jesus Vasquez, Jr.
Pat Hacker	Bart Koch	Eric Crofts
Sikha Kundu	Tiffany Lee	Himansu Mehta

U.S. EPA National Exposure Research Laboratory, Athens, GA

Terrance L. Floyd
F. Gene Crumley

We also need to express appreciation to Leif Kronberg and Angel Messegauer for providing samples of furanone standards, as well as Bruce McKague (Can Syn Chem Co.), Francesc Ventura (Aigues of Barcelona, Spain) and George Majetich (Majestic Research) for providing standards for quantitative methods and new DBP identification work.

Last, but not least, we would like to gratefully acknowledge the assistance of the participating utilities that collected the samples, provided operational and water quality data, and ensured a successful survey. Without their generous cooperation, this study would not have been possible.

We are also extremely grateful to the U.S. EPA Office of Water and Office of Prevention, Pesticides, and Toxic Substances scientists who undertook the initial DBP prioritization effort that provided the focus for this study. Thank you to Vicki Dellarco, Yin-Tak Woo, David Lai, Jennifer McLain, and Mary Ko Manibusan.

GLOSSARY OF TERMS

AOC	Assimilable organic carbon
BEMX	Brominated forms of EMX
BF_3/MeOH	Boron trifluoride methanol complex
BMX-1	3-Chloro-4-(bromochloromethyl)-5-hydroxy-2(5H)-furanone
BMX-2	3-Chloro-4-(dibromomethyl)-5-hydroxy-2(5H)-furanone
BMX-3	3-Bromo-4-(dibromomethyl)-5-hydroxy-2(5H)-furanone
CCF	Carbon contactor filtered
CH_2N_2	Diazomethane
CI	Chemical ionization
Cl_2	Chlorine
CLSA	Closed-loop stripping analysis
ClO_2	Chlorine dioxide
ClO_2^-	Chlorite
CT	Concentration-time
DCAN	Dichloroacetonitrile
DIW	Deionized water
DBP	Disinfection by-product
DCP	Dichloropropanone
DOC	Dissolved organic carbon
DS	Distribution system
DXAA	Sum of dihaloacetic acids (dichloro-, bromochloro-, dibromoacetic acid)
EBCT	Empty bed contact time
ECD	Electron capture detector
EI	Electron ionization
EMX	(E)-2-Chloro-3-(dichloromethyl)-4-oxobutenoic acid
EtAc	Ethyl acetate
FE	Filter effluent
FI	Filter influent
GAC	Granular activated carbon
GC	Gas chromatography or Gas chromatograph
H_2SO_4/MeOH	Sulfuric acid in methanol
HAAs	Haloacetic acids
HAA5	Sum of 5 HAAs (monochoro-, monobromo-, dichloro-, dibromo-, trichloroacetic acid)
HAA9	Sum of 9 HAAs (HAA5 + bromochloro-, bromodichloro-, dibromochloro-, tribromoacetic acid)
HANs	Haloacetonitriles

HKs	Haloketones
HNMs	Halonitromethanes
HPLC	High performance liquid chromatography
HRMS	High resolution mass spectrometry
ICR	Information Collection Rule
ID	Inner diameter
IS	Internal standard
KHP	Potassium hydrogen phosphate
LLE	Liquid-liquid extraction
MBA	Mucobromic acid
MCA	Mucochloric acid
MCL	Maximum contaminant level
MDL	Method detection limit
MEK	Methyl ethyl ketone
MeOH	Methanol
MG	Million gallons
mgd	Million gallons per day
MS	Mass spectrometry
MtBE	Methyl *tertiary*-butyl ether
MW	Molecular weight
MWDSC	Metropolitan Water District of Southern California
MX	3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone
MX-analogues	MX, ZMX, EMX, ox-MX, ox-EMX, red-MX, MCA, BMX-1,2,3
MXR	Esterified form of MX
MXR-analogues	Esterified forms of MX-analogues
NA	Not available
ND	Not detected at or above minimum reporting level (MRL)
NH_2Cl	Chloramines
NMR	Nuclear magnetic resonance
NR	Not reported
NS	Not sampled
N_2	Nitrogen gas
NH_3	Ammonia
NOM	Natural organic matter
O_3	Ozone
OE	Ozone contactor effluent
Ox-EMX	Oxidized EMX, (E)-2-Chloro-3-(dichloromethyl)butenedioic acid
Ox-MX	Oxidized MX, (Z)-2-Chloro-3-(dichloromethyl)butenedioic acid
Ox-NOM	Oxidized NOM
PE	Plant effluent
PFBHA	Pentafluorobenzylhydroxylamine

P&T	Purge-and-trap
Red-MX	Reduced MX, 3-Chloro-4-(dichloromethyl)-2(5H)-furanone
RDL	Reporting detection level
RM	Rapid mix
SDS	Simulated distribution system
SIR	Selected ion monitoring
SPE	Solid phase extraction
SPME	Solid phase microextraction
SUVA	Specific ultraviolet absorbance
TCP	Trichloropropanone
THMs	Trihalomethanes
THM4	Sum of 4 regulated THMs (chloroform, bromoform, bromodichloromethane, dibromochloromethane)
TIC	Total ion chromatogram
TLC	Thin layer chromatography
TOC	Total organic carbon
TT	Treatment tank effluent
TXAA	Sum of trihaloacetic acids (trichloro-, bromodichloro-, dibromochloro-, tribromoacetic acid)
UNC	University of North Carolina
USEPA	United States Environmental Protection Agency
UV	Ultraviolet light
VOC	Volatile organic compound
WTP	Water treatment plant
ZMX	(Z)-2-Chloro-3-(dichloromethyl)-4-oxobutenoic acid

EXECUTIVE SUMMARY

The motivation for this Nationwide Disinfection By-product (DBP) Occurrence Study was two-fold: First, more than 500 DBPs have been reported in the literature, yet there is almost no quantitative occurrence information for most. As a result, there is significant uncertainty over the identity and levels of DBPs that people are exposed to in their drinking water. Second, only a limited number of DBPs have been studied for adverse health effects. So, it is not known whether other DBPs (besides the few that are currently regulated) pose a risk to human health. To determine whether other DBPs pose an adverse health risk, more comprehensive quantitative occurrence and toxicity data are needed.

Because health effects studies are very expensive, it is not possible to test all DBPs that have been reported. It is also not feasible to measure >500 DBPs in waters across the United States. Thus, results of a DBP prioritization effort by scientists at the U.S. Environmental Protection Agency (USEPA) Office of Water and the USEPA Office of Prevention, Pesticides, and Toxic Substances were used to focus this study on those DBPs that were the most toxicologically significant. These EPA experts applied an in-depth mechanism-based structural activity relationship analysis to the more than 500 DBPs reported in the literature, supplemented by an extensive literature search for genotoxicity and other data, and ranked the carcinogenic potential of these DBPs. Approximately 50 DBPs that received the highest ranking for potential toxicity and that were not included in the USEPA's Information Collection Rule (ICR) were selected for this occurrence study. These DBPs, denoted as 'high priority' DBPs in this report, included such compounds as MX [3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone], brominated forms of MX (BMXs), halonitromethanes, iodo-trihalomethanes, and many brominated species of halomethanes, haloacetonitriles, haloketones, and haloamides.

For this Nationwide Occurrence Study, scientists from the USEPA's National Exposure Research Laboratory (NERL) initiated a collaboration with scientists at the University of North Carolina (UNC, Howard Weinberg, PI) and the Metropolitan Water District of Southern California (MWDSC, Stuart Krasner, co-PI). The 'high priority' DBPs, along with regulated and Information Collection Rule DBPs for comparison, were quantified in drinking waters across the United States. These waters represented diverse geographic regions with different source water quality. Several source waters contained relatively high bromide levels (where brominated DBPs would be expected to form). In addition, many of the waters selected for study were relatively high in total organic carbon (TOC). Waters treated with all four major disinfectants (chlorine, chloramines, ozone, and chlorine dioxide) were studied. In addition, the fate and transport of these DBPs was studied in the real distribution systems and in simulated distribution system (SDS) tests. Prior to this study, there was almost nothing known about the stability of these DBPs in the distribution system.

Because no quantitative analytical methods existed for most of the high priority DBPs, optimized analytical methods were initially developed at UNC and MWDSC. No one single analytical method could be used for all DBPs, so different methods were developed and optimized for specific groups of DBPs. Also, because there were no commercially available standards for many of these compounds, many had to be synthesized.

Another goal of this project was to use this opportunity to look for other DBPs that have not been previously identified in order to provide a more complete assessment of DBPs formed by different treatments in different regions of the United States. This work was carried out at the USEPA NERL-Athens laboratory. For this research, a combination of advanced mass spectrometric tools was used to identify the new DBPs.

Results revealed the presence of many of the high priority DBPs in the waters sampled. Important observations included finding the highest levels of iodo-trihalomethanes (THMs) at a plant that used chloramination without pre-chlorination. Levels of individual iodo-THMs ranged from 0.2 to 15 µg/L. Another important observation involved finding the highest concentration of dichloroacetaldehyde at a plant that used chloramine and ozone disinfection. Therefore, although the use of alternative disinfectants minimized the formation of the four regulated THMs, certain dihalogenated DBPs and iodo-THMs were formed at significantly higher levels than in waters treated with chlorine. Thus, the formation and control of the four regulated THMs is not necessarily an indicator of the formation and control of other halogenated DBPs, and the use of alternative disinfectants does not necessarily control the formation of all halogenated DBPs, and can even result in increased concentrations of some. Moreover, many of these halogenated DBPs—including certain dihalogenated and brominated species—were not studied in the ICR.

Halogenated furanones, including MX and brominated MX (BMX) analogues, were widely observed in these samplings. Another finding was the high levels of MX and MX-analogues in many samples. It was previously observed that MX did not exceed a concentration of 60 to 90 ng/L (the few measurements that had been conducted generally showed levels <60 ng/L). In this study, however, MX was often observed at levels significantly greater than 100 ng/L, with a maximum level of 310 ng/L observed in finished water from a treatment plant that disinfected a high-TOC water with chlorine dioxide, chlorine, and chloramines. These findings are significant because the levels of MX are much higher than previously reported. Likewise, several other analogues of MX were identified, including BMX analogues. Results include 170 ng/L and 200 ng/L levels for BMX-1 and BEMX-3, respectively (at a treatment plant that disinfected a high-bromide water with chlorine dioxide, chlorine, and chloramines). It is interesting that the drinking water utilities with the highest MX and BMX levels were from treatment plants that use chlorine dioxide for primary disinfection. MX did not form from chlorine dioxide disinfection *per se*, rather chlorine dioxide oxidation appeared to not destroy MX precursors (as ozone, another alternative disinfectant, does). Thus, MX and BMX formation was highest at treatment plants with high levels of TOC and bromide, respectively.

Halonitromethanes, including dihalogenated and brominated species not included in the ICR, were found in some of the samples; levels of individual species ranged from 0.1 to 3 µg/L. In some cases, pre-ozonation was found to increase the formation of the trihalonitromethanes (brominated analogues of chloropicrin [trichloronitromethane]). Many brominated acids were also identified in several finished waters that contained elevated levels of bromide in their source waters. A number of brominated acids were identified for the first time (i.e., brominated propanoic, propenoic, butanoic, butenoic, oxopentanoic, heptanoic, nonanoic, and butenedioic acids), with most being observed in the finished water from a treatment plant that has significant

bromide levels in its source water. One of the high priority DBPs, 3,3-dichloropropenoic acid, was found in several finished waters, giving further evidence that haloacids with longer carbon chains are prevalent DBPs (i.e., haloacetic acids are not the only haloacids formed during disinfection).

Dihaloacetaldehydes and brominated analogues of chloral hydrate (trichloroacetaldehyde) were detected in many samples, as were mono-, di-, tri-, and/or tetra-species of halomethanes and haloketones. Several haloamides were also found in finished waters at levels similar to DBPs that are commonly measured (low µg/L levels). This is a class of DBPs that has not been previously quantified, but the levels observed in this study indicate that their levels in finished waters are not trivial. In addition, carbon tetrachloride was detected in some of the waters measured, with a maximum of 0.8 µg/L observed. Although carbon tetrachloride was present in sampled finished drinking waters, its identity as a DBP could not be proven, since carbon tetrachloride is sometimes used to clean out chlorine cylinders before they are filled. Thus, it could be either a DBP or a contaminant from the cleaning process.

Another finding in this study was the discovery of iodoacids for the first time. Five new iodoacid species were tentatively identified: iodoacetic acid, iodobromoacetic acid, iodobromopropenoic acid (2 isomers), and 2-iodo-3-methylbutenedioic acid. High resolution mass spectrometry confirmed the presence of iodine in their structures and the overall empirical formulas for these new DBPs. One of these—iodoacetic acid—has been confirmed through the analysis of an authentic chemical standard (match of retention time and mass spectrum). Additional synthetic standards are currently being prepared to confirm the other iodoacid identifications. These iodoacids were observed as DBPs in a high-bromide water from a treatment plant that uses only chloramine disinfection. Another iodinated DBP, tentatively identified as iodobutanal, was found in finished waters from treatment plants on both coasts that can be impacted by saltwater intrusion (sea water is a source of iodide in addition to a major source of bromide in some drinking waters). This DBP has also not been reported previously.

In addition to the new iodinated DBPs and new brominated acids, another brominated ketone was identified for the first time: 1-bromo-1,3,3-trichloropropanone, which was found in many of the waters sampled.

The stability of DBPs in actual distribution systems and in simulated distribution system (SDS) tests varied. In most cases where chloramination was used, the DBPs were relatively stable. However, when free chlorine was used, THMs and other DBPs, including haloacetic acids, increased in concentration both in the actual distribution system and in SDS tests. Haloacetonitriles generally were stable (at the distribution-system pH levels encountered in this study) and increased in concentration, but many of the haloketones were found to degrade in the distribution system and SDS tests. Halonitromethanes and dihaloacetaldehydes were found to be stable in these systems and tests. Although controlled laboratory studies had suggested instability of halogenated furanones, particularly MX, in water, MX and MX-analogues were sometimes stable, and sometimes they degraded somewhat in the distribution systems and SDS tests. When the MX analogues showed some degradation in the distribution system, they were generally still present at detectable levels, indicating that they do not completely degrade in the distribution system. Many times, the BMXs were stable.

INTRODUCTION

More than 500 disinfection by-products (DBPs) have been reported in the literature for the major disinfectants currently used (chlorine, ozone, chlorine dioxide, chloramines), as well as their combinations (Richardson, 1998). Of these reported DBPs, only a small percentage have been quantified in drinking waters. Thus, there is significant uncertainty over the identity and levels of DBPs that people are actually exposed to in their drinking water. Moreover, only a limited number of DBPs have been studied for adverse health effects. To determine whether the other DBPs pose an adverse health risk, more comprehensive quantitative occurrence and toxicity data are needed. To address this issue, scientists at the U.S. Environmental Protection Agency's (USEPA's) National Exposure Research Laboratory (NERL) initiated a proposal for a Nationwide DBP Occurrence Study.

Due to the large number of DBPs identified in drinking waters in the United States and other countries, it is not feasible to quantify all of them, so a way of prioritizing them was needed. Prior to this occurrence study, a multidisciplinary group of experts from the USEPA Office of Water and the USEPA Office of Prevention, Pesticides, and Toxic Substances had initiated a prioritization effort for the >500 DBPs reported in the literature according to their predicted adverse health effects (Woo et al., 2002). An in-depth, mechanism-based, structural activity relationship (SAR) analysis, supplemented by an extensive literature search for genotoxicity and other data, was used to rank the carcinogenic potential of these DBPs. Approximately 50 DBPs that received the highest ranking for potential toxicity, and that were not already included in the USEPA's Information Collection Rule (ICR), were selected for this occurrence study. Those ~50 DBPs are denoted 'high priority' DBPs in this report.

The 'high priority' DBPs include brominated, chlorinated, and iodinated species of halomethanes, brominated and chlorinated forms of haloacetonitriles, haloketones, haloacids, and halonitromethanes, as well as analogues of MX [3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone] (Table 1). Chemical Abstract Services (CAS) numbers are provided in Table 1 when they were available. Previously, MX had been determined to be the most mutagenic (to *Salmonella* bacteria) DBP ever identified in drinking water, accounting for as much as 20-50% of the total mutagenic activity measured in chlorinated drinking water samples (Kronberg and Vartiainen, 1988; Backlund et al., 1988; Meier et al., 1987). MX has also been shown to be carcinogenic in laboratory animals (Komulainen et al., 1997). Yet, very little drinking water occurrence data has been obtained for MX, so its potential hazard to humans has not been determined. There have also been recent reports of brominated DBP forms of MX (BMXs) (Suzuki and Nakanishi, 1995). These brominated DBP species are of concern because brominated species of DBPs have been shown to be significantly more carcinogenic than their chlorinated analogues. Brominated nitromethanes have also been recently shown to be extremely cytotoxic and genotoxic in mammalian cells (Plewa et al., 2002; Kargalioglu et al., in press). Specifically, they have been shown to be at least an order of magnitude more genotoxic to mammalian cells than MX and have genotoxicities greater than all of the regulated DBPs, except for monobromoacetic acid. It is interesting that dibromonitromethane and

bromonitromethane received the highest priority ranking of all DBPs in the SAR toxicity analysis effort.

It should be noted that Table 1 lists the identity of more than 50 high priority target species. During method development, additional species in the same analyte group were included for some of the drinking water plant surveys.

Because most of the high priority DBPs were from chlorine or chloramine disinfection, a few additional ozone and chlorine dioxide DBPs that were not ranked as a high priority were also included for completeness (i.e., to provide more information on those alternative disinfectants). In addition, methyl *tert*-butyl ether (MtBE) and methyl bromide, which are volatile organic compounds (VOCs) but not DBPs, were included in the list of target analytes because they are important source water pollutants, and their measurement would provide valuable occurrence information. Regulated and some ICR DBPs were also included in this study for comparison purposes (Table 2). In addition, routine water quality measurements, such as total organic carbon (TOC), total organic halide (TOX), assimilable organic carbon (AOC), and bromide were determined.

Table 1. Priority DBPs selected for Nationwide Occurrence Study [a]

MX and MX-Analogues:
3-Chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX)
3-Chloro-4-(dichloromethyl)-2-(5H)-furanone (red-MX)
(E)-2-Chloro-3-(dichloromethyl)-butenedioic acid (ox-MX)
(E)-2-Chloro-3-(dichloromethyl)-4-oxobutenoic acid (EMX)
2,3-Dichloro-4-oxobutenoic acid (Mucochloric acid) [87-56-9]
3-Chloro-4-(bromochloromethyl)-5-hydroxy-2(5H)-furanone (BMX-1) [132059-51-9]
3-Chloro-4-(dibromomethyl)-5-hydroxy-2(5H)-furanone (BMX-2) [132059-52-0]
3-Bromo-4-(dibromomethyl)-5-hydroxy-2(5H)-furanone (BMX-3) [132059-53-1]
(E)-2-Chloro-3-(bromochloromethyl)-4-oxobutenoic acid (BEMX-1) [c]
(E)-2-Chloro-3-(dibromomethyl)-4-oxobutenoic acid (BEMX-2) [c]
(E)-2-Bromo-3-(dibromomethyl)-4-oxobutenoic acid (BEMX-3) [c]

Haloacids:
3,3-Dichloropropenoic acid

Halomethanes:
Chloromethane [74-87-3]
Bromomethane (methyl bromide) [74-83-9] [b]
Dibromomethane [74-95-3]
Bromochloromethane [74-97-5]
Bromochloroiodomethane [34970-00-8]
Dichloroiodomethane [594-04-7]
Dibromoiodomethane [c] [593-94-2]
Chlorodiiodomethane [c] [638-73-3]
Bromodiiodomethane [c] [557-95-9]
Iodoform [75-47-8] [c]
Chlorotribromomethane [594-15-0]
Carbon tetrachloride [56-23-5]

Halonitromethanes:
Bromonitromethane [563-70-2]
Chloronitromethane [c] [1794-84-9]
Dibromonitromethane [598-91-4]
Dichloronitromethane [c] [7119-89-3]
Bromochloronitromethane [c] [135531-25-8]
Bromodichloronitromethane [c] [918-01-4]
Dibromochloronitromethane [c] [1184-89-0]
Tribromonitromethane (bromopicrin) [c] [464-10-8]

Table 1 (Continued)

Haloacetonitriles:
Bromoacetonitrile [590-17-0]
Chloroacetonitrile [107-14-2]
Tribromoacetonitrile [75519-19-6]
Bromodichloroacetonitrile [60523-73-1]
Dibromochloroacetonitrile [144772-39-4]

Haloketones:
Chloropropanone [78-95-5]
1,3-Dichloropropanone [534-07-6]
1,1-Dibromopropanone
1,1,3-Trichloropropanone [921-03-9]
1-Bromo-1,1-dichloropropanone
1,1,1,3-Tetrachloropropanone [16995-35-0]
1,1,3,3-Tetrachloropropanone [632-21-3]
1,1,3,3-Tetrabromopropanone [c] [22612-89-1]
1,1,1,3,3-Pentachloropropanone [1768-31-6]
Hexachloropropanone [116-16-5]

Haloaldehydes:
Chloroacetaldehyde [107-20-0]
Dichloroacetaldehyde [70-02-7]
Bromochloroacetaldehyde [c] [98136-99-3]
Tribromoacetaldehyde [115-17-3] [c]

Haloacetates:
Bromochloromethyl acetate [247943-54-0]

Haloamides:
Monochloroacetamide [79-07-2] [c]
Monobromoacetamide [683-57-8] [c]
Dichloroacetamide [683-72-7]
Dibromoacetamide [c] [598-70-9]
Trichloroacetamide [594-65-0] [c]

Table 1 (Continued)

Non-Halogenated Aldehydes and Ketones:
2-Hexenal [505-57-7]; [6728-26-3]
5-Keto-1-hexanal [d]
Cyanoformaldehyde [4471-47-0]
Methylethyl ketone (2-butanone) [78-93-3] [d]
6-Hydroxy-2-hexanone [d]
Dimethylglyoxal (2,3-butanedione) [431-03-8]
Volatile organic compounds (VOCs) and Miscellaneous DBPs:
1,1,1,2-Tetrabromo-2-chloroethane
1,1,2,2-Tetrabromo-2-chloroethane [c]
Methyl-*tert*-butyl ether [1634-04-4] [b]
Benzyl chloride [100-44-7]

[a] Chemical Abstracts Services (CAS) numbers provided in brackets when available.
[b] Not a DBP, but included because it is an important source water contaminant.
[c] DBP not originally prioritized (identified in drinking water after initial prioritization), but included due to similarity to other priority compounds.
[d] DBP not given a high priority, but included for completeness sake to provide more representation to ozone DBPs for occurrence.

Table 2. Information Collection Rule and regulated DBPs included for comparison [a]

Halomethanes	Haloacetic acids (cont).
Chloroform	Dibromoacetic acid
Bromodichloromethane	Trichloroacetic acid
Dibromochloromethane	Bromodichloroacetic acid
Bromoform	Dibromochloroacetic acid
	Tribromoacetic acid
Haloacetonitriles	
Dichloroacetonitrile	Halonitromethanes
Bromochloroacetonitrile	Chloropicrin (trichloronitromethane)
Dibromoacetonitrile	
Trichloroacetonitrile	Haloaldehydes
	Chloral hydrate
Haloketones	(trichloroacetaldehyde)
1,1-Dichloropropanone	
1,1,1-Trichloropropanone	Oxyhalides
	Bromate
Haloacetic acids	Chlorate
Monochloroacetic acid	Chlorite
Monobromoacetic acid	
Dichloroacetic acid	
Bromochloroacetic acid	

[a] Five HAAs are regulated; six HAAs were required in the ICR, however some utilities reported data on the complete set of 9 HAAs.

The design of this study involved the study of drinking waters disinfected with the four common disinfectants: chlorine, chloramines, ozone, and chlorine dioxide. Because many of the high priority DBPs were brominated, it was important to include drinking waters that contained relatively high bromide levels. In addition, many of the waters selected for study were relatively high in TOC. Drinking water samples were selected from across the United States to assess the distribution and speciation of by-products in a variety of different waters from geographically diverse regions, with differing water quality, treatment, and distribution system characteristics (Figure 1). Moreover, pairs of treatment plants were chosen that used source waters from the same (or similar) watersheds but employed different treatment technologies and disinfection scenarios. This permitted an evaluation of the impact of technology and disinfectant combinations on by-product formation, while minimizing confounding factors related to differing source water quality. Each of the plants provided operational information and complementary water quality analyses. Drinking water was also sampled at typically two points in each distribution system to determine the fate and transport of DBPs—as well as actual occurrence in the distribution system—and simulated distribution system (SDS) tests were conducted to determine the formation and stability of DBPs in the presence of chlorine or chloramines. Previously, most of the newly identified DBPs were detected in drinking waters that had been sampled only at the treatment plant; very little was known about the fate and transport (and stability) of most of the newly identified DBPs in the distribution system. To this end, the influence of water quality parameters, treatment, and distribution system conditions on DBP concentrations and persistence (stability) was a major objective of this work. The drinking water utilities that were sampled are shown in Table 3.

Sampling Survey: 12 plants sampled quarterly

2 plants - same watershed - different treatment/disinfection

Plants sampled in EPA Regions 3, 4, 5, 6, 7, and 9

Figure 1. Sampling survey.

Table 3. Drinking water utilities sampled

Utility[a] (EPA Region[b])	Disinfection Used
Plant 1 (EPA Region 9)	Ozone-chlorine-chloramines
Plant 2 (EPA Region 9)	Chlorine-chloramines
Plant 12 (EPA Region 6)	(Chlorine dioxide-)Chloramines
Plant 11 (EPA Region 6)	Chlorine dioxide-chlorine-chloramines
Plant 8 (EPA Region 4)	Chlorine-chloramines
Plant 7 (EPA Region 4)	Chloramines-ozone
Plant 6 (EPA Region 4)	Chlorine dioxide-chlorine-chloramines
Plant 5 (EPA Region 4)	Ozone-chlorine
Plant 3 (EPA Region 3)	Chlorine-chloramines
Plant 4 (EPA Region 3)	Chlorine
Plant 10 (EPA Region 5)	Chlorine-chloramines
Plant 9 (EPA Region 7)	Chlorine-chloramines

[a]The following pairs of plants treated water from the same or similar watersheds: plants 1and 2; 3 and 4; 5 and 6; 7 and 8; 9 and 10; and 11 and 12**.**

[b]The 12 plants in this survey were located in six of the nine regions defined by the EPA. The states included in each of these six regions are as follows:

EPA Region 9—Arizona, California Hawaii, Nevada
EPA Region 6—Arkansas, Louisiana, New Mexico, Oklahoma, Texas
EPA Region 4—Alabama, Florida, Georgia, Kentucky, Mississippi, North Carolina, South Carolina, Tennessee
EPA Region 3—Delaware, Maryland, Pennsylvania, Virginia, West Virginia, Washington D.C.
EPA Region 5—Illinois, Indiana, Michigan, Minnesota, Ohio, Wisconsin
EPA Region 7—Iowa, Kansas, Missouri, Nebraska

Because there were no existing quantitative analytical methods for most of the high priority DBPs, methods were initially developed at UNC and MWDSC. The high priority DBPs were divided between UNC and MWDSC for method development and quantitative analyses (UNC measured the MX analogues, carbonyls, 3,3-dichloropropenoic acid, haloacetates, haloamides, and some haloaldehydes; MWDSC measured bromate, chlorate, chlorite, halomethanes, haloacetic acids, haloacetonitriles, haloacetaldehydes, haloketones, halonitromethanes, methyl ethyl ketone, methyl *tertiary* butyl ether (MTBE), tetrabromochloroethane, and benzyl chloride). In addition, a method was used at UNC for differentiating the total organic chlorine and bromine. No one single analytical method could be used for all DBPs, so different methods were developed and optimized for specific groups of DBPs. Also, because there were no commercially available standards for many of these compounds, a significant number had to be synthesized. A combination of extraction and derivatization techniques were utilized that minimized artifact formation and maximized recovery of the target analytes from the aquatic matrix. Positive identification was achieved through use of a combination of complementary spectroscopic tools, some of which were designed to target a broader range of by-products than those listed, and/or dual-column gas chromatography. Once methods for the target by-products were established, studies of their formation and stability were conducted at full-scale treatment plants and their respective distribution systems.

Another goal of this project was to use this opportunity to look for other DBPs that had not been previously identified in order to provide a more complete assessment of DBPs formed by different treatments in different regions of the U.S. This work was carried out at the USEPA NERL-Athens laboratory. For this research, a combination of mass spectrometric techniques (gas chromatography with high and low resolution electron ionization mass spectrometry, and with chemical ionization mass spectrometry) was used to aid in the identification of these new DBPs. Mass spectra for those DBPs that had not been previously reported (i.e., those identified in this study for the first time) are provided in the Appendix of this report.

Presentations of preliminary results from this Nationwide DBP Occurrence Study have been given at several scientific meetings over the last three years. Citations of the more comprehensive proceedings articles appear below for reference (Krasner et al., 2002; Sclimenti

et al., 2002; Krasner et al., 2001; Weinberg et al., 2001; Gonzalez et al., 2000; Onstad et al., 2000, Onstad and Weinberg, 2001).

This report is presented in multiple chapters, each of which represents a specific component of the research, method development, and DBP analysis in the treatment plants after different unit processes and/or disinfectant addition and in the distribution systems.

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RESULTS

EPA REGION 9: PLANTS 1 AND 2

Plant Operations and Sampling

On October 30, 2000, January 23, 2001, July 17, 2001, and March 19, 2002, two treatment plants in EPA Region 9 were sampled.

The treatment processes at plant 1 (Figure 1) included ozonation, flocculation, coagulation, sedimentation, and filtration. A secondary disinfectant was not applied until after the filters, so the filters were operated biologically. After the filters, the water was chlorinated with a short, free chlorine contact time, and then ammonia was added to form chloramines. Note, the basins at plant 1 were chlorinated (using sodium hypochlorite) on average twice per week for approximately four hours. This chlorine was applied to the effluent of the ozone contactors to help control algae and other growths in the basins.

Plant 1 was sampled at the following locations:
(1) raw water before the ozone contactor
(2) the ozone (O_3) contactor effluent
(3) the filter influent
(4) the filter effluent
(5) the clearwell effluent
(6) the finished water

The treatment processes at plant 2 (Figure 2) included coagulation and filtration. Chlorine was applied to the raw, settled, and filtered waters. Ammonia was added to the finished water to form chloramines.

Plant 2 was sampled at the following locations:
(1) filter influent (settled water) or filter effluent
(2) the effluent of the treated water tank
(3) the finished water

In addition, finished water was collected from both plants, and simulated distribution system (SDS) testing conducted for average and maximum detention times for that time of the year (Table 1). Furthermore, the distribution system was sampled at two locations, one representing an average detention time and the other representing a maximum detention time. (Raw water was not sampled at plant 2, as it was the same as was used at plant 1.)

Table 1. SDS holding times (hr) at the EPA Region 9 treatment plants

Sample	10/30/00	1/23/01	7/17/01	3/19/02
Plant 1 average detention time	18	23	6	65
Plant 1 maximum detention time	NS[a]	48	28	70
Plant 2 average detention time	18	22	4	5
Plant 2 maximum detention time	NS	38	5	10

[a]NS = Not sampled

Figure 1

Plant 1 Schematic

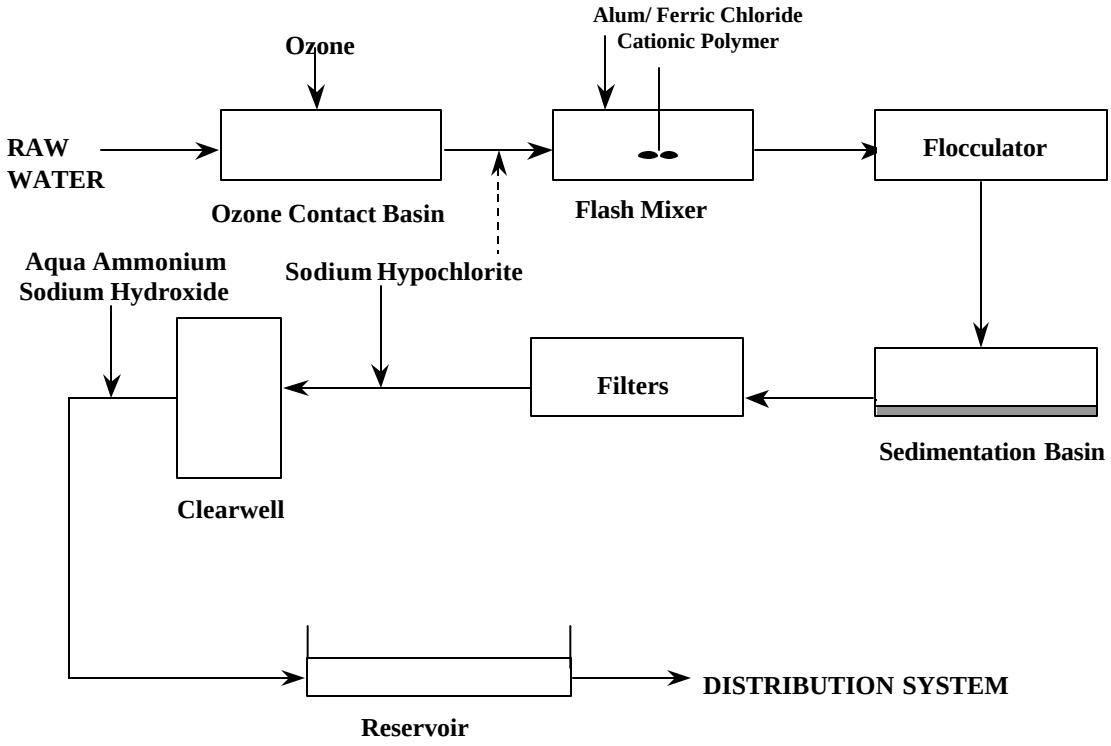
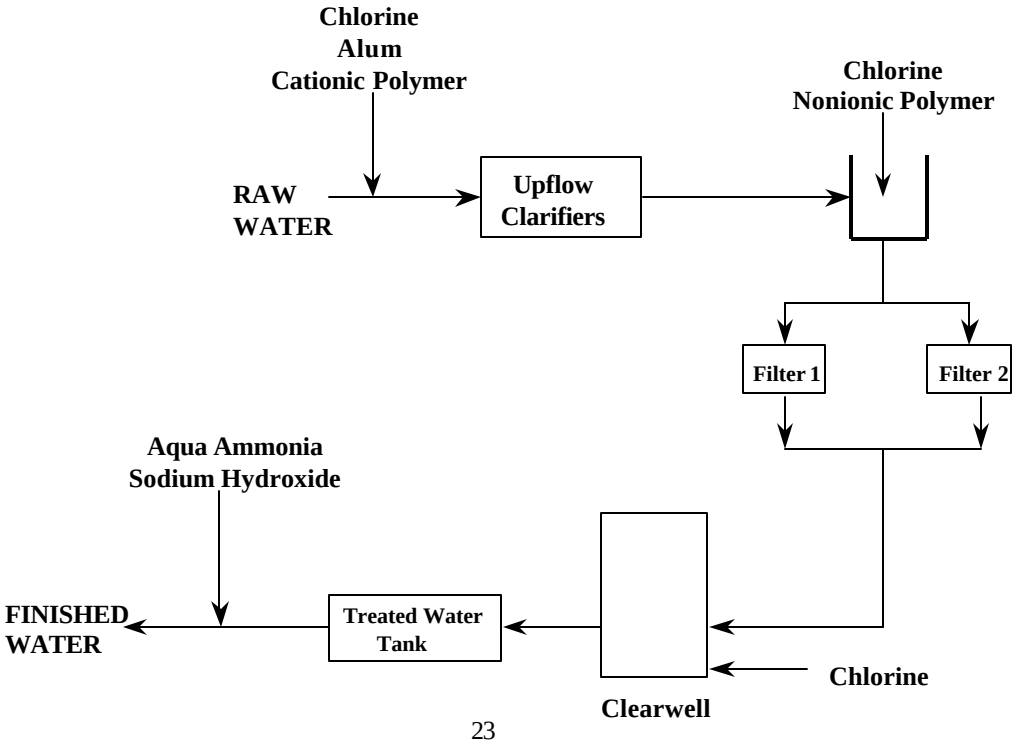


Figure 2

Plant 2 Schematic



On the day of sampling, information was collected on the operations at each plant (Tables 2-3).

Table 2. Operational information at plant 1

Parameter	10/30/00	1/23/01	7/17/01	3/19/02
Plant flow (mgd)	11.0	16.2	22.0	15.8
Ozone dose (mg/L)	1.84	2.53	2.43	2.33
HRT[a] in ozone contactor (min)	4.9	9.5	6	9.8
CT achieved from ozonation (mg/L-min)	1.67	1.24	0.20	3.6
Giardia inactivation achieved from ozonation (logs)	0.75	2.82	1.31	NA[c]
Coagulant[b] dose (mg/L)	14	13	18	16
Filter loading rate (gpm/sq ft)	2.8	3.4	4.7	4.8
Filter EBCT[d] (min)	6.7	7.7	5.5	9
Chlorine dose at ozone contactor effluent (mg/L)	0	0	0	0
Chlorine dose at filter effluent (mg/L)	2.93	4.65	2.15	3.6
Ammonia dose at clearwell effluent (mg/L as N)	0.56	0.72	0.48	0.55

[a]Hydraulic retention time in cells 1 and 2 only
[b]Ferric chloride ($FeCl_3$)
[c]NA = Not available
[d]Empty bed contact time through both media layers

Table 3. Operational information at plant 2

Parameter	10/30/00	1/23/01	7/17/01	3/19/02
Plant flow (mgd)	6.8	5.6	7.7	4.4
Coagulant[a] dose (mg/L)	20	19	25	12
Chlorine dose at plant influent (mg/L)	1.11	1.3	1.5	1.2
Chlorine dose at filter influent (mg/L)	0.65	0.60	0.8	0.75
Chlorine dose at filter effluent (mg/L)	1.93	2.31	1.95	3.7
Ammonia dose at effluent of treated water tank (mg/L as N)	0.46	0.44	0.5	0.62

[a]Alum [$Al_2(SO_4)_3$ $14H_2O$] on 10/30/00 and 1/23/01, ferric chloride ($FeCl_3$) on 7/17/01 and 3/19/02

Water Quality

On the day of sampling, information was also collected on the water quality at each plant (Tables 4-5).

Table 4. Water quality information at plant 1

	pH				Temperature (ºC)				Disinfectant Residual[a] (mg/L)			
Location	10/30/00	1/23/01	7/17/01	3/19/02	10/30/00	1/23/01	7/17/01	3/19/02	10/30/00	1/23/01	7/17/01	3/19/02
Raw	8.16	8.3	7.7	9.07	17.3	10.6	20.7	13.6	---	---	---	---
O_3 eff.	8.13	7.89	7.4	7.14	17	10.4	22.3	13.4	**0.34**	**0.26**	**0.20**	**0.37**
Filt. inf.	7.73	7.20	6.8	6.78	17.3	10.9	21.5	13.8	---	---	---	---
Filt. eff.	7.84	6.90	6.7	6.82	17.1	10.6	21.0	13.9	---	---	---	---
Clear. eff.	7.59	9.0	6.7	6.73	17	10.5	21.4	13.7	*2.26*	*3.61*	*2.05*	*2.64*
Fin. water	8.20	8.63	8.7	8.22	16	9.7	20.7	13.2	1.81	3.65	1.86	2.81
DS[b]/ave.	8.1	8.74	8.2	8.54	17.1	11.9	22.3	14.7	1.61	1.62	1.81	>2.20
DS/max	8.35	8.65	8.3	8.61	17.9	11.8	21.8	14.4	1.14	0.26	1.78	>2.20
SDS/ave.	8.19	8.09	8.6	8.43	15.6	12.4	21.3	14.2	1.67	1.59	1.86	2.11
SDS/max	NS	8.57	8.2	8.34	NS	10.2	20.8	14.9	NS	1.21	1.80	2.08

[a]Ozone residuals (**values shown in bold**) in effluent of cell 2 of ozone contactor; chlorine residuals (values shown in italics) at clearwell effluent; chloramine residuals at other locations.
[b]DS = Distribution system

Table 5. Water quality information at plant 2

	pH				Temperature (ºC)				Disinfectant Residual[a] (mg/L)			
Location	10/30/00	1/23/01	7/17/01	3/19/02	10/30/00	1/23/01	7/17/01	3/19/02	10/30/00	1/23/01	7/17/01	3/19/02
Filt. eff.[b]	7.5	7.4	6.7	7.35	17.8	10.7	21.5	13.0	*0.72*	*0.33*	*0.22*	*0.26*
Treat. tank[c]	7.5	7.3	6.6	7.21	16.4	11.5	21.8	13.2	*1.69*	*1.83*	*1.91*	*2.71*
Fin. water	7.88	8.3	8.6	8.74	16.3	11.6	21.7	13.4	1.85	1.88	1.84	2.43
DS/ave.	8.23	8.95	8.5	8.98	14.6	10.9	21.4	13.5	1.38	1.35	2.00	1.83
DS/max	8.35	8.69	8.5	8.72	19.6	12.4	21.8	14.0	0.96	0.97	1.78	1.92
SDS/ave.	8.16	8.51	8.14	8.56	17.6	11.4	21.2	14.3	1.55	1.46	1.93	2.13
SDS/max	NS	8.51	8.10	8.67	NS	10.1	20.9	16.1	NS	1.50	2.05	2.20

[a]Chlorine residuals (values shown in italics) at filter effluent and at effluent of treated water tank; chloramine residuals at other locations.
[b]Sampled settled water (filter influent) rather than filter effluent on 10/30/00
[c]Effluent of treated water tank

Other data collected included total organic carbon (TOC) and ultraviolet (UV) absorbance (Table 6). The TOC ranged from 3.0 to 4.5 mg/L and the UV was 0.076 to 0.136 cm^{-1}. Typically, ozonation had little effect on TOC. In July 2001, ozonation resulted in a slight increase in the value of the TOC. This phenomenon is due to the conversion of "recalcitrant" TOC by ozone to a form that can be more readily measured by a TOC analyzer. On the other hand, a significant portion of the UV absorbance was reduced by ozone. At plant 1, coagulation removed 27-47 % of the TOC and biofiltration removed another 14-21 %. In addition, coagulation reduced the UV by 38-63 %. The overall (cumulative) removal of TOC at plant 1 was 37-53 % and the UV reduction was 70-81 %. At plant 2, 8-47 % of the TOC was removed and UV reduced by 51-80 % by the coagulation/filtration process.

Table 6. TOC and UV removal at the EPA Region 9 treatment plants

Location	TOC (mg/L)	UV (cm^{-1})	SUVA[a] (L/mg-m)	Removal/Unit (%)		Removal/Cumulative (%)	
				TOC	UV	TOC	UV
10/30/2000							
Plant 1 Raw	3.1	0.076	2.4	---	---	---	---
Plant 1 O3 Eff.	3.1	0.039	1.3	1.3%	49%	1.3%	49%
Plant 1 Filter Inf.	2.3	0.024	1.1	27%	38%	27%	68%
Plant 1 Filter Eff.	2.0	0.023	1.2	14%	4.2%	37%	70%
Plant 2 Filt. Eff.	2.9	0.037	1.3	7.7%	51%	7.7%	51%
1/23/2001							
Plant 1 Raw	4.48	0.136	3.0	---	---	---	---
Plant 1 O3 Eff.	4.34	0.070	1.6	3.1%	49%	3.1%	49%
Plant 1 Filter Inf.	3.11	0.031	1.0	28%	56%	31%	77%
Plant 1 Filter Eff.	2.47	0.031	1.3	21%	0%	45%	77%
Plant 2 Filt. Eff.	3.00	0.055	1.8	33%	60%	33%	60%
7/17/2001							
Plant 1 Raw	2.99	0.093	3.1	---	---	---	---
Plant 1 O3 Eff.	3.11	0.048	1.5	-4.0%	48%	-4.0%	48%
Plant 1 Filter Inf.	1.64	0.018	1.1	47%	63%	45%	81%
Plant 1 Filter Eff.	1.4	0.018	1.3	15%	0%	53%	81%
Plant 2 Filt. Eff.	1.57	0.019	1.2	47%	80%	47%	80%
3/19/2002							
Plant 1 Raw	4.5	0.132	2.9	---	---	---	---
Plant 1 O3 Eff.	4.4	0.069	1.6	2.2%	48%	2.2%	48%
Plant 1 Filter Inf.	2.69	0.030	1.1	39%	57%	40%	77%
Plant 1 Filter Eff.	2.2	0.029	1.3	18%	3.3%	51%	78%
Plant 2 Filt. Eff.	3.02	0.060	2.0	33%	55%	33%	55%

[a]SUVA = Specific ultraviolet absorbance = 100*UV/DOC,
where DOC = dissolved organic carbon, which typically = 90-95% TOC
(used TOC values in calculating SUVA)

Table 7 shows the values of miscellaneous other water quality parameters in the EPA Region 9 treatment plants' raw source water. Bromide ranged from 0.12 to 0.40 mg/L. At both plant 1 and plant 2, they treated surface water impacted by saltwater intrusion.

Table 7. Miscellaneous water quality parameters in plant 1 and 2's raw water

Date	Bromide (mg/L)	Alkalinity (mg/L)	Ammonia (mg/L as N)
10/30/2000	0.16	106	ND[a]
01/23/2001	0.40	66	0.04
07/17/2001	0.14	72	0.04
03/19/2002	0.12	82	ND

[a]ND = Not detected

The source water was moderate in alkalinity. The raw-water pH varied from 7.7 to 9.1 (Table 4). The source water can have significant variability in these inorganic parameters.

DBPs

Oxyhalides. Ozonation resulted in the formation of <3 to 26 µg/L of bromate (Table 8). Bromate formation was highest in January 2001 when the bromide concentration in the raw water was highest (Table 7).

Table 8. Oxyhalide formation at the EPA Region 9 treatment plants

Location	Bromate (µg/L)	Chlorate (µg/L)	Bromate/Bromide (µmol/µmol)
10/30/2000			
Plant 1 O3 eff.	5.7	10	2.2%
Plant 1 clear. eff.	5.2	157	
1/23/2001			
Plant 1 O3 eff.	26	5.9	4.0%
Plant 1 clear. eff.	22	121	
Plant 2 fin. water	ND	114	
7/17/2001			
Plant 1 O3 eff.	4.9	9.8	2.2%
Plant 1 clear. eff.	5.5	133	
Plant 2 fin. water	ND	93	
3/19/2002			
Plant 1 O3 eff.	ND[a] (2)	10	1.0%
Plant 1 clear. eff.	4	80	2.1%
Plant 2 fin. water	ND (1)	127	

[a]ND = Not detected
(bromate minimum reporting level [MRL] = 3 µg/L;
value in parenthesis is < MRL)

The conversion of bromide to bromate was 1-4 % (on a molar basis), which is a typical conversion rate for an ozone plant operating for *Giardia* inactivation (Douville and Amy, 2000). In addition, sodium hypochlorite can be contaminated with low or sub-µg/L levels of bromate (Delcomyn et al., 2000). In March 2002, there was an increase in the concentration of bromate in the treated water at plant 1 after secondary disinfection (4 versus <3 µg/L). Bromate was not detected (minimum reporting level of 3 µg/L) at plant 2. However, some chlorate was

introduced into the finished waters at both plants from secondary disinfection (Table 8) (chlorate is a by-product formed during the decomposition of the hypochlorite stock solution [Bolyard et al. [1992]).

Biodegradable Organic Matter. Ozone can convert natural organic matter in water to carboxylic acids (Kuo et al., 1996) and other assimilable organic carbon (AOC) (van der Kooij et al., 1982). Table 9 shows the carboxylic acid and AOC data for plant 1. Because AOC data are expressed in units of micrograms of carbon per liter (µg C/L), the carboxylic acid data were converted to the same units. A portion of the molecular weight (MW) of each carboxylic acid is due to carbon atoms (i.e., 27-49 %) and the remainder is due to oxygen and hydrogen atoms. The sums of the five carboxylic acids (on a µg C/L basis) were compared to the AOC data. On a median basis for each sample date, 19 to 30 % of the AOC was accounted for by the carboxylic acids.

Figures 3 and 4 show the AOC and the carboxylic acid results, respectively, for the July 2001 sample date. Ozonation resulted in a significant increase in AOC and the concentration of the carboxylic acids, especially oxalate. (Note, one of the bacterial strains used in the AOC method [i.e., *Spirillum NOX*] is used to estimate oxalate-carbon equivalents of the AOC [van der Kooij and Hijnen, 1984].) The carboxylic acids and AOC were both significantly reduced in concentration in the downstream treatment processes (coagulation/sedimentation) prior to biological filtration. Because chlorine was not applied until after the filters, there may have been biological activity in the basins that degraded the AOC. Also, some of the AOC may have been removed by the coagulation process (Volk and LeChevallier, 2002) along with the TOC (Table 6).

Figures 5 and 6 show the formation and removal of AOC and oxalate, respectively, for all of the sample dates. AOC increased from 16-83 µg C/L in the raw water to 504-707 µg C/L in the ozonated water. AOC decreased to 148-333 µg C/L in the settled water and to 131-224 µg C/L in the filtered water. Oxalate increased from 14-18 µg/L in the raw water to 314-409 µg/L in the ozonated water. Oxalate decreased to 56-223 µg/L in the settled water and to 9-33 µg/L in the filtered water. The formation and removal of carboxylic acids—in particular that of oxalate—and AOC tended to follow the same trends through the different treatment processes.

Halogenated Organic and Other Non-halogenated Organic DBPs. Tables 10 and 11 (10/30/00), Tables 13 and 14 (1/23/01), Tables 16 and 17 (7/17/01), and Tables 20 and 21 (3/19/02) show results for the halogenated organic DBPs that were analyzed by MWDSC.

Table 9. Formation and removal of carboxylic acids and AOC at plant 1

	Concentration[a] (µg/L)					Concentration (µg C/L)									Sum/
Location	Acetate	Propionate	Formate	Pyruvate	Oxalate	Acetate	Propionate	Formate	Pyruvate	Oxalate	Sum	AOC-P17	AOC-NOX	AOC	AOC
10/30/2000															
Raw water	ND	ND	ND	ND	17	ND	ND	ND	ND	4.6	4.6	N/A[b]	N/A		
Ozone effluent	ND	ND	ND	ND	314	ND	ND	ND	ND	86	86	168	336	504	17%
Filter influent	ND	ND	32	19	70	ND	ND	8.6	7.8	19	36	N/A	N/A		
Filter effluent	ND	ND	25	25	33	ND	ND	6.6	10	9.0	26	72	101	173	21%
													median		19%
1/23/2001															
Raw water	N/A	N/A	N/A	N/A	N/A							13	3.4	16	
Ozone effluent	N/A	N/A	N/A	N/A	N/A							191	386	578	
Filter influent	N/A	N/A	N/A	N/A	N/A							54	279	333	
Filter effluent	N/A	N/A	N/A	N/A	N/A							50	91	141	
7/17/2001															
Raw water	*13*	ND	15	*13*	*14*	5.3	ND	3.9	5.5	3.9	19	54	29	83	22%
Ozone effluent	80	*8.8*	223	50	378	32	4.4	60	21	103	220	186	516	703	31%
Filter influent	16	*5.5*	43	19	56	6.4	2.7	11	7.9	15	44	41	107	148	30%
Filter effluent	45	ND	43	*14*	22	18	ND	12	5.7	5.9	41	43	89	131	33%
													median		30%
3/19/2002															
Raw water	*11*	ND	*12*	*7.1*	18	4.3	ND	3.2	2.9	5.0	15	48	4.7	53	29%
Ozone effluent	77	ND	206	31	409	31	ND	55	13	112	211	266	441	707	30%
Filter influent	40	ND	125	23	223	16	ND	33	9.5	61	120	38	205	243	49%
Filter effluent	ND	ND	ND	*4.0*	*8.7*	ND	ND	ND	1.7	2.4	4.0	51	173	224	2%
													median		29%
Formula	$CH3COO^-$	$CH_3CH_2COO^-$	$HCOO^-$	CH_3COCOO^-	$C_2O_4^{2-}$										
MW (gm/mole)	59	73	45	87	88										
C portion (gm/mole)	24	36	12	36	24										
C% of MW	41%	49%	27%	41%	27%										

[a]Method detection limit (MDL) = 3 µg/L; reporting detection level (RDL) = 15 µg/L; value in italics < RDL

Figure 3

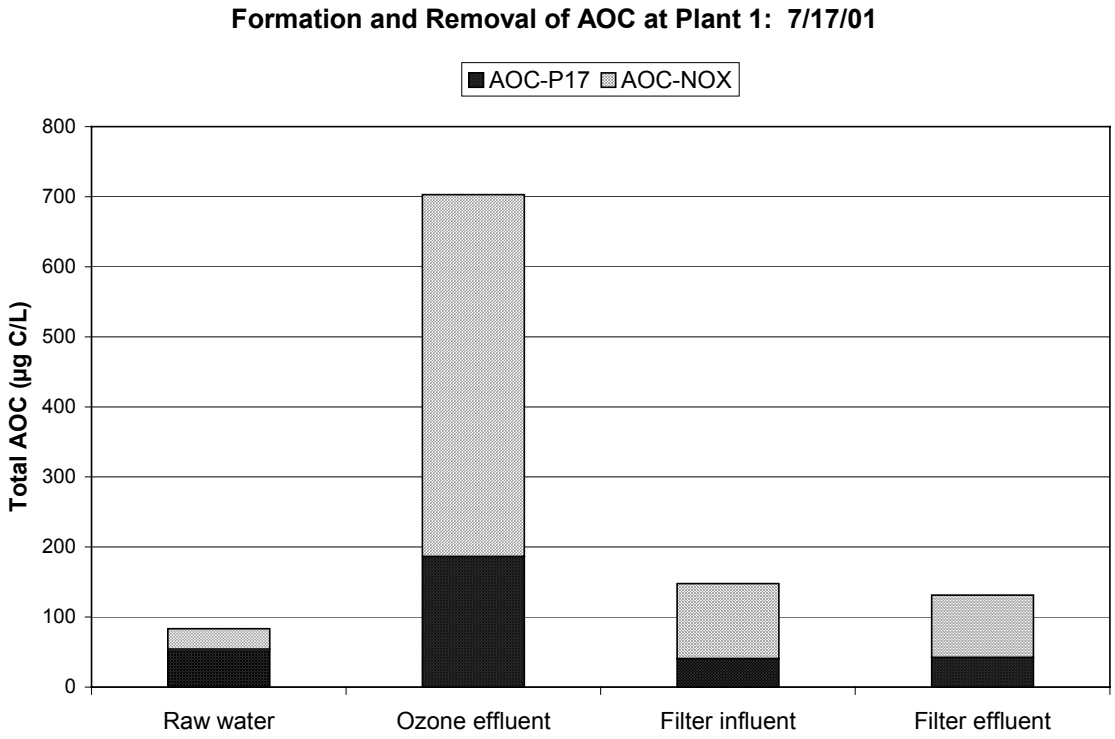


Figure 4

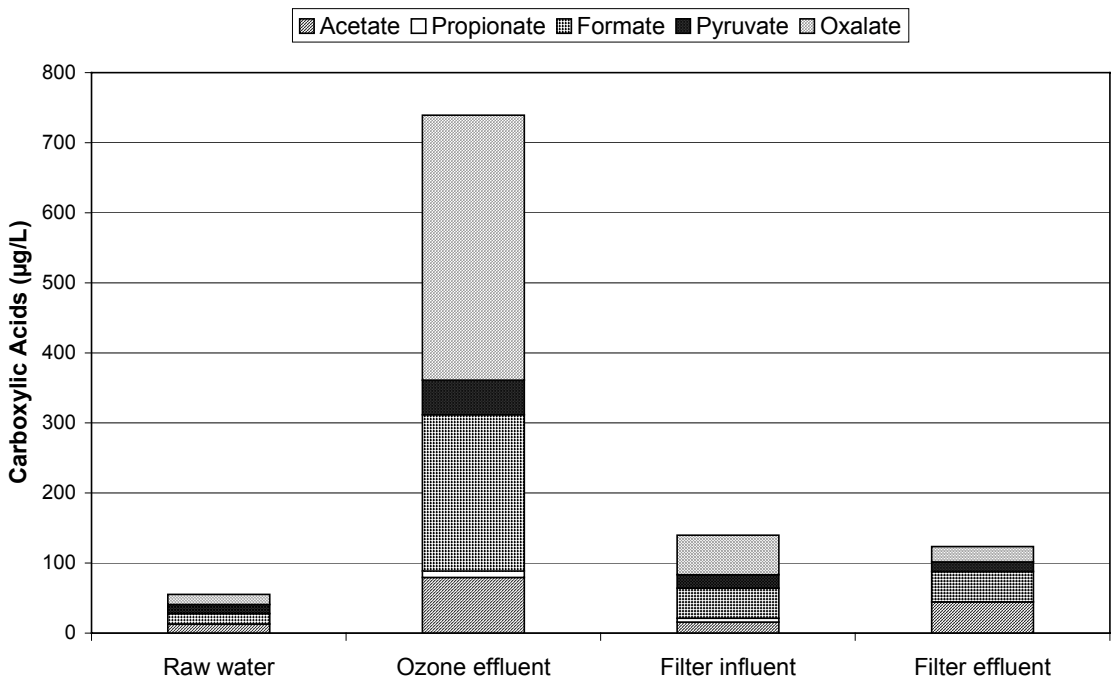


Figure 5

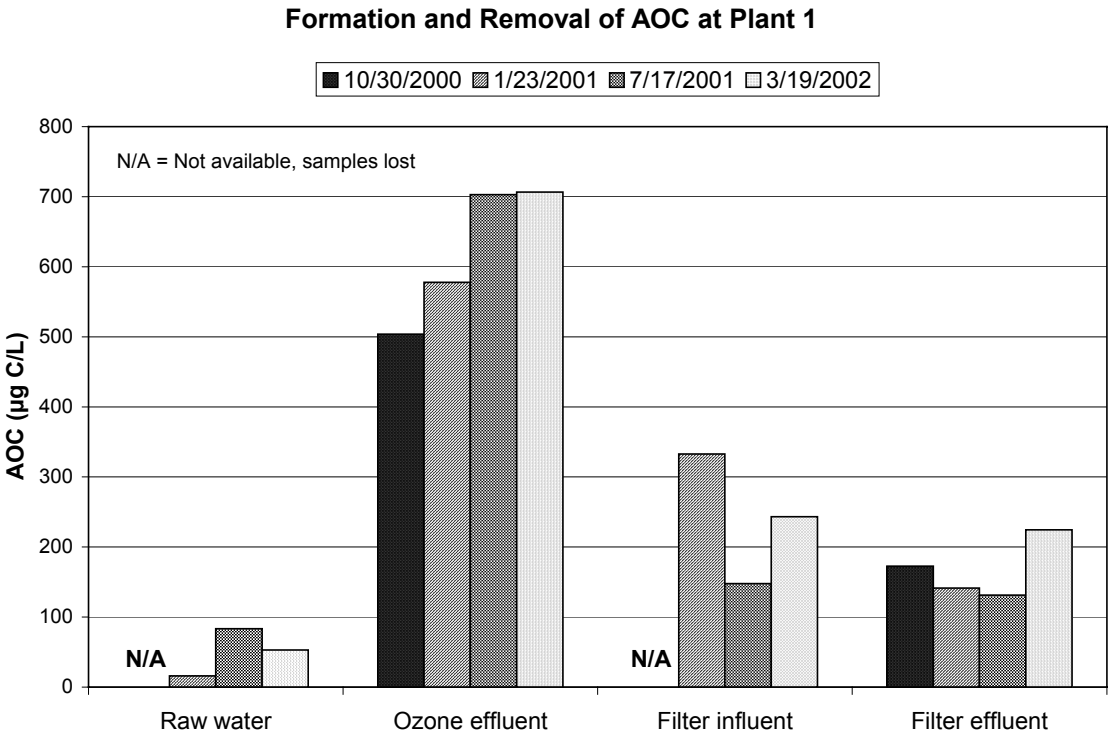


Figure 6

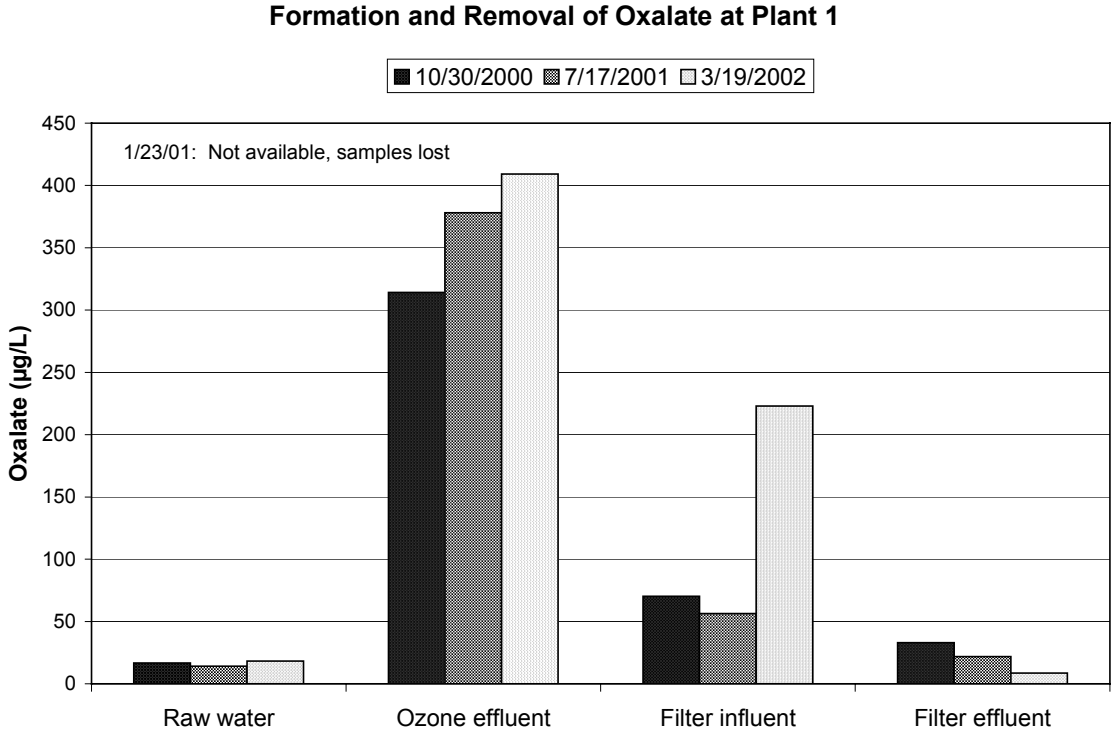


Table 10. DBP results at plant 1 (10/30/00)

10/30/2000	MRL[a]	Plant 1[b]						
Compound	µg/L	Raw	O_3 Eff	Clear. Eff	Fin. Water	SDS	DS/Ave.	DS/Max.
Halomethanes								
Chloromethane	0.15	ND[d]	ND	ND	ND	ND	ND	
Bromomethane	0.20	ND	ND	ND	ND	ND	ND	
Bromochloromethane	0.14	ND	ND	ND	ND	ND	ND	
Dibromomethane	0.11	ND	ND	ND	ND	ND	ND	
Chloroform[e]	0.1	ND	0.7	1	1	2	8	4
Bromodichloromethane[e]	0.1	ND	0.7	1	3	3	3	4
Dibromochloromethane[e]	0.19	ND	1	4	8	8	7	11
Bromoform[e]	0.14	ND	0.2	2	4	4	3	5
THM4[f]		ND	3	8	16	17	21	24
Dichloroiodomethane	0.5	ND	ND	NR[g]	NR	1	1	NR
Bromochloroiodomethane	0.5	ND	NR	NR	NR	NR	NR	NR
Dibromoiodomethane	0.5	ND	ND	ND	NR	NR	NR	NR
Chlorodiiodomethane	0.59	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.53	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.22	ND	NR	ND	ND	ND	ND	ND
Carbon tetrachloride	0.06	ND	ND	ND	ND	ND	ND	
Tribromochloromethane	0.1	ND	ND	ND	0.1	0.1	ND	0.1
Haloacetic acids								
Monochloroacetic acid[e]	2			ND	ND	ND	ND	
Monobromoacetic acid[e]	1			ND	ND	ND	ND	
Dichloroacetic acid[e]	1			ND	1.3	1.8	5.8	
Bromochloroacetic acid[e]	1			ND	1.6	2.0	2.2	
Dibromoacetic acid[e]	1			ND	2.1	2.9	2.1	
Trichloroacetic acid[e]	1			ND	ND	ND	1.8	
Bromodichloroacetic acid	1			ND	ND	ND	ND	
Dibromochloroacetic acid	1			ND	ND	ND	ND	
Tribromoacetic acid	2			ND	ND	ND	ND	
HAA5[h]				ND	3.4	4.7	10	
HAA9[i]				ND	5.0	6.7	12	
DXAA[j]				ND	5.0	6.7	10	
TXAA[k]				ND	ND	ND	1.8	
Haloacetonitriles								
Chloroacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[e]	0.1	ND	ND	ND	0.2	0.2	0.4	0.3
Bromochloroacetonitrile[e]	0.1	ND	ND	0.2	0.4	0.4	0.4	0.6
Dibromoacetonitrile[e]	0.11	ND	ND	0.3	0.6	0.6	0.4	0.7
Trichloroacetonitrile[e]	0.1	ND	ND	ND	ND	ND	ND	ND
Haloacetaldehydes								
Dichloroacetaldehyde	0.16	ND	ND	ND	0.4	0.7	0.4	0.7
Bromochloroacetaldehyde[l]								
Chloral hydrate[e]	0.2	ND	ND	ND	1	2	2	0.6
Tribromoacetaldehyde	0.1	0.2	ND	0.2	0.1	ND	ND	0.2

Table 10 (continued)

10/30/2000	MRL[a]	Plant 1[b]						
Compound	µg/L	Raw	O_3 Eff	Clear. Eff	Fin. Water	SDS	DS/Ave.	DS/Max.
Haloketones								
Chloropropanone	0.1	ND	ND	ND	0.2	0.3	ND	0.2
1,1-Dichloropropanone[e]	0.1	ND	ND	ND	ND	0.2	ND	0.2
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	3	ND	ND	ND	ND	ND	ND	
1,1,1-Trichloropropanone[e]	0.1	ND	ND	ND	ND	ND	0.2	0.1
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	0.1
1-Bromo-1,1-dichloropropanone	3	ND	ND	ND	ND	ND	ND	
1,1,1-Tribromopropanone	3	ND	ND	ND	ND	ND	ND	
1,1,3-Tribromopropanone	3	ND	ND	ND	ND	ND	ND	
1,1,3,3-Tetrachloropropanone	0.1	ND	ND	1	ND	ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes								
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	3	ND	ND	ND	ND	ND	ND	
Dibromonitromethane	0.11	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[e]	0.1	ND	ND	ND	0.2	0.3	0.2	0.2
Miscellaneous Compounds								
Methyl ethyl ketone	1.9	ND	ND	ND	ND	ND	ND	
Methyl *tertiary* butyl ether	0.16	0.9	0.6	0.6	0.8	0.7	0.4	
Benzyl chloride	0.5-3	ND	ND	ND	NR	NR	NR	NR

[a]MRL = Minimum reporting level, which equals method detection limit (MDL) or lowest calibration standard or concentration of blank

[b]Plant 1 sampled at (1) raw water, (2) ozone contactor effluent, (3) clearwell effluent, (4) finished water, (5) SDS testing of finished water, (6) distribution system at average detention time and (7) at maximum detention time.

[c]Plant 2 sampled at (1) filter influent, (2) effluent of treated water tank, (3) finished water, (4) SDS testing of finished water, (5) distribution system at average detention time and (6) at maximum detention time.

[d]ND = Not detected at or above MRL

[e]DBP in the Information Collection Rule (ICR) (note: some utilities collected data for all 9 haloacetic acids for the ICR, but monitoring for only 6 haloacetic acids was required)

[f]THM4 = Sum of 4 THMs (chloroform, bromodichloromethane, dibromochloromethane, bromoform)

[g]NR = Not reported, due to interference problem on gas chromatograph or to problem with quality assurance

[h]HAA5 = Sum of 5 haloacetic acids (monochloro-, monobromo-, dichloro-, dibromo-, trichloroacetic acid)

[i]HAA9 = Sum of 9 haloacetic acids

[j]DXAA = Sum of dihaloacetic acids (dichloro-, bromochloro-, dibromoacetic acid)

[k]TXAA = Sum of trihaloacetic acids (trichloro-, bromodichloro-, dibromochoro-, tribromoacetic acid)

[l]Bromochloroacetaldehyde and chloral hydrate co-eulte; result = sum of 2 DBPs

[m]<3: Concentration less than MRL of 3 µg/L

Table 11. DBP results at plant 2 (10/30/00)

10/30/2000	MRL[a]	Plant 2[c]					
Compound	µg/L	Filt. Inf	Treat. Tank	Fin. Water	SDS	DS/Ave.	DS/Max.
Halomethanes							
Chloromethane	0.15		ND	ND	ND	ND	
Bromomethane	0.20		ND	ND	ND	ND	
Bromochloromethane	0.14		ND	ND	ND	ND	
Dibromomethane	0.11		ND	ND	ND	ND	
Chloroform[e]	0.1	10	11	14	15	14	17
Bromodichloromethane[e]	0.1	8	15	14	17	23	20
Dibromochloromethane[e]	0.19	16	25	25	26	35	31
Bromoform[e]	0.14	4	5	5	5	6	6
THM4[f]		38	56	58	63	78	74
Dichloroiodomethane	0.5	NR	NR	NR	3	4	NR
Bromochloroiodomethane	0.5	NR	1	1	1	1	NR
Dibromoiodomethane	0.5	NR	NR	NR	NR	1	NR
Chlorodiiodomethane	0.59	ND	ND	ND	ND	0.7	ND
Bromodiiodomethane	0.53	ND	ND	ND	ND	ND	ND
Iodoform	0.22	NR	ND	ND	ND	ND	ND
Carbon tetrachloride	0.06		ND	ND	ND	ND	
Tribromochloromethane	0.1	ND	ND	ND	ND	ND	ND
Haloacetic acids							
Monochloroacetic acid[e]	2		ND	ND	ND	ND	
Monobromoacetic acid[e]	1		ND	ND	ND	ND	
Dichloroacetic acid[e]	1		9.9	9.5	11	11	
Bromochloroacetic acid[e]	1		9.4	9.1	10	11	
Dibromoacetic acid[e]	1		6.9	6.6	7.1	8.1	
Trichloroacetic acid[e]	1		8.4	7.9	8.6	8.4	
Bromodichloroacetic acid	1		6.0	5.6	3.4	ND	
Dibromochloroacetic acid	1		2.5	2.4	1.6	ND	
Tribromoacetic acid	2		ND	ND	ND	ND	
HAA5[h]			25	24	27	28	
HAA9[i]			43	41	42	39	
DXAA[j]			26	25	28	30	
TXAA[k]			17	16	14	8.4	
Haloacetonitriles							
Chloroacetonitrile	0.1	ND	ND	ND	ND	ND	ND
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[e]	0.1	1	2	2	2	2	2
Bromochloroacetonitrile[e]	0.1	1	2	2	2	2	2
Dibromoacetonitrile[e]	0.11	0.8	1	1	1	2	1
Trichloroacetonitrile[e]	0.1	ND	ND	ND	ND	ND	ND
Haloacetaldehydes							
Dichloroacetaldehyde	0.16	0.6	0.9	1	2	1	2
Bromochloroacetaldehyde[l]							
Chloral hydrate[e]	0.2	3	4	4	4	4	5
Tribromoacetaldehyde	0.1	0.5	0.6	0.4	ND	0.3	ND

Table 11 (continued)

10/30/2000	MRL[a]	Plant 2[c]					
Compound	µg/L	Filt. Inf	Treat. Tank	Fin. Water	SDS	DS/Ave.	DS/Max.
Haloketones							
Chloropropanone	0.1	ND	ND	ND	0.1	0.2	0.2
1,1-Dichloropropanone[e]	0.1	0.4	0.3	0.3	0.4	0.4	0.4
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	3		ND	ND	ND	ND	
1,1,1-Trichloropropanone[e]	0.1	0.9	2	1	0.7	1	0.3
1,1,3-Trichloropropanone	0.1	0.1	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	3		<3[m]	<3	ND	ND	
1,1,1-Tribromopropanone	3		ND	ND	ND	ND	
1,1,3-Tribromopropanone	3		ND	ND	ND	ND	
1,1,3,3-Tetrachloropropanone	0.1	0.2	0.2	0.2	0.1	0.2	ND
1,1,3,3-Tetrabromopropanone	0.1	ND	ND	ND	ND	ND	ND
Halonitromethanes							
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND
Dichloronitromethane	3		ND	ND	ND	ND	
Dibromonitromethane	0.11	ND	ND	ND	ND	ND	ND
Chloropicrin[e]	0.1	ND	ND	ND	0.2	0.2	0.3
Miscellaneous Compounds							
Methyl ethyl ketone	1.9		ND	ND	ND	ND	
Methyl *tertiary* butyl ether	0.16		0.9	0.9	0.9	0.9	
Benzyl chloride	0.5-3	NR	NR	NR	NR	NR	NR

Table 12. Additional target DBP results (µg/L) at the EPA Region 9 treatment plants (10/30/00)

10/30/00	Plant 1[a]					Plant 2[b]				
Compound	Raw	OE	FE	PE	DS	Raw	FI	TT	PE	DS
Monochloroacetaldehyde	0	0	0	0	0	0	0.1	0.1	0.1	0.2
Dichloroacetaldehyde	0	0	0	0.6	0.7	0	0.9	1.1	1.4	1.7
Bromochloroacetaldehyde	0	0	0	1.0	1.3	0	1.7	1.9	1.3	1.1
3,3-Dichloropropenoic acid	0	0	0	0.1	0.1		0.3	0.4	0.7	0.2
Bromochloromethylacetate	0.5	0.1	0.1	0.1	0.1		0	0	0	0
2,2-Dichloroacetamide	0	0	0	0.2	0.3		0	0	0.8	1.4
TOX (µg/L as Cl^-)	NA[c]	NA	10.2	75.5	109		NA	NA	199	135
Cyanoformaldehyde	<0.1	<0.1	<0.1	0.2	0.2		0.1	<0.1	0.3	0.3
5-Keto-1-hexanal	<0.4	<0.4	<0.4	<0.4	<0.4		<0.4	<0.4	<0.4	<0.4
6-Hydroxy-2-hexanone	<0.4	<0.4	<0.4	<0.4	<0.4		<0.4	<0.4	<0.4	<0.4
Dimethylglyoxal	<0.4	1.3	1.1	<0.4	<0.4		<0.4	<0.4	<0.4	<0.4
trans-2-Hexenal	<0.5	<0.5	<0.5	<0.5	<0.5		<0.5	<0.5	<0.5	<0.5

[a]Plant 1 sampled at (1) raw water, (2) ozone contactor effluent (OE), (3) filter effluent (FE), (4) finished water at plant effluent (PE), and (5) distribution system (DS) at average detention time.
[b]Plant 2 sampled at (1) filter influent (FI), (2) effluent of treated water tank (TT), (3) finished water at PE, and (4) DS at average detention time.
[c]NA = Not available

Table 13. DBP results at plant 1 (1/23/01)

1/23/2001	MRL[a]	Plant 1[n]							
Compound	µg/L	Raw	O_3 Eff	Clear. Eff	Fin. Water	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes									
Chloromethane	0.15	ND[d]	ND	ND	ND	ND		ND	
Bromomethane	0.20	ND	ND	ND	ND	ND		ND	
Bromochloromethane	0.14	ND	ND	ND	ND	ND		ND	
Dibromomethane	0.11	ND	ND	ND	ND	ND		ND	
Chloroform[e]	0.1	ND	0.2	0.5	NR[g]	2	NR	1	NR
Bromodichloromethane[e]	0.1	ND	1	2	NR	7	NR	6	NR
Dibromochloromethane[e]	0.12	ND	1	4	NR	16	NR	20	NR
Bromoform[e]	0.12	ND	0.5	3	NR	20	NR	30	NR
THM4[f]		ND	3	10	NR	45	NR	57	NR
Dichloroiodomethane	0.25	ND	ND	ND	0.2	0.3	NR	0.2	NR
Bromochloroiodomethane	0.20	ND	ND	ND	ND	0.2	NR	ND	NR
Dibromoiodomethane	0.64	ND	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.52	ND	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.60	ND	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.70	ND	1	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.06	ND	ND	ND	ND	ND		ND	
Haloacetic acids									
Monochloroacetic acid[e]	2			ND	ND	ND		ND	
Monobromoacetic acid[e]	1			1.1	1.4	1.2		1.4	
Dichloroacetic acid[e]	1			2.1	2.0	3.6		2.4	
Bromochloroacetic acid[e]	1			3.0	3.0	7.0		4.9	
Dibromoacetic acid[e]	1			14	13	13		11	
Trichloroacetic acid[e]	1			ND	ND	1.0		ND	
Bromodichloroacetic acid	1			1.0	ND	1.4		ND	
Dibromochloroacetic acid	1			2.2	1.4	2.1		1.4	
Tribromoacetic acid	2			ND	ND	ND		ND	
HAA5[h]				17	16	19		15	
HAA9[i]				23	21	29		21	
DXAA[j]				19	18	24		18	
TXAA[k]				3.2	1.4	4.5		1.4	
Haloacetonitriles									
Chloroacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[e]	0.1	ND	ND	0.1	0.1	0.2	0.4	0.2	0.2
Bromochloroacetonitrile[e]	0.1	ND	ND	0.3	0.3	0.3	1	0.9	0.9
Dibromoacetonitrile[e]	0.10	ND	ND	0.6	0.7	0.7	2	2	2
Trichloroacetonitrile[e]	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetaldehydes									
Dichloroacetaldehyde	0.16	ND	0.3	0.8	NR	0.8	1	2	2
Bromochloroacetaldehyde	0.1	ND	0.6	3	3	3	6	7	6
Chloral hydrate[e]	0.1	ND	0.2	0.1	NR	0.2	0.3	0.2	0.2
Tribromoacetaldehyde	0.1	ND	0.1	1	NR	0.5	0.4	0.2	ND

Table 13 (continued)

1/23/2001	MRL	Plant 1							
Compound	µg/L	Raw	O_3 Eff	Clear. Eff	Fin. Water	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloketones									
Chloropropanone	0.5	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloropropanone[e]	0.10	ND	0.2	0.3	0.2	0.3	0.2	0.1	0.2
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	N/A[p]	NR		NR	NR	NR		NR	
1,1,1-Trichloropropanone[e]	0.10	ND	ND	0.2	0.3	0.2	0.2	0.2	ND
1,1,3-Trichloropropanone	0.5	ND	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	N/A	NR		NR	NR	NR		NR	
1,1,1-Tribromopropanone	N/A	NR		NR	NR	NR		NR	
1,1,3-Tribromopropanone	N/A	NR		NR	NR	NR		NR	
1,1,3,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	N/A	NR		NR	NR	NR		NR	
1,1,3,3-Tetrabromopropanone	0.5	ND	ND	0.2-0.6[q]	ND	ND	ND	ND	ND
Halonitromethanes									
Bromonitromethane	0.1	ND	ND	0.1	0.1	0.1	0.2	0.2	0.2
Dichloronitromethane	N/A	NR		NR	NR	NR		NR	
Bromochloronitromethane	N/A	NR		NR	NR	NR		NR	
Dibromonitromethane	0.10	ND	ND	0.1-0.2[q]	0.1-0.2	0.1-0.2	0.2-0.3	0.1-0.2	ND
Chloropicrin[e]	0.1	ND	ND	ND	ND	ND	0.2	0.2	0.4
Miscellaneous Compounds									
Methyl ethyl ketone	1.9	ND	ND	ND	ND	ND		ND	
Methyl *tertiary* butyl ether	0.16	0.3	0.2	0.2	0.2	0.2		0.2	
Benzyl chloride	2	ND	ND	ND	ND	ND	ND	ND	ND

[n]Plant 1 sampled at (1) raw water, (2) ozone contactor effluent, (3) clearwell effluent, (4) finished water, (5) SDS testing of finished water at average detention time and (6) at maximum detention time, and (7) distribution system at average detention time and (8) at maximum detention time.

[o]Plant 2 sampled at (1) filter effluent, (2) effluent of treated water tank, (3) finished water, (4) SDS testing of finished water at average detention time and (5) at maximum detention time, and (6) distribution system at average detention time and (7) at maximum detention time.

[p]N/A = Not applicable

[q]Spike recovery >>100%; range of values represents reported values and values corrected for recovery

Table 14. DBP results at plant 2 (1/23/01)

1/23/2001	MRL	Plant 2[o]						
Compound	µg/L	Filt. Eff	Treat. Tank	Fin. Water	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes								
Chloromethane	0.15		ND	ND	ND		ND	
Bromomethane	0.20		ND	ND	ND		ND	
Bromochloromethane	0.14		ND	ND	ND		ND	
Dibromomethane	0.11		ND	ND	ND		ND	
Chloroform[e]	0.1	NR	8	11	18	NR	17	NR
Bromodichloromethane[e]	0.1	NR	20	30	40	NR	40	NR
Dibromochloromethane[e]	0.12	NR	30	40	50	NR	50	NR
Bromoform[e]	0.12	NR	18	18	19	NR	20	NR
THM4[f]		NR	76	99	127	NR	127	NR
Dichloroiodomethane	0.25	NR	0.5	0.6	0.4	NR	0.5	NR
Bromochloroiodomethane	0.20	NR	0.6	0.8	0.4	NR	0.5	NR
Dibromoiodomethane	0.64	ND	ND	0.6	0.8	ND	ND	0.8
Chlorodiiodomethane	0.52	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.60	0.6	ND	ND	ND	ND	ND	ND
Iodoform	0.70	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.06		ND	ND	ND		ND	
Haloacetic acids								
Monochloroacetic acid[e]	2		ND	ND	ND		ND	
Monobromoacetic acid[e]	1		1.2	1.2	1.3		1.4	
Dichloroacetic acid[e]	1		14	14	15		15	
Bromochloroacetic acid[e]	1		19	18	19		19	
Dibromoacetic acid[e]	1		18	18	20		20	
Trichloroacetic acid[e]	1		9.7	8.6	8.6		9.1	
Bromodichloroacetic acid	1		16	15	15		15	
Dibromochloroacetic acid	1		15	15	14		15	
Tribromoacetic acid	2		3.9	3.6	3.3		3.5	
HAA5[h]			43	42	45		46	
HAA9[i]			97	93	96		98	
DXAA[j]			51	50	54		54	
TXAA[k]			45	42	41		43	
Haloacetonitriles								
Chloroacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[e]	0.1	2	2	2	2	2	2	2
Bromochloroacetonitrile[e]	0.1	2	3	3	3	3	3	3
Dibromoacetonitrile[e]	0.10	2	3	2	3	3	3	3
Trichloroacetonitrile[e]	0.1	ND	ND	ND	ND	ND	ND	ND
Haloacetaldehydes								
Dichloroacetaldehyde	0.16	1	2	2	3	4	3	3
Bromochloroacetaldehyde	0.1	4	4	4	4	3	4	4
Chloral hydrate[e]	0.1	0.6	1	1	2	2	2	2
Tribromoacetaldehyde	0.1	1	3	3	1	0.2	1	0.5

Table 14 (continued)

1/23/2001	MRL	Plant 2						
Compound	µg/L	Filt. Eff	Treat. Tank	Fin. Water	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloketones								
Chloropropanone	0.5	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloropropanone[e]	0.10	0.4	0.4	0.4	0.4	0.5	0.6	0.6
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	N/A		NR	NR	NR		NR	
1,1,1-Trichloropropanone[e]	0.10	1	1	1	1	0.7	1	1
1,1,3-Trichloropropanone	0.5	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	N/A		NR	NR	NR		NR	
1,1,1-Tribromopropanone	N/A		NR	NR	NR		NR	
1,1,3-Tribromopropanone	N/A		NR	NR	NR		NR	
1,1,3,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	N/A		NR	NR	NR		NR	
1,1,3,3-Tetrabromopropanone	0.5	0.7-2	0.5-2	0.6-2	0.3-0.9	ND	ND	ND
Halonitromethanes								
Bromonitromethane	0.1	0.2	0.2	0.1	ND	ND	ND	ND
Dichloronitromethane	N/A		NR	NR	NR		NR	
Bromochloronitromethane	N/A		NR	NR	NR		NR	
Dibromonitromethane	0.10	0.2-0.4	0.2-0.5	0.2-0.4	0.2-0.3	<0.1-0.1	ND	ND
Chloropicrin[e]	0.1	0.2	0.3	ND	0.5	0.8	1	2
Miscellaneous Compounds								
Methyl ethyl ketone	1.9		ND	ND	ND		ND	
Methyl *tertiary* butyl ether	0.16		0.3	0.3	0.3		0.3	
Benzyl chloride	2	ND	ND	ND	ND	ND	ND	ND

Table 15. Occurrence of other DBPs[a] at plant 1 (1/23/01)

Compound	OE	PE
Halomethanes		
Bromochloromethane	x	-
Dibromomethane	x	-
Bromodichloromethane[b]	x	x
Dibromochloromethane	x	x
Bromoform	x	-
Dichloroiodomethane	-	x
Bromochloroiodomethane	-	x
Dibromoiodomethane	-	x
Haloacids		
Bromoacetic acid	-	x
Dichloroacetic acid	-	x
Bromochloroacetic acid	x	x
Dibromoacetic acid	x	x
Dibromochloroacetic acid	-	x
Tribromoacetic acid	-	x
2,2-Dibromopropanoic acid	-	x
3,3-Dibromopropenoic acid	-	x
cis-2,3-Dibromopropenoic acid	-	x
Tribromopropenoic acid	-	x
2-Bromobutanoic acid	-	x
trans-4-Bromo-2-butenoic acid	-	x
cis-4-Bromo-2-butenoic acid	-	x
2,3-Dibromo-2-butenoic acid	-	x
Bromodichloro-butenoic acid[c]	-	x
Bromochloro-4-oxopentanoic acid	-	x
3,3-Dibromo-4-oxopentanoic acid	-	x
cis-2-Bromo-butenedioic acid	-	x
trans-2,3-Dibromo-butenedioic acid	-	x
cis-2-Bromo-3-methylbutenedioic acid	-	x
Haloacetonitriles		
Dichloroacetonitrile	-	x
Bromochloroacetonitrile	-	x
Dibromoacetonitrile	-	x

Compound	OE	PE
Haloaldehydes		
Dichloroacetaldehyde	x	-
Bromochloroacetaldehyde	x	x
Trichloroacetaldehyde	x	-
Tribromoacetaldehyde	x	-
2-Bromo-2-methylpropanal	-	x
Haloketones		
1,1-Dichloropropanone	x	x
1-Bromo-1-chloropropanone	-	x
1,1-Dibromopropanone	x	x
1,1,1-Trichloropropanone	x	x
1,1,3-Trichloropropanone	-	x
1-Bromo-1,1-dichloropropanone	-	x
1,1,1-Tribromopropanone	-	x
1,1,3,3-Tetrachloropropanone	x	x
1,1,3-Tribromo-3-chloropropanone	-	x
1,1,3,3-Tetrabromopropanone	x	x
Halonitromethanes		
Bromonitromethane	-	x
Dibromonitromethane	-	x
Miscellaneous Halogenated DBPs		
Chlorobenzene	x	x
Tribromophenol	-	x
Non-halogenated DBPs		
Glyoxal	x	x
Pentanoic acid	x	x
Hexanoic acid	x	x
Heptanoic acid	x	x
Octanoic acid	x	x
Nonanoic acid	x	x
Decanoic acid	x	x
Undecanoic acid	-	x
Dodecanoic acid	-	x
Tetradecanoic acid	x	x
Pentadecanoic acid	x	x
Hexadecanoic acid	x	x
Octadecanoic acid	x	x
Ethanedioic acid	-	x
Octanedioic acid	-	x
Nonanedioic acid	x	x

[a]DBPs detected by broadscreen gas chromatography/mass spectrometry (GC/MS) technique
[b]Compounds listed in italics were confirmed through the analysis of authentic standards; haloacids and non-halogenated carboxylic acids identified as their methyl esters.
[c]Exact isomer not known

Table 16. DBP results at plant 1 (7/17/01)

07/17/2001	MRL[a]	Plant 1[n]							
Compound	µg/L	Raw	O_3 Eff	Clear. Eff	Fin. Water	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes									
Chloromethane	0.2	ND[d]	ND	ND	ND	ND		ND	
Bromomethane	0.2	ND	ND	ND	ND	ND		ND	
Bromochloromethane	0.5	ND	ND	ND	ND	ND		ND	
Dibromomethane	0.5	ND	ND	ND	ND	ND		ND	
Chloroform[e]	0.1	ND	0.1	0.2	0.4	1	1	0.3	0.4
Bromodichloromethane[e]	0.1	ND	0.1	0.7	2	3	3	2	2
Dibromochloromethane[e]	0.1	ND	ND	1	4	4	NR[g]	3	NR
Bromoform[e]	0.11	ND	ND	0.8	3	3	3	3	3
THM4[f]		ND	0.2	3	9	11	NR	8	NR
Dichloroiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND
Bromochloroiodomethane	0.25	ND	ND	ND	ND	ND	NR	ND	NR
Dibromoiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.1-0.5	ND	ND	0.2	ND	0.3	ND	ND	ND
Bromodiiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.5	ND	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.2	ND	ND	ND	ND	ND		ND	
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids									
Monochloroacetic acid[e]	2			ND	ND	ND		ND	
Monobromoacetic acid[e]	1			ND	ND	ND		ND	
Dichloroacetic acid[e]	1			1.1	2.2	4.8		2.2	
Bromochloroacetic acid[e]	1			2.4	2.2	3.6		3.8	
Dibromoacetic acid[e]	1			4.2	3.6	4.3		6.4	
Trichloroacetic acid[e]	1			ND	ND	1.2		ND	
Bromodichloroacetic acid	1			ND	ND	1.1		ND	
Dibromochloroacetic acid	1			ND	ND	ND		ND	
Tribromoacetic acid	2			ND	ND	ND		ND	
HAA5[h]				5.3	5.8	10		9	
HAA9[i]				7.7	8.0	15		12	
DXAA[j]				7.7	8.0	13		12	
TXAA[k]				ND	ND	2.3		ND	
Haloacetonitriles									
Chloroacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[e]	0.10	ND	ND	ND	0.1	0.2	0.2	0.1	ND
Bromochloroacetonitrile[e]	0.1	ND	ND	ND	0.3	0.1	0.3	0.3	0.2
Dibromoacetonitrile[e]	0.14	ND	ND	0.6	0.6	0.6	0.6	0.6	0.4
Trichloroacetonitrile[e]	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Bromodichloroacetonitrile	0.5	ND	ND		ND				ND
Dibromochloroacetonitrile	0.5	ND	ND		ND				ND
Tribromoacetonitrile	0.5	ND	ND		ND				ND
Haloacetaldehydes									
Dichloroacetaldehyde	0.22	ND	ND	2	0.2	1	2	0.7	2
Bromochloroacetaldehyde	0.1	ND	ND	1	0.4	ND	ND	ND	0.1
Chloral hydrate[e]	0.1	ND	ND	2	ND	ND	ND	ND	ND
Tribromoacetaldehyde	0.1	ND	ND	2	0.1	ND	ND	ND	ND

Table 16 (continued)

07/17/2001	MRL[a]	Plant 1[n]							
Compound	µg/L	Raw	O_3 Eff	Clear. Eff	Fin. Water	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloketones									
Chloropropanone	0.1	ND	ND	0.1	0.1	0.1	ND	0.1	ND
1,1-Dichloropropanone[e]	0.10	ND	ND	0.2	0.2	0.3	0.3	0.2	0.2
1,3-Dichloropropanone	0.1	ND	ND	0.5	ND	ND	ND	ND	ND
1,1-Dibromopropanone	0.10	ND	ND	0.3	0.1	ND	ND	ND	ND
1,1,1-Trichloropropanone[e]	0.1	ND	ND	0.5	0.1	ND	ND	ND	ND
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	0.1	ND	ND	0.4	ND	ND	ND	ND	ND
1,1,1-Tribromopropanone	0.29	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3-Tribromopropanone	0.14	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes									
Bromonitromethane	0.1	ND	ND	ND	0.2	ND	0.1	0.1	0.1
Dichloronitromethane	0.1	ND	ND	ND	0.1	0.2	0.2	ND	0.2
Bromochloronitromethane	0.1	ND	ND	ND	0.2	0.1	0.1	0.2	0.1
Dibromonitromethane	0.10	ND	ND	0.1	0.5	0.2	0.2	0.4	0.2
Chloropicrin[e]	0.1	0.1	0.2	0.1	ND	0.2	0.1	0.1	0.2
Bromodichloronitromethane	0.5	ND	ND		0.7				0.9
Dibromochloronitromethane	0.5	ND	ND		1.5				1.7
Bromopicrin	0.5	ND	ND		2.5				2.8
Miscellaneous Compounds									
Methyl ethyl ketone	0.5	ND	1	ND	ND	ND		ND	
Methyl *tertiary* butyl ether	0.2	ND	ND	ND	ND	ND		ND	
1,1,2,2-Tetrabromo-2-chloroethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Benzyl chloride	0.25	ND	NR	ND	ND	ND	NR	ND	NR

[r]<0.5 = Detected by GC/MS below its MRL of 0.5 µg/L; interference problem with GC/ECD analysis

Table 17. DBP results at plant 2 (7/17/01)

07/17/2001	MRL	Plant 2[o]						
Compound	µg/L	Filt. Eff	Treat. Tank	Fin. Water	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes								
Chloromethane	0.2		ND	ND	ND		ND	
Bromomethane	0.2		ND	ND	ND		ND	
Bromochloromethane	0.5		ND	ND	ND		ND	
Dibromomethane	0.5		ND	ND	ND		ND	
Chloroform[e]	0.1	5	6	7	7	9	8	8
Bromodichloromethane[e]	0.1	9	11	13	15	16	16	16
Dibromochloromethane[e]	0.1	NR	7	10	11	NR	11	NR
Bromoform[e]	0.11	2	2	2	2	2	2	2
THM4[f]		NR	26	32	35	NR	37	NR
Dichloroiodomethane	0.5	5	4	4	3	0.6	3	2
Bromochloroiodomethane	0.25	NR	1	1	1	NR	1	NR
Dibromoiodomethane	0.5	NR	<0.5[r]	<0.5	<0.5	ND	0.7	NR
Chlorodiiodomethane	0.1-0.5	0.4	<0.5	<0.5	<0.5	ND	0.5	NR
Bromodiiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.5	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.2		ND	ND	ND		ND	
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids								
Monochloroacetic acid[e]	2		ND	ND	ND		ND	
Monobromoacetic acid[e]	1		ND	ND	ND		ND	
Dichloroacetic acid[e]	1		12	12	12		13	
Bromochloroacetic acid[e]	1		12	11	11		12	
Dibromoacetic acid[e]	1		6.2	6.2	6.2		6.6	
Trichloroacetic acid[e]	1		9.2	9.0	7.5		9.3	
Bromodichloroacetic acid	1		7.9	7.8	7.0		8.3	
Dibromochloroacetic acid	1		3.7	3.6	3.0		3.8	
Tribromoacetic acid	2		ND	ND	ND		ND	
HAA5[h]			27	27	26		29	
HAA9[i]			51	50	47		53	
DXAA[j]			30	29	29		32	
TXAA[k]			21	20	18		21	
Haloacetonitriles								
Chloroacetonitrile	0.1	ND	0.1	0.1	0.1	0.1	0.1	0.1
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[e]	0.10	1	2	2	2	2	2	2
Bromochloroacetonitrile[e]	0.1	1	2	2	2	2	2	2
Dibromoacetonitrile[e]	0.14	1	2	2	2	2	1	2
Trichloroacetonitrile[e]	0.1	ND	ND	ND	ND	ND	ND	ND
Bromodichloroacetonitrile	0.5			ND	ND			ND
Dibromochloroacetonitrile	0.5			ND	ND			ND
Tribromoacetonitrile	0.5			ND	ND			ND
Haloacetaldehydes								
Dichloroacetaldehyde	0.22	2	1	1	0.9	1	1	2
Bromochloroacetaldehyde	0.1	2	1	1	1	0.6	1	1
Chloral hydrate[e]	0.1	1	2	2	2	1	2	2
Tribromoacetaldehyde	0.1	0.3	0.2	0.2	0.1	ND	0.1	0.1

Table 17 (continued)

07/17/2001	MRL	Plant 2[o]						
Compound	µg/L	Filt. Eff	Treat. Tank	Fin. Water	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloketones								
Chloropropanone	0.1	ND	ND	0.1	0.1	0.1	0.1	0.1
1,1-Dichloropropanone[e]	0.10	0.7	0.8	0.7	0.5	0.5	0.6	0.7
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	0.10	0.6	0.3	0.3	0.2	ND	0.2	0.1
1,1,1-Trichloropropanone[e]	0.1	0.7	1	1	0.9	0.2	0.8	0.7
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	0.1	NR	1	1	0.3	ND	ND	ND
1,1,1-Tribromopropanone	0.29	ND	ND	ND	ND	ND	ND	ND
1,1,3-Tribromopropanone	0.14	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes								
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	0.1	0.2	0.2	0.2	0.2	0.1	0.2	0.1
Bromochloronitromethane	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Dibromonitromethane	0.10	0.1	0.1	0.1	0.1	ND	ND	ND
Chloropicrin[e]	0.1	0.1	0.2	0.2	0.2	0.1	0.1	0.2
Bromodichloronitromethane	0.5			0.8	0.6			0.8
Dibromochloronitromethane	0.5			1.0	0.8			0.9
Bromopicrin	0.5			ND	ND			ND
Miscellaneous Compounds								
Methyl ethyl ketone	0.5		ND	ND	ND		ND	
Methyl *tertiary* butyl ether	0.2		ND	ND	ND		ND	
1,1,2,2-Tetrabromo-2-chloroethane	0.1	ND	ND	ND	ND	ND	ND	ND
Benzyl chloride	0.25	NR	ND	ND	ND	NR	ND	NR

Table 18. Additional target DBP results (µg/L) at the EPA Region 9 treatment plants (7/17/01)

7/17/01	Plant 1[a]						Plant 2[a]				
Compound	Raw	OE	FE	PE	DS	SDS	FI	TT	PE	DS	SDS
Monochloroacetaldehyde											
Dichloroacetaldehyde											
Bromochloroacetaldehyde											
3,3-Dichloropropenoic acid	0	0	0	0	0	0	0	0	0	0	0
Bromochloromethylacetate	0	0	0	0	0	0	0	0	0	0	0
2,2-Dichloroacetamide	0	0	0	0	0	0	0	0	0	0	0
TOX (µg/L as Cl^-)	NA	NA	10.2	21.1	25.3	43.2	75.6	84.5	91.3	106	114
Cyanoformaldehyde	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
5-Keto-1-hexanal	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
6-Hydroxy-2-hexanone	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
Dimethylglyoxal	<0.4	0.8	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
trans-2-Hexenal	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4

[a]SDS testing of finished water at maximum detention time

Table 19. Halogenated furanone results (µg/L) at the EPA Region 9 treatment plants (7/17/01)

7/17/01	Plant 1		Plant 2	
Compound	FE	PE	FE	DS
Mucochloric acid (ring)	<0.04	<0.04	<0.04	<0.04
Mucochloric acid (open)	<0.04	<0.04	0.07	<0.04
MX	<0.04	<0.04	0.12	0.07
ZMX	<0.04	<0.04	0.05	<0.04
EMX	<0.04	<0.04	<0.04	<0.04

Table 20. DBP results at plant 1 (3/19/02)

03/19/2002	MRL[a]	Plant 1[n]							
Compound	µg/L	Raw	O_3 Eff	Clear. Eff	Fin. Water	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes									
Chloromethane	0.2	ND[d]	ND	ND	ND	ND		ND	
Bromomethane	0.2	ND	ND	ND	ND	ND		ND	
Bromochloromethane	0.5	ND	ND	ND	ND	ND		ND	
Dibromomethane	0.5	ND	ND	ND	ND	ND		ND	
Chloroform[e]	0.2	ND	1	2	2	3	NR[g]	2	2
Bromodichloromethane[e]	0.2	ND	1	2	3	4	NR	4	5
Dibromochloromethane[e]	0.2	ND	0.4	2	3	4	NR	4	7
Bromoform[e]	0.2	ND	ND	0.6	0.8	2	NR	2	1
THM4[f]		ND	2	7	9	13	NR	12	15
Dichloroiodomethane	0.25	ND	0.3	ND	NR	ND	NR	ND	0.4
Bromochloroiodomethane	0.25	ND	ND	ND	ND	<0.25[s]	0.6	<0.25	ND
Dibromoiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.52	ND	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.5	ND	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.2	ND	ND	ND	ND	ND		ND	ND
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids									
Monochloroacetic acid[e]	2			ND	ND	ND		ND	
Monobromoacetic acid[e]	1			ND	ND	ND		ND	
Dichloroacetic acid[e]	1			1.9	2.1	4.2		3.9	
Bromochloroacetic acid[e]	1			2.3	1.3	3.9		3.6	
Dibromoacetic acid[e]	1			2.7	2.1	5.4		5.9	
Trichloroacetic acid[e]	1			1.5	1.6	1.6		2.0	
Bromodichloroacetic acid	1			2.0	1.0	1.6		2.3	
Dibromochloroacetic acid	1			ND	ND	1.8		2.0	
Tribromoacetic acid	2			ND	ND	ND		ND	
HAA5[h]				6.1	5.8	11		12	
HAA9[i]				10	8.1	19		20	
DXAA[j]				6.9	5.5	14		13	
TXAA[k]				3.5	2.6	5.0		6.3	
Haloacetonitriles									
Chloroacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[e]	0.2	ND	0.2	ND	0.2	ND	NR	ND	0.5
Bromochloroacetonitrile[e]	0.5	ND	ND	<0.5	0.8	1	2	1	2
Dibromoacetonitrile[e]	0.1	ND	ND	0.5	0.6	0.8	0.8	0.3	0.8
Trichloroacetonitrile[e]	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Bromodichloroacetonitrile	0.5	ND	ND		ND				
Dibromochloroacetonitrile	0.5	ND	ND		ND				
Tribromoacetonitrile	0.96	ND	ND		ND				
Haloacetaldehydes									
Dichloroacetaldehyde	0.98	ND	ND	1	1	2	2	2	2
Bromochloroacetaldehyde	0.5	ND	0.1	0.9	1	2	2	2	2
Chloral hydrate[e]	0.1	ND	0.2	0.7	0.6	0.5	0.8	1	1
Tribromoacetaldehyde	0.1	ND	ND	0.8	0.5	ND	ND	ND	ND

Table 20 (continued)

03/19/2002	MRL[a]	Plant 1[n]							
Compound	µg/L	Raw	O_3 Eff	Clear. Eff	Fin. Water	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloketones									
Chloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloropropanone[e]	0.10	ND	0.4	NR	0.8	NR	NR	1	2
1,3-Dichloropropanone	0.1	ND	ND	0.2	ND	ND	ND	ND	ND
1,1-Dibromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloropropanone[e]	0.1	ND	0.5	<0.5	0.5	0.6	0.6	0.3	0.3
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	0.1	ND	ND	0.1	0.2	ND	ND	ND	ND
1,1,1-Tribromopropanone	NA[t]	ND	ND	NR	ND	NR	NR	NR	ND
1,1,3-Tribromopropanone	0.1	ND	ND	0.5	ND	ND	ND	ND	ND
1,1,3,3-Tetrachloropropanone	0.5	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	0.10	ND	ND	0.4	ND	ND	ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.1	ND	0.1	ND	ND	ND	ND	ND	ND
Halonitromethanes									
Chloronitromethane	NA	ND	ND	ND	ND	ND		ND	ND
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	0.1	ND	ND	ND	ND	0.2	0.2	0.3	0.1
Bromochloronitromethane	0.1	ND	ND	ND	0.1	0.2	ND	ND	ND
Dibromonitromethane	0.10	ND	ND	ND	0.1	ND	ND	ND	ND
Chloropicrin[e]	0.5	ND	NR	ND	ND	<0.5	NR	<0.5	NR
Bromodichloronitromethane	0.5	ND	ND		ND				
Dibromochloronitromethane	2	ND	ND		ND				
Bromopicrin	0.5	ND	ND		ND				
Miscellaneous Compounds									
Methyl ethyl ketone	0.5	ND	ND	ND	ND	ND		ND	
Methyl *tertiary* butyl ether	0.2	ND	ND	ND	ND	ND		ND	
1,1,2,2-Tetrabromo-2-chloroethane	0.54	ND	ND	ND	ND	ND	ND	ND	ND
Benzyl chloride	0.5	ND	ND	ND	ND	ND	NR	ND	ND

[s]<0.25 or <0.5 or <1 = Detected by GC/MS below its MRL of 0.25 or 0.5 or 1 µg/L; quality assurance problem with gas chromatograph method

[t]NA = Not available.

Table 21. DBP results at plant 2 (3/19/02)

03/19/2002	MRL	Plant 2[o]						
Compound	µg/L	Filt. Eff	Treat. Tank	Fin. Water	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes								
Chloromethane	0.2		ND	ND	ND		ND	
Bromomethane	0.2		ND	ND	ND		ND	
Bromochloromethane	0.5		ND	ND	ND		ND	
Dibromomethane	0.5		ND	ND	ND		ND	
Chloroform[e]	0.2	NR	15	16	28	NR	25	34
Bromodichloromethane[e]	0.2	NR	17	19	23	NR	25	27
Dibromochloromethane[e]	0.2	NR	6	7	8	NR	8	11
Bromoform[e]	0.2	NR	0.7	0.6	0.7	NR	0.9	0.4
THM4[f]	0	NR	39	43	60	NR	59	72
Dichloroiodomethane	0.25	NR	2	2	2	2	3	2
Bromochloroiodomethane	0.25	1	1	1	1	2	1	2
Dibromoiodomethane	0.5	0.7	0.5	0.6	<0.5	ND	0.5	ND
Chlorodiiodomethane	0.1	NR	<0.5	<0.5	<0.5	NR	<0.5	NR
Bromodiiodomethane	0.52	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.5	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.2		ND	ND	ND		ND	ND
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids								
Monochloroacetic acid[e]	2		ND	2.1	ND		2.2	
Monobromoacetic acid[e]	1		ND	ND	ND		ND	
Dichloroacetic acid[e]	1		18	19	20		22	
Bromochloroacetic acid[e]	1		9.6	6.1	6.2		10	
Dibromoacetic acid[e]	1		3.5	3.4	3.7		4.0	
Trichloroacetic acid[e]	1		14	13	13		16	
Bromodichloroacetic acid	1		9.7	9.2	9.5		11	
Dibromochloroacetic acid	1		2.7	2.4	2.4		3.0	
Tribromoacetic acid	2		ND	ND	ND		ND	
HAA5[h]	0		36	38	37		44	
HAA9[i]	0		58	55	55		68	
DXAA[j]	0		31	29	30		36	
TXAA[k]	0		26	25	25		30	
Haloacetonitriles								
Chloroacetonitrile	0.1	ND	0.1	0.1	0.1	0.2	0.2	0.2
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[e]	0.2	NR	1	2	2	NR	2	3
Bromochloroacetonitrile[e]	0.5	2	1	2	2	1	1	2
Dibromoacetonitrile[e]	0.1	0.8	0.5	0.9	0.5	0.7	0.6	1
Trichloroacetonitrile[e]	0.1	ND	ND	ND	ND	ND	ND	ND
Bromodichloroacetonitrile	0.5			ND	ND			ND
Dibromochloroacetonitrile	0.5			ND	ND			ND
Tribromoacetonitrile	0.96			ND	ND			ND
Haloacetaldehydes								
Dichloroacetaldehyde	0.98	2	2	2	2	2	2	3
Bromochloroacetaldehyde	0.5	0.6	0.7	0.5	ND	ND	ND	ND
Chloral hydrate[e]	0.1	2	4	3	4	4	4	4
Tribromoacetaldehyde	0.1	ND	0.4	0.1	ND	ND	ND	ND

Table 21 (continued)

03/19/2002	MRL	Plant 2[o]						
Compound	µg/L	Filt. Eff	Treat. Tank	Fin. Water	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloketones								
Chloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloropropanone[e]	0.10	NR	2	1	1	NR	1	1
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloropropanone[e]	0.1	NR	3	3	2	NR	2	2
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	0.1	0.4	<1	0.9	ND	ND	ND	ND
1,1,1-Tribromopropanone	NA	NR	NR	ND	ND	NR	NR	ND
1,1,3-Tribromopropanone	0.1	0.2	ND	0.1	ND	ND	ND	ND
1,1,3,3-Tetrachloropropanone	0.5	ND	ND	ND	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes								
Chloronitromethane	NA		ND	ND	ND		ND	ND
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	0.1	0.2	0.3	0.2	0.2	0.3	0.3	0.2
Bromochloronitromethane	0.1	0.2	ND	0.3	ND	0.1	ND	ND
Dibromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[e]	0.5	NR	<0.5	<0.5	<0.5	NR	0.5	NR
Bromodichloronitromethane	0.5			1	0.8			1
Dibromochloronitromethane	2			ND	ND			ND
Bromopicrin	0.5			ND	ND			ND
Miscellaneous Compounds								
Methyl ethyl ketone	0.5		ND	ND	ND		ND	
Methyl *tertiary* butyl ether	0.2		ND	ND	ND		ND	
1,1,2,2-Tetrabromo-2-chloroethane	0.54	ND	ND	ND	ND	ND	ND	ND
Benzyl chloride	0.5	NR	ND	ND	ND	NR	ND	NR

Table 22. Additional Target DBP Results (µg/L) at the EPA Region 9 treatment plants (3/19/02)

3/19/02	Plant 1[a]					Plant 2[b]					
Compound	Raw	OE	FE	PE	DS	FE	TT	PE	DS/a	DS/m	SDS
Monochloroacetaldehyde	0	1.8	2.2	2.4	0	0.2		0		0.3	
Dichloroacetaldehyde	0	0	0	3.5	1.5	2.9		4.2		5.8	
Bromochloroacetaldehyde	0	0	0	1.8	3.0	1.3		1.1		1.2	
3,3-Dichloropropenoic acid	0		0	0	0	0		0		0	
Bromochloromethylacetate	0		0	0	0	0		0		0	
Monochloroacetamide	0		0	0	0	0		0		0	
Monobromoacetamide	0		0	0	0	0		0		0	
2,2-Dichloroacetamide	0		0	0.6	1.1	1.2		3.9		4.5	
Dibromoacetamide	0		0.1	1.6	1.6	0.4		0.8		0.7	
Trichloroacetamide	0		0.1	0.1	0.2	0.3		0.3		0.3	
TOX (µg/L as Cl^-)	11.3		18.3	145	164	191	234	200	164	243	246
TOBr (µg/L as Br^-)	4.6		2.0	79.7	50.0	67.0	72.0	76	76	84	86
TOCl (µg/L as Cl^-)	9.3		20.5	87.2	142	116	202	185	155	195	204
Cyanoformaldehyde	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
5-Keto-1-hexanal	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6-Hydroxy-2-hexanone	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Dimethylglyoxal	<0.1	0.4	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
trans-2-Hexenal	<0.1	<0.1	<0.1	<0.1	1.0	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

[a]Plant 1 DS sampled at maximum detention time

[b]Plant 2 DS sampled at average (a) and maximum (m) detention times

Table 23. Halogenated furanone results (µg/L) at the EPA Region 9 treatment plants (3/19/02)

3/19/02	Plant 1		Plant 2		
Compound	FE	PE	FE	PE	DS/max
BMX-1	<0.02	<0.02	<0.02	<0.02	<0.02
BEMX-1	<0.02	0.02	<0.02 (0.01)	0.29	0.18
BMX-2	<0.02	<0.02	<0.02 (0.01)	0.02	<0.02 (0.01)
BEMX-2	<0.02	<0.02	<0.02 (0.01)	0.03	0.04
BMX-3	<0.02	<0.02	<0.02	<0.02	<0.02
BEMX-3	<0.02	<0.02 (0.01)	0.04	0.17	0.06
MX	<0.02	<0.02	<0.02	<0.02	<0.02
EMX	<0.02	<0.02	<0.02	<0.02	<0.02
ZMX	<0.02	<0.02	<0.02	<0.02	<0.02
Ox-MX	<0.02	<0.02	<0.02	<0.02	<0.02
Mucochloric acid (ring)	<0.02	<0.02	<0.02	<0.02	<0.02
Mucochloric acid (open)	<0.02	0.03	0.09	0.10	0.11

Table 12 (10/30/00), Table 18 (7/17/01), and Table 22 (3/19/02) show results for additional target DBPs that were analyzed at the University of North Carolina (UNC). Table 15 (1/23/01) shows results from broadscreen DBP analyses conducted at the U.S. Environmental Protection Agency (USEPA). Table 19 (7/17/01) and Table 23 (3/19/02) show results for halogenated furanones that were analyzed at UNC.

Summary of tables for halogenated organic and other nonhalogenated organic DBPs

DBP Analyses (Laboratory)	10/30/00	1/23/01	7/17/01	3/19/02
Halogenated organic DBPs (MWDSC)	Tables 10-11	Tables 13-14	Tables 16-17	Tables 20-21
Additional target DBPs (UNC)	Table 12		Table 18	Table 22
Halogenated furanones (UNC)			Table 19	Table 23
Broadscreen analysis (USEPA)		Table 15		

Halomethanes. Figure 7 shows the effect of the different treatment/disinfection scenarios at plant 1 and at plant 2 (for July 2001) on trihalomethane (THM) formation and speciation. The use of ozonation/chloramination significantly reduced THM formation. However, at plant 1, there was a shift to the formation of the more brominated species. Jacangelo and colleagues (1989) also observed that pre-ozonation in bromide-containing waters could result in a shift in speciation upon post-chlorination. In addition, because chlorine was not added until after coagulation at plant 1, the bromide-to-TOC ratio was higher (since coagulation removes TOC, but not bromide), which can also result in a shift in THM speciation (Symons et al., 1993).

Figure 7

Effect of Ozone/Chlorine/Chloramines at Plant 1 and Chlorine/Chloramines at Plant 2 on Trihalomethane Formation and Speciation in Finished Waters (July 17, 2001)

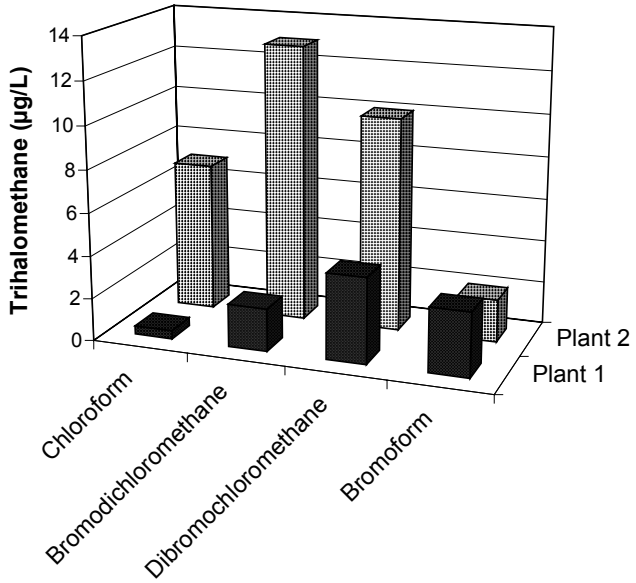
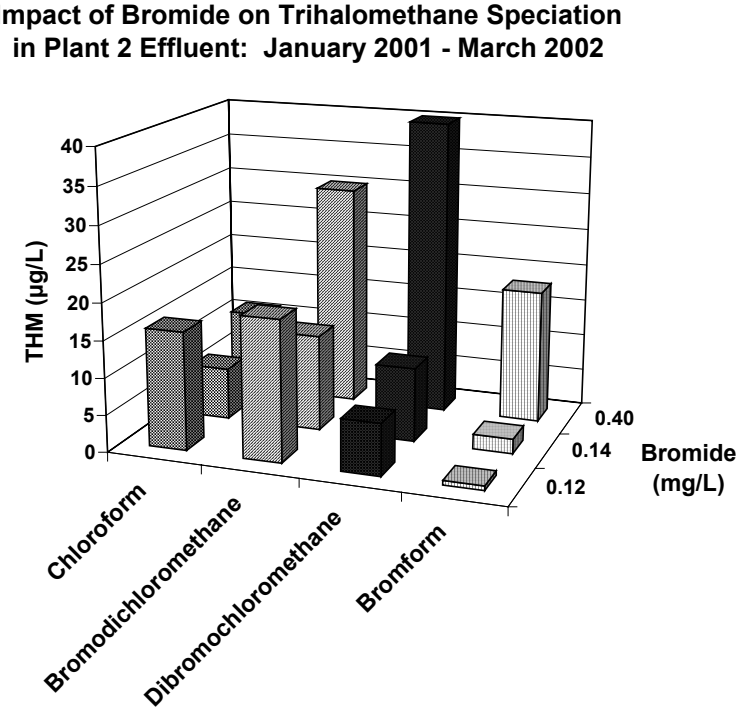


Figure 8 shows the effect of bromide on THM formation and speciation in the finished water at plant 2 for the January 2001, July 2001, and March 2002 samplings. The increase in bromide resulted in more THM formation, as well as a shift in speciation. For example, dibromochloromethane and bromoform formation were significantly higher when the bromide level in the source water increased.

Figure 8



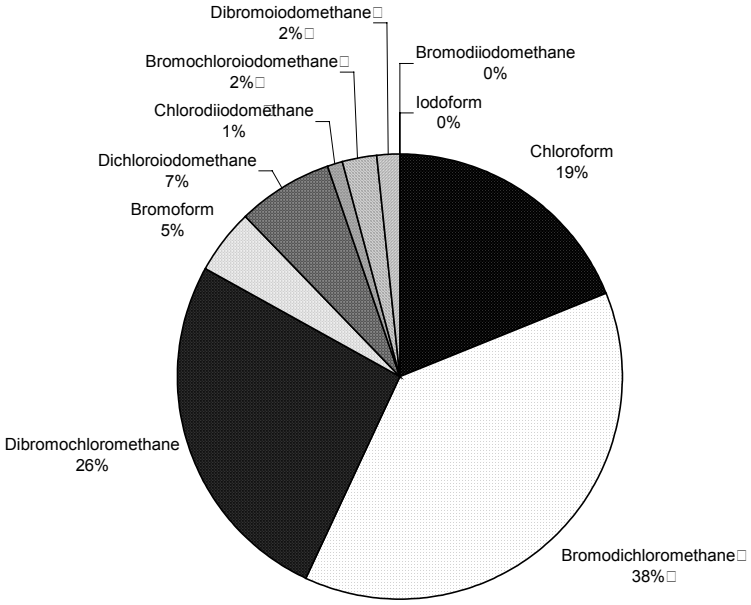
In addition, low or sub-µg/L levels of iodinated THMs were detected, primarily at plant 2. (At plant 1 and plant 2, saltwater intrusion is the source of bromide and, thus, should also be a source of iodide). For example, in January 2001 (bromide = 0.40 mg/L), 1 µg/L of iodoform was detected in the ozone contactor effluent at plant 1, but was not detected (with a minimum reporting level [MRL] of 0.7 µg/L) in downstream locations. However, 0.3 and 0.2 µg/L of dichloroiodo- and bromochloroiodomethane, respectively, were detected in the chloraminated, distributed water. Broadscreen GC/MS analyses also revealed the presence of dichloroiodomethane and bromochloroiodomethane, as well as dibromoiodomethane in finished water from plant 1 (January 2001) (Table 15). At plant 2, 0.5 and 0.6 µg/L of dichloroiodo- and bromochloroiodomethane, respectively, were detected in the plant after chlorination, and 0.6 µg/L of dibromoiodomethane was detected after chloramination.

Iodide is oxidized to hypoiodous acid in the presence of ozone, chlorine, or chloramines. Bichsel and von Gunten (2000) found that when ozone (O_3 , 1.0 mg/L) was used on a low-TOC (1.3 mg/L) water (O_3:TOC = 0.77 mg/mg), no iodinated THMs were detected and $\geq$90 % of the iodide was transformed to iodate, whereas chlorine led to the formation of iodate and iodinated THMs. At plant 1 in January 2001, 2.5 mg/L ozone was used on a moderate-TOC (4.5 mg/L)

water (O_3:TOC = 0.56 mg/mg). Although iodate was not measured in this study, the formation of iodoform after ozonation and other iodinated THMs after chloramination suggests that the lower O_3:TOC ratio did not result in a quantitative conversion of iodide to iodate. However, the use of ozone at plant 1 did result in the formation of less iodinated THMs in the finished water than at plant 2.

Figure 9 shows the THM speciation—including the iodomethanes—at plant 2 in July 2001 (bromide = 0.14 mg/L). Bromodichloromethane was the major species of the four regulated THMs, and dichloroiodomethane was the major iodomethane. In both cases, the major THM formed for each group of halomethanes was dichlorinated, with either a bromine or iodine atom as the third halogen.

Figure 9

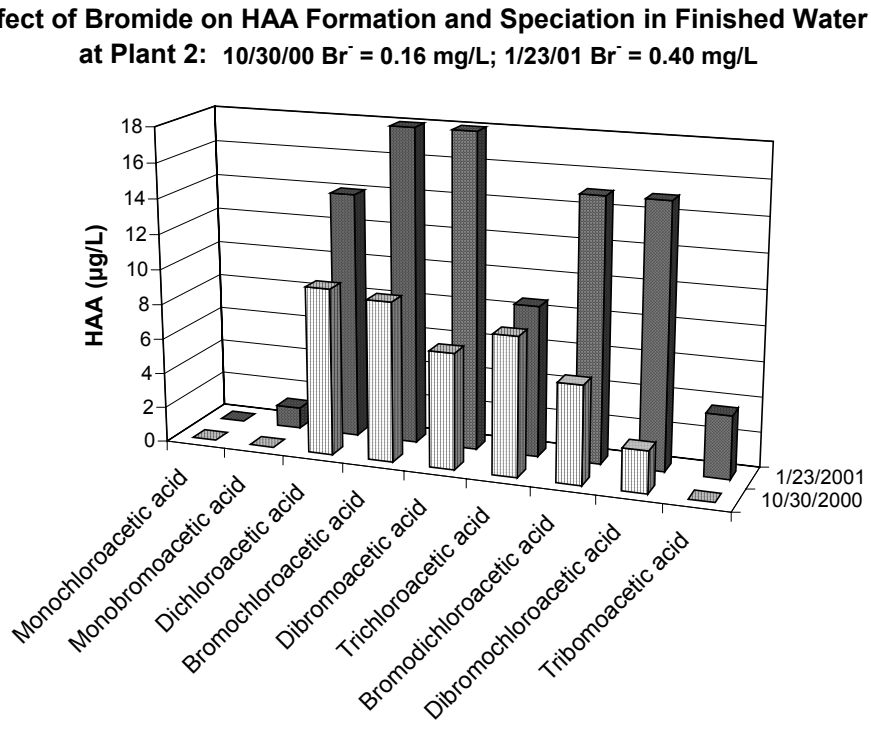


Trihalomethane Speciation at Plant 2
SDS (Average Detention Time) Sample (July 17, 2001)

Haloacids. Figure 10 shows the effect of bromide (Br^-) on haloacetic acid (HAA) formation and speciation in the finished water at plant 2 for the October 2000 and the January 2001 samplings. For example, tribromoacetic acid was detected when the bromide level in the source water increased, whereas it was not detected when the bromide level was lower. In addition, there was a shift to the formation of the other bromine-containing HAAs.

At plant 2, the sum of the dihalogenated HAAs (DXAAs) was somewhat higher than the sum of the trihalogenated HAAs (TXAAs), whereas at plant 1 the formation of HAAs was almost due only to the DXAAs. In other research, ozonation had been shown to be able to destroy THM and TXAA precursors better than DXAA precursors (Reckhow and Singer, 1984).

Figure 10



Similarly, chloramination has been shown to be more effective at controlling the formation of THMs and TXAAs than the formation of DXAAs (Krasner et al., 1996).

In addition to the target HAAs, other haloacids were detected in selected drinking water samples by the broadscreen GC/MS methods (Table 15). Plant 1—whose source water had 0.40 mg/L bromide in January 2001—had numerous brominated acids. Fourteen brominated acids (2,2-dibromopropanoic acid, 3,3-dibromopropenoic acid, *cis*-2,3-dibromopropenoic acid, tribromopropenoic acid, 2-bromobutanoic acid, *trans*-4-bromo-2-butenoic acid, *cis*-4-bromo-2-butenoic acid, 2,3-dibromo-2-butenoic acid, bromodichlorobutenoic acid, bromochloro-4-oxopentanoic acid, 3,3-dibromo-4-oxopentanoic acid, 2-bromobutenedioic acid, *trans*-2,3-dibromobutenedioic acid, *cis*-2-bromo-3-methylbutenedioic acid) had not been previously reported in drinking water. Several of these bromo-acids were also seen in finished waters from plant 11 (EPA Region 6), and also in drinking waters from Israel that had been treated with chlorine or chlorine dioxide-chloramine (Richardson et al., submitted).

October 2000 results from UNC indicated the presence of another target halo-acid, 3,3-dichloropropenoic acid, at levels of 0.1 and 0.7 µg/L, respectively, in finished waters from the plant 1 and plant 2 (Table 12).

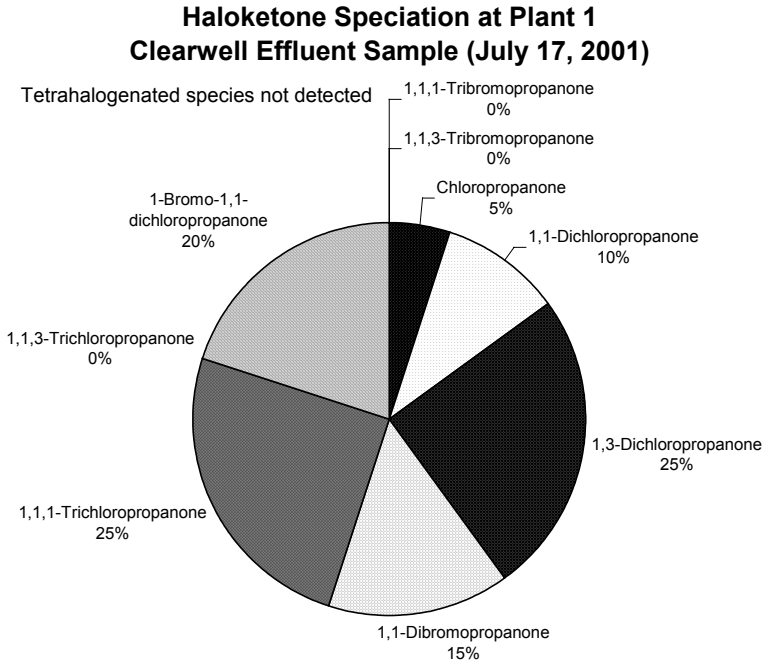
Haloacetonitriles. In other DBP research, haloacetonitriles (HANs) were found to be produced at approximately one-tenth the level of the THMs (Krasner et al., 1989). This was also observed in the plant 1 and plant 2 samples. Dichloro-, bromochloro-, and dibromoacetonitrile—

Information Collection Rule (ICR) DBPs—were detected at both treatment plants. Trichloroacetonitrile—another ICR DBP—was not detected; likewise, the brominated analogues of trichloroacetonitrile were not detected. Sub-µg/L levels of chloroacetonitrile were detected at plant 2 in July 2001 and March 2002.

Haloketones. In addition to the formation of low levels of haloketone (HK) compounds from the ICR, low levels of 1,1,3,3-tetrabromopropanone were detected in January 2001, primarily at plant 2. The concentration of this HK at plant 2 decreased in the distribution system, and was not detected in the SDS samples. The distribution-system and SDS samples were at a pH of 8.5 to 9.0, thus the disappearance of this HK was probably due to base-catalyzed hydrolysis. (For example, Croué and Reckhow (1989) found that 1,1,1-trichloropropanone—another HK—undergoes base-catalyzed hydrolysis at pH 8.5.) During the October 2000 sampling, this brominated HK was not detected, instead its chlorinated analogue, 1,1,3,3-tetrachloropropanone, was detected. Thus, the higher bromide level in the source water in January 2001 also changed the speciation of this HK.

Low levels of other HKs were also detected in July 2001 (Figure 11). These included a monohalogenated HK (i.e., chloropropanone) and other di- and trihalogenated HKs in which the halogens were not all on the same carbon atom and/or there was bromine substitution.

Figure 11

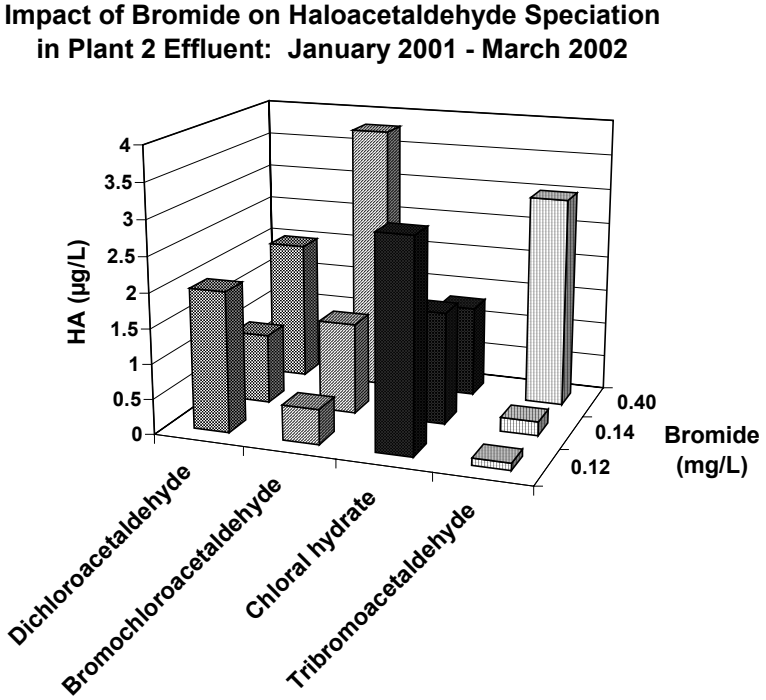


In addition to the target HKs, other HKs were detected by the broadscreen GC/MS methods (Table 15). A number of these HKs were analogous to the di-, tri-, and tetrahalogenated

HKs quantified by MWDSC, except that these were brominated or mixed bromochloro species. For example, in January 2001, when the raw-water bromide was at 0.40 mg/L, MWDSC detected 1,1-dichloro-, 1,1,1-trichloro-, and 1,1,3,3-tetrabromopropanone after chloramination and ozonation at plant 1. Broadscreen GC/MS analysis of this same water also detected two brominated analogues of 1,1-dichloropropanone, two brominated analogues of 1,1,1-trichloropropanone, and a bromochloro analogue of 1,1,3,3-tetrabromopropanone. Most were observed in the finished water that had been treated with secondary chlorine and chloramine, but some were also seen in waters from the ozone contactor effluent. The chlorinated species were likely formed by the twice-a-week treatment of the flocculation and sedimentation basins with chlorine (which was applied at the ozone contactor effluent) to control algal growth, and not by the treatment with ozone. Alternatively, the brominated species may have been formed by ozone, as ozone can oxidize bromide to hypobromous acid, which can react with TOC to form brominated DBPs.

Haloaldehydes. Figure 12 shows the impact of bromide on haloacetaldehyde speciation in the plant effluent of plant 2. When the bromide level was the highest (0.40 mg/L), there was a significant formation of bromochloro- and tribromoacetaldehyde. When the bromide

Figure 12



concentration was lower (0.12-0.14 mg/L), both of these brominated species were formed at lower levels and the formation of the chlorinated species (dichloroacetaldehyde and chloral hydrate) were the major haloacetaldehydes produced.

Likewise, when the bromide level was the highest, there was a significant formation of the bromine-containing THMs (bromodichloromethane, dibromochloromethane, and bromoform) (Figure 8). When the bromide concentration was lower, bromoform was formed at lower levels, and the formation of the chlorine-containing species (chloroform and bromodichloromethane) were typically the major THMs produced.

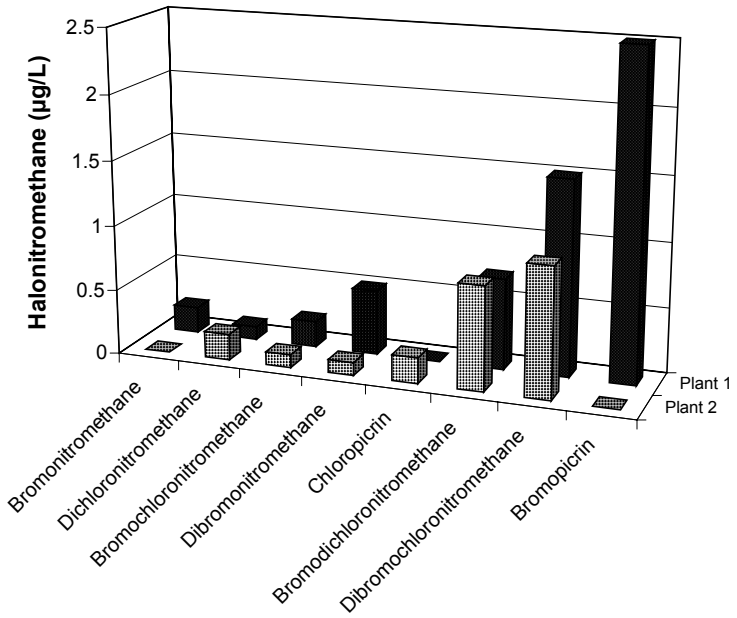
In January 2001, tribromoacetaldehyde decreased in concentration in both sets of distribution-system and SDS samples, whereas the dihalogenated acetaldehydes increased in concentration in the distribution-system and SDS samples for plant 1. Moreover, the concentration of bromochloroacetaldehyde was higher in the distribution-system and SDS samples at plant 1 than at MSWTP. The results for tribromoacetaldehyde are consistent with the research of Xie and Reckhow (1996), who found that tribromoacetaldehyde degraded quickly at pH 9.0. In other research, acetaldehyde (an ozone by-product) was found to react with chlorine to form chloroacetaldehyde, which in the presence of free chlorine rapidly reacted to form chloral hydrate (McKnight and Reckhow, 1992). At plant 1, chlorine (in the presence of ammonia and bromide) may have reacted with acetaldehyde formed by the ozonation process to produce dichloro- and bromochloroacetaldehyde.

In addition to the target haloacetaldehydes, another brominated aldehyde (2-bromo-2-methylpropanal) was detected by the broadscreen GC/MS methods (Table 15).

Halonitromethanes. In addition to low levels of chloropicrin (trichloronitromethane) (an ICR DBP), low or sub-µg/L levels of other halonitromethanes (HNMs) were detected in the selected samples (Figure 13). Although ozone/chlorine/chloramines at plant 1 produced less THMs than chlorine/chloramines produced at plant 2 (Figure 7), a higher concentration of the trihalogenated HNMs was detected at plant 1 in July 2001 (Figure 13) (this was not the situation in March 2002). In other research, pre-ozonation was found to increase chloropicrin formation upon post-chlorination (Hoigné and Bader, 1988). In addition, the speciation of the trihalogenated HNMs was similar to the speciation of the THMs. At plant 2, the bromochloro species predominated, whereas at plant 1 there was more of a shift to the formation of the more fully brominated species.

Figure 13

Effect of Ozone/Chlorine/Chloramines at Plant 1 and Chlorine/Chloramines at Plant 2 on Halonitromethane Formation and Speciation in Finished Waters (July 17, 2001)



Halogenated furanones. Tables 19 and 23 show results for halogenated furanones in the July 2001 and March 2002 samplings for the EPA Region 9 treatment plants. Data are included for 3-chloro-4-(dichloromethyl)-5-hydroxy-2[5H]-furanone, otherwise known as MX; (E)-2-chloro-3-(dichloromethyl)-4-oxobutenoic acid, otherwise known as EMX; (Z)-2-chloro-3-(dichloromethyl)-4-oxobutenoic acid (ZMX); the oxidized form of MX (Ox-MX); brominated forms of MX and EMX (BMXs and BEMXs); and mucochloric acid (MCA), which can be found as a closed *ring* or in an *open* form. Results are displayed graphically in Figure 14.

In July 2001, 3-chloro-4-(dichloromethyl)-5-hydroxy-2[5H]-furanone, otherwise known as MX, was detected at plant 2 but not at plant 1 (with an MRL of 0.04 µg/L) (Table 19; Figure 14). This is probably because ozone in the plant 1 treatment scheme removes MX precursors from the raw TOC, while chlorine in the plant 2 treatment scheme reacts with the raw TOC to form MX . Likewise, plant 1 produced less THMs than plant 2 (Figure 7). The filter effluent sample from plant 2 contained a higher concentration of MX (120 ng/L) than reported in a survey of Australian waters (<90 ng/L) (Simpson and Hayes, 1998). However, water quality and treatment/disinfection schemes may be different in Australia than in the United States. In particular, regulatory requirements in Australia are significantly different than in the United States. MX appears to degrade between the filter effluent and the distribution system (DS)/ average sample of plant 2. However, water in the distribution system may represent a blend of water from more than one treatment plant. In addition, water in the distribution system may represent water produced at plant 2 on a previous day, as the survey was not set up to follow a "plug" of water *per se*. The second sampling of plant 1 and plant 2 (March 2002) for

halogenated furanones showed similar trends, such as removal of MX-analogue precursors by ozonation in plant 1, when compared to plant 2 (Table 23, Figure 15). Overall, plant 2 exhibited higher concentrations of mucochloric acid (MCA *open*) and brominated MX-analogues than plant 1. Within the distribution system of plant 2, BEMX-1 appeared to decrease (from 290 ng/L in the plant effluent to 180 ng/L in the DS/maximum sample) and BEMX-3 appeared to decrease (from 170 ng/L in the plant effluent to 60 ng/L in the DS/maximum sample). Because TOC and bromide levels in the source water of this treatment plant can vary frequently (Krasner et al., 1994)—as well as the pH of the water (which can significantly vary on a diurnal basis)—differences between the plant effluent and the distribution system (particularly at a maximum detention time) may be due (in part) to a comparison of different "packets" of water treated at different points in time. Alternatively, analysis of SDS samples for halogenated furanones would have allowed for a more direct assessment of the impact of distribution system detention time, etc., on the formation and stability of these DBPs.

Figure 14

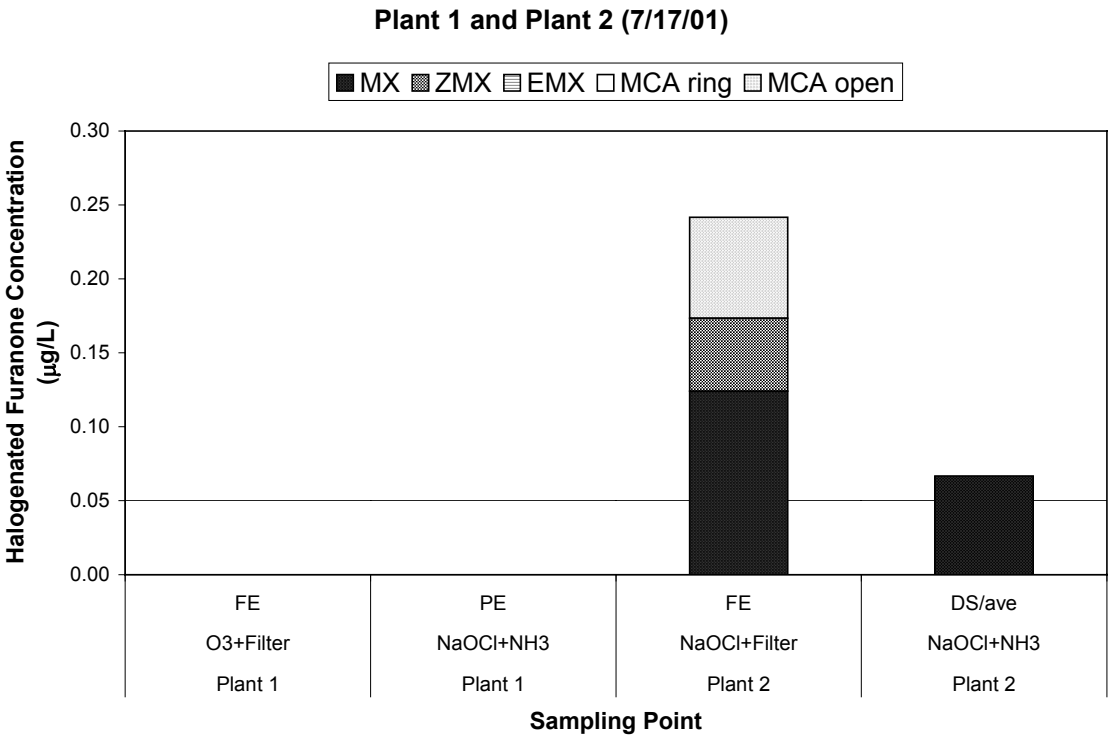
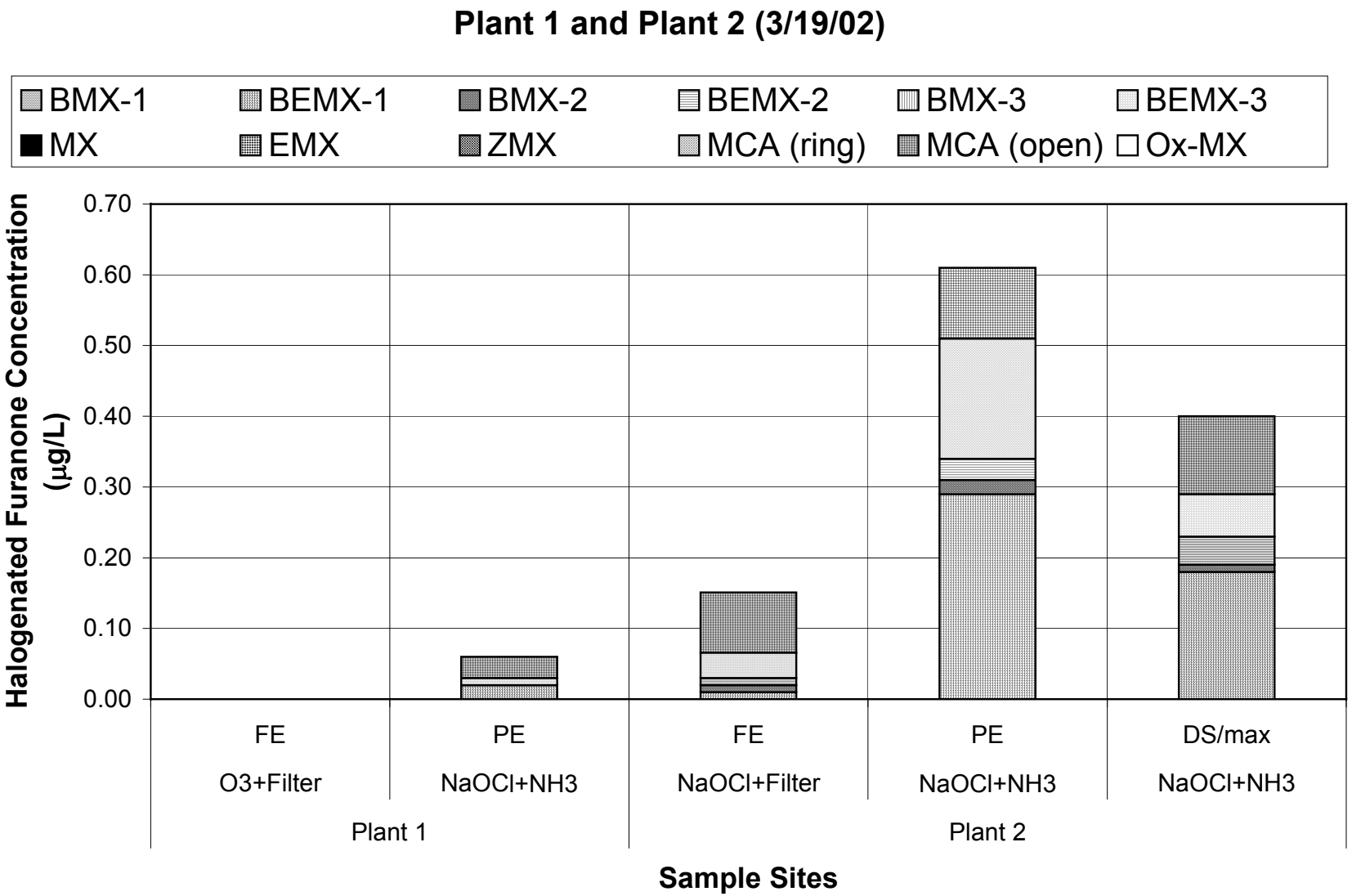


Figure 15


Plant 1 and Plant 2 (3/19/02)
BMX-1
BEMX-1
BMX-2
BEMX-2
BMX-3
BEMX-3
MX
EMX
ZMX
MCA (ring)
MCA (open)
Ox-MX
Halogenated Furanone Concentration (µg/L)
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
FE
O3+Filter
PE
NaOCl+NH3
FE
NaOCl+Filter
PE
NaOCl+NH3
DS/max
NaOCl+NH3
Plant 1
Plant 2
Sample Sites

VOCs. Although methyl *tertiary* butyl ether (MtBE) is not a DBP, it is a VOC that was included in this study. In January 2001, 0.3 µg/L of MtBE was detected in the raw water sample. The same level of MtBE was detected in the treated waters at plant 2, whereas a somewhat lower level (i.e., 0.2 µg/L) was detected at plant 1. In other research, ozone has been shown to destroy (at least in part) MtBE (Liang et al., 1999). If the decrease in MtBE at plant 1 was real, this could have been due to ozonation.

Methyl ethyl ketone (MEK) is also a VOC. In addition, it was detected after ozonation at plant 1 in July 2001. Non-halogenated ketones can be formed by ozone (Glaze et al., 1989). MEK was not detected downstream of the ozone contactor effluent (with an MRL of 0.5 µg/L), perhaps due to biodegradation through the downstream treatment processes.

Other Halogenated DBPs. A few additional, miscellaneous halogenated DBPs were also detected. UNC methods detected dichloroacetamide at 0.2 and 0.8 µg/L in finished water, respectively, from plant 1 and plant 2 in October 2000 (Table 12). Bromochloromethylacetate was also detected in finished waters from plant 1 at 0.1 µg/L (Table 12). In addition, broadscreen GC/MS analyses revealed the presence of chlorobenzene and tribromophenol (Table 15) in finished waters from plant 1 (January 2001). None of these compounds were observed in the corresponding raw, untreated water.

Non-Halogenated DBPs. The plant 1 ozonated drinking water offered one of the few times that cyanoformaldehyde was detected in the Nationwide DBP Occurrence Study. Cyanoformaldehyde had been first identified in a DBP study published in 1999 on ozonated drinking waters from a pilot plant (Richardson et al, 1999). Cyanoformaldehyde was found in the finished water at plant 1 in October 2000 at 0.2 µg/L, and its concentration remained steady at 0.2 µg/L in the distribution system (Table 12). Cyanoformaldehyde was also found in finished waters from plant 2 (which used chlorine disinfection) at 0.3 µg/L (October 2000). Dimethylglyoxal was also seen in ozone contactor effluent samples from plant 1 in both October 2000 and July 2001, but was below detection in the finished water (plant effluent). In the July 2001 sampling, it appeared to be removed by biological filtration, but in the October 2000 sampling, its levels decreased between the filter effluent sampling and the plant effluent, indicating a possible reaction with the secondary chlorine-chloramine that was added following filtration. Broadscreen GC/MS analysis also revealed the presence of glyoxal and several non-halogenated carboxylic acids in samples from plant 1 in January 2001 (Table 15). Several of these carboxylic acids were also seen in the raw, untreated water, but those listed as DBPs in Table 15 represent those whose levels increased substantially (2-3X) in the treated waters vs. the raw, untreated waters.

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EPA REGION 6: PLANTS 11 AND 12

Plant Operations and Sampling

Plant 11 treated water from a river in EPA Region 6 (Figure 1) and plant 12 treated water from another river basin and lake in EPA Region 6. On March 26, 2001, September 10, 2001, November 5 or 15, 2001, and February 11 or 12, 2002, plants 11 and 12 were sampled.

Plant 11 operated a chlorine dioxide plant (Figure 2):

- Ferric sulfate [$Fe_2(SO_4)_3$] and cationic polymer were used for coagulation.
- There was up-flow solids contact flocculation/clarification and dual-media filtration.
- The disinfection strategy used a combination of free chlorine and chlorine dioxide to achieve disinfection requirements through the plant clearwell.
- In March 2001, chlorine dioxide was only added post-filtration, in September 2001 and February 2002 chlorine dioxide was added to the clarified water and post-filtration, and in November 2001 chlorine dioxide was added before the clarifier and after the filters (after the sampling point for the clearwell influent).
- The free chlorine residual was quenched with ammonia to form a chloramine residual prior to the storage tank and distribution.

At plant 12 (Figure 3):

- Alum was used for coagulation.
- There was dual-media filtration. (They were in the process of scrapping the granular activated carbon [GAC] filter media and going back to dual media.)
- The disinfection strategy used a combination of chlorine and ammonia to form chloramines. In February 2002, they used chlorine dioxide during pre-treatment. (They did not use chlorine dioxide as part of their treatment process in March, September, and November 2001.)

Plant 11 was sampled at the following locations:

(1) raw water
(2) filter influent
(3) filter effluent or clearwell influent
(4) clearwell effluent (not sampled in November 2001 and February 2002)
(5) the plant effluent

In addition, the distribution system was sampled at two locations, one representing an average detention time and the other representing a maximum detention time. Furthermore, plant effluent was collected, and simulated distribution system (SDS) testing conducted with a 24- and a 48-hr holding time to represent the average and maximum detention times, respectively, in March 2001, September 2001, and February 2002. In November 2001, the SDS tests were conducted with holding times of 36 and 72 hr, respectively.

However, the plant 11 SDS samples that were shipped on September 12, 2001 were not delivered to Metropolitan Water District of Southern California (MWDSC) until September 17, 2001, since Federal Express could not use air delivery at that time. Because the samples were

not kept cold for that entire period of time, the SDS samples for the September 2001 sampling represent a test of the long-term stability of the DBPs when held at room temperature.

Figure 1. EPA Region 6

New Mexico - Oklahoma - Arkansas - Louisiana - Texas

Figure 2. Plant 11 schematic

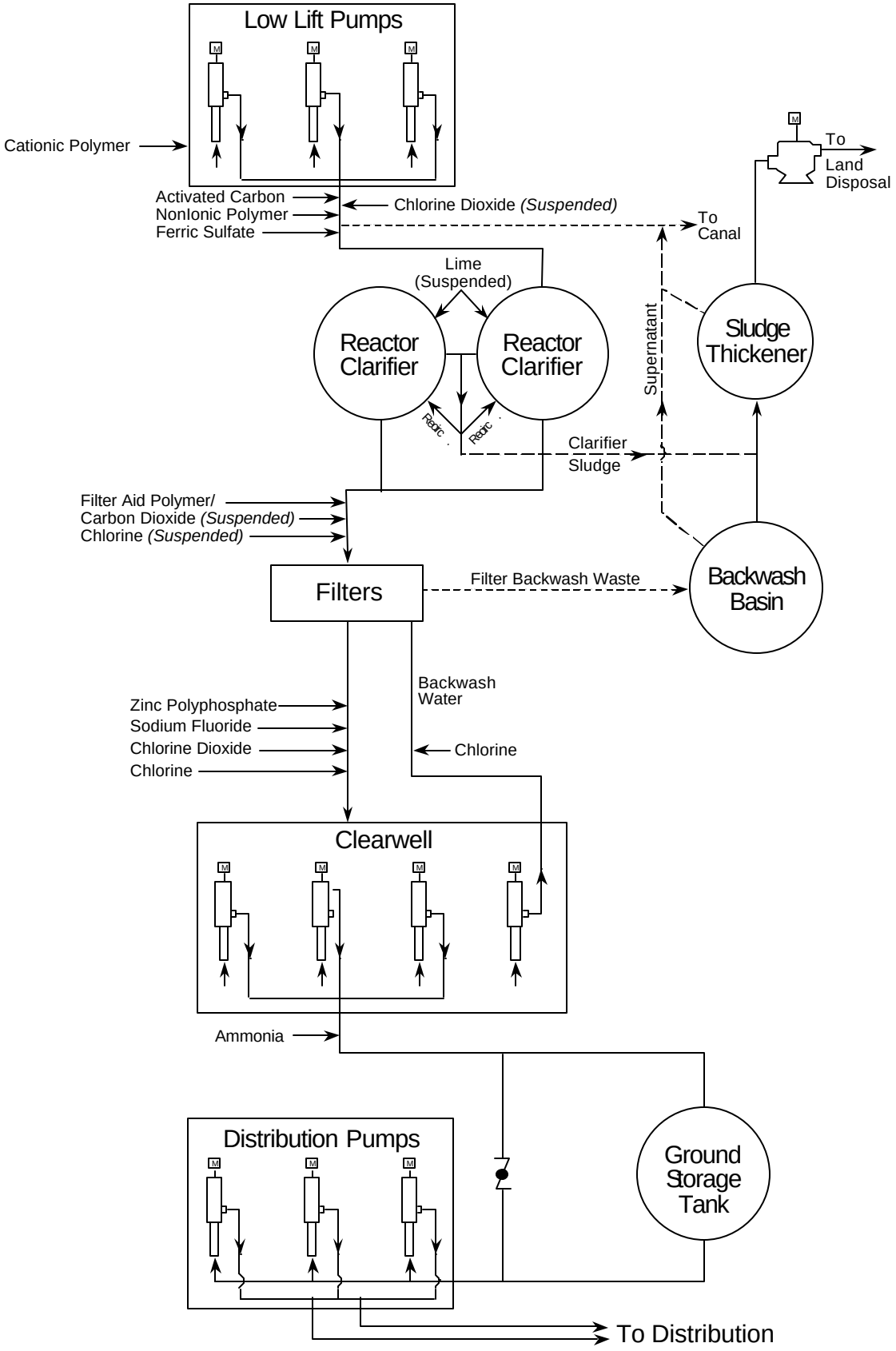
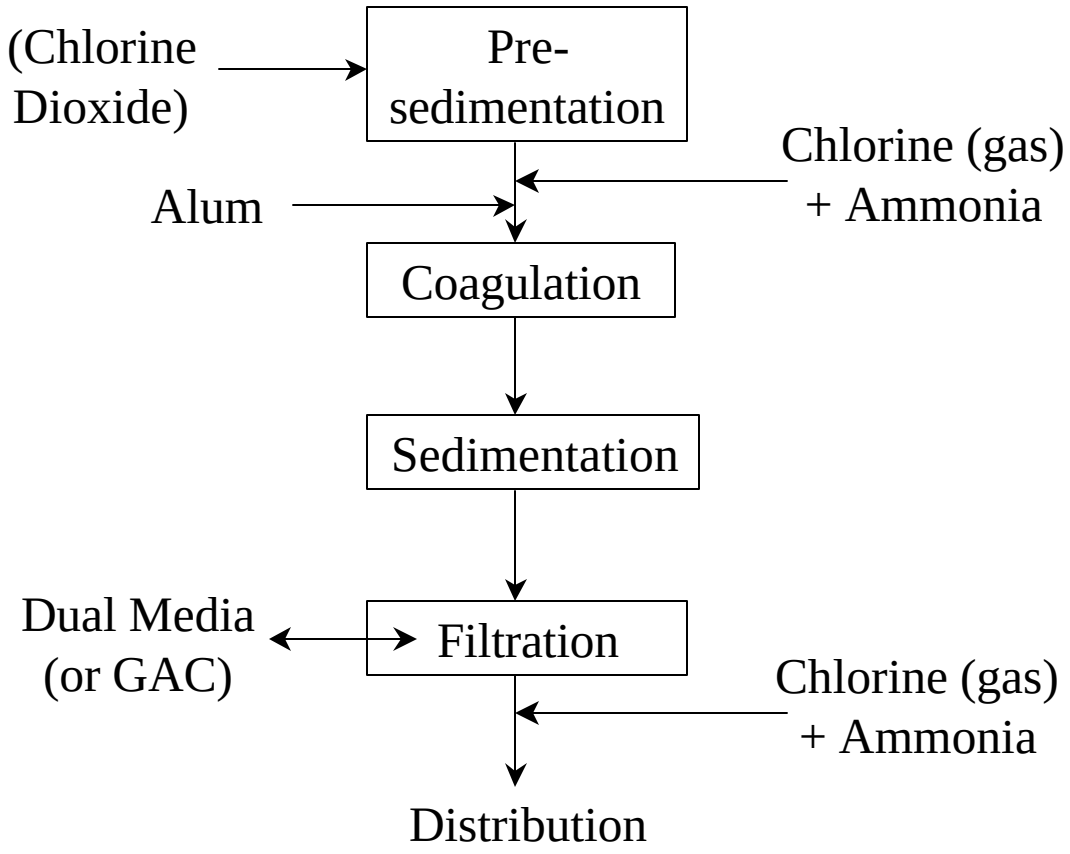


Figure 3. Plant 12 schematic



Plant 12 was sampled at the following locations:

(1) raw water,
(2) after pre-treatment,
(3) filter influent,
(4) filter effluent,
(5) and the plant effluent.

In addition, the distribution system was sampled at two locations, one representing an average detention time and the other representing a maximum detention time. In March 2001, plant effluent was collected and SDS testing was conducted with a 18- and a 30-hr holding time to represent the average and maximum detention times, respectively. SDS testing was not performed in September 2001. In November 2001, the SDS tests were conducted with holding times of 24 and 48 hr, respectively. In February 2002, the SDS samples were held for less than one day (holding times are not available). On the day of sampling, information was collected on the operations at each plant (Tables 1-2).

Table 1. Operational information at plant 11

Parameter	3/26/01	9/10/01	11/5/01	2/11/02
Plant flow (mgd)	12.96	37.4	31.7	28.8
$Fe_2(SO_4)_3$ dose (mg/L)	18.7	7.6	8.5	10.4
Polymer (coagulant aid) dose (mg/L)	3.9	2.7	2.4	7.1
Polymer (filter aid) dose (mg/L)	0.024	0.048	0.048	0.048
Chlorine dioxide dose before clarifier (mg/L as ClO_2)	0	0	0.35	0
Chlorine dioxide dose at clarifier (mg/L as ClO_2)	0	0.35	0	0.25
Chlorine dioxide dose post-filtration (mg/L as ClO_2)	0.75	0.5	0.5	0.5
Chlorine dose at filter effluent (mg/L as Cl_2)	4.5	4.1	4.1	4.0
Ammonia dose at clearwell effluent (mg/L as NH_3-N)	1.25	1.15	1.15	0.86

Table 2. Operational information at plant 12

Parameter	3/26/01	9/10/01	11/15/01	2/12/02
Plant flow (mgd)	72	64	60	60
Coagulant dose used for pre-treatment (mg/L)	0	0	0	0
Chlorine dioxide dose (mg/L as ClO_2)	0	0	0	1.0
Potassium permanganate ($KMnO_4$) dose used for pre-treatment (mg/L)	NA[a]	1	1.0	1.0
Chlorine dose after pre-treatment (mg/L as Cl_2)	4.6	6.0	6.5	5.0
Ammonia dose after pre-treatment (mg/L as NH_3-N)	0.72	1.5	1.2	0.82
Aluminum sulfate dose used in sed. basins (mg/L)	80	95	80	80
No. filters contained GAC, contained dual media	8, 9	0, all	0, 22	0, 22
Chlorine dose at filter effluent (mg/L as Cl_2)	5.5	4.8	3.3	2.4
Ammonia dose at filter effluent (mg/L as NH_3-N)	0.71	1.2	0.61	0.44

[a]NA = Not available

Water Quality

On the day of sampling, information was collected on water quality at each plant (Tables 3-4). Additional data were collected for total organic carbon (TOC) and ultraviolet (UV) absorbance (Tables 5-6). At plant 12, the raw water equaled a blend from two lakes. The blend ratio changed from day to day. Water after pre-treatment equaled a blend of raw and pre-treated ($KMnO_4$) water. The detention time in the pre-sedimentation basin lead to a mixture of current and previous blends. Thus, the difference in water quality between the raw and pre-treated water at plant 12 represented, in part, changes in the blend ratio.

At plant 12 in March 2001, September 2001, November 2001, and February 2002, the water after pre-treatment had 2-19 % less TOC than the raw water, and coagulation subsequently removed 21-40 % of the remaining TOC in the pre-treated water. The water after pre-treatment had a 13-28 % reduction in UV, and coagulation reduced the UV of the pre-treated water by an additional 38-54 %. At plant 11 in March 2001, September 2001, November 2001, and February 2002, coagulation and filtration cumulatively removed 17-30 % of the TOC and reduced the UV by 23-65 %.

Table 3. Water quality information at plant 11

	pH				Temperature (ºC)				Disinfectant Residual[a] (mg/L)			
Location	3/26/01	9/10/01	11/5/01	2/11/02	3/26/01	9/10/01	11/5/01	2/11/02	3/26/01	9/10/01	11/5/01	2/11/02
Raw water	8.14	8.12	8.33	NA	19.2	26.2	21.2	11.2	---	---	---	---
Filter influent	7.54	7.86	8.13	7.98	19.0	26.8	21.3	11.6	---	**0.31**	---	---
Filter eff. or clear. inf.	7.65	7.38	7.47	7.49	19.0	26.4	22.3	11.4	---	*3.3*	---	**0.17**/ *3.7*
Clearwell effluent	7.30	7.48	NS[b]	NS	18.0	27.8	NS	NS	**0.31**/ 2.5	2.6	NS	NS
Plant effluent	7.40	7.52	7.52	7.47	18.2	24.8	21.9	11.4	**0.02**/ 2.7	3.0	**0.10**/ 2.9	**0.13**/ 3.2
Dist. system/average	7.52	7.62	7.62	7.62	19.3	27.6	23.3	12.1	2.6	2.6	2.7	2.7
Dist. system/maximum	7.44	7.58	7.68	7.68	20.2	27.8	22.9	12.3	2.5	2.5	2.4	2.5
SDS/average	7.63	7.53	7.52	7.53	20.0	26.0	21.4	13.9	2.7	2.4	2.5	2.8
SDS/maximum	7.52	7.57	7.56	7.52	18.1	25.8	21.6	14.1	2.5	2.3	2.2	2.7

[a]Chlorine dioxide residuals (values shown in bold) in clearwell effluent and plant effluent in March 2001, in filter influent in September 2001, in plant effluent in November 2001, and in clearwell influent and in plant effluent in February 2002; chlorine residuals (values shown in italics) in clearwell influent in September 2001 and in February 2002; chloramine residuals at other locations.

[b]NS = Not sampled

Table 4. Water quality information at plant 12

	pH				Temperature (ºC)				Disinfectant Residual[a] (mg/L)			
Location	3/26/01	9/10/01	11/15/01	2/12/02	3/26/01	9/10/01	11/15/01	2/12/02	3/26/01	9/10/01	11/15/01	2/12/02
Raw water	8.3	7.7	7.6	7.8	20.9	28	23.6	16	---	---	---	---
After pre-treatment	8.4	7.8	8.0	7.8	19.9	28	23.4	14	---	---	---	**0.15**
Filter influent	8.8	8.3	8.1	8.4	19.0	27	24.1	17	2.1	1.6	2.3	1.7
Filter effluent	8.2	7.6	NA	8.1	20.8	27	23.1	16	1.6	4.8	2.1	1.4
Plant effluent	8.1	7.6	8.3	7.6	20.8	27	23.4	14	4.9	4.7	4.3	4.6
Dist. system/average	7.8	7.7	NA	7.4	15.4	26	NA	16	3.6	3.2	NA	NA
Dist. system/maximum	7.7	7.7	NA	7.4	21.3	25	NA	18	2.2	2.6	NA	NA
SDS/average	NA	NS[b]	7.3	7.4	NA	NS	25	16	NA	NS	3.4	2.7
SDS/maximum	NA	NS	7.3	7.4	NA	NS	25	18	NA	NS	2.8	2.4

[a]Chlorine dioxide residual (value shown in bold) at pre-treatment sample location in February 2002; chloramine residuals at other locations.

[b]NS = Not sampled

Table 5. TOC and UV removal at plant 11

Location	TOC (mg/L)	UV[a] (cm^{-1})	SUVA[b] (L/mg-m)	Removal/Unit (%)		Removal/Cumulative (%)	
				TOC	UV	TOC	UV
03/26/2001							
Raw	5.66	0.137	2.42	---	---	---	---
Filter Inf.	4.08	0.083	2.03	28%	39%	28%	39%
Filter Eff.	4.24	0.089	2.10	-3.9%	-7.2%	25%	35%
09/10/2001							
Raw	3.51	0.079	2.25	---	---	---	---
Filter Inf.	3.24	0.069	2.13	7.7%	13%	7.7%	13%
Clearwell Inf.	2.89	0.044	1.52	11%	36%	18%	44%
11/5/2001							
Raw	4.68	0.115	2.46	---	---	---	---
Filter Inf.	4.0	0.094	2.35	15%	18%	15%	18%
Clearwell Inf.	3.87	0.088	2.27	3.3%	6.4%	17%	23%
02/11/2002							
Raw	4.26	0.108	2.54	---	---	---	---
Filter Inf.	3.25	0.055	1.69	24%	49%	24%	49%
Clearwell Inf.	3.0	0.038	1.27	7.7%	31%	30%	65%

[a]UV = Ultraviolet absorbance reported in units of "inverse centimeters" (APHA, 1998)

[b]SUVA (L/mg-m) = Specific ultraviolet absorbance = 100*UV (cm^{-1})/DOC (mg/L) or UV (m^{-1})/DOC (mg/L), where DOC = dissolved organic carbon, which typically = 90-95% TOC (used TOC values in calculating SUVA) (e.g., UV = 0.137/cm = 0.137/(0.01 m) = 13.7/m, DOC = 5.66 mg/L, SUVA = (13.7 m^{-1})/(5.66 mg/L) = 2.42 L/mg-m)

Table 6. TOC and UV removal at plant 12

Location	TOC (mg/L)	UV[a] (cm^{-1})	SUVA[b] (L/mg-m)	Removal/Unit (%)		Removal/Cumulative (%)	
				TOC	UV	TOC	UV
03/26/2001							
Raw	6.72	0.184	2.74	---	---	---	---
After Pre-Treat.	6.12	0.160	2.61	8.9%	13%	8.9%	13%
Filter Inf.	4.48	0.095	2.12	27%	41%	33%	48%
Filter Eff.	4.52	0.086	1.90	-0.9%	9.5%	33%	53%
09/10/2001							
Raw	7.52	0.273	3.63	---	---	---	---
After Pre-Treat.	6.20	0.196	3.16	18%	28%	18%	28%
Filter Inf.	3.70	0.091	2.46	40%	54%	51%	67%
Filter Eff.	3.80	0.089	2.34	-2.7%	2.2%	49%	67%
11/15/2001							
Raw	7.01	0.233	3.32	---	---	---	---
After Pre-Treat.	5.71	0.188	3.29	19%	19%	19%	19%
Filter Inf.	4.51	0.117	2.59	21%	38%	36%	50%
Filter Eff.	4.42	0.115	2.60	2.0%	1.7%	37%	51%
02/12/2002							
Raw	5.33	0.176	3.30	---	---	---	---
After Pre-Treat.	5.24	0.129	2.46	1.7%	27%	1.7%	27%
Filter Inf.	3.30	0.070	2.12	37%	46%	38%	60%
Filter Eff.	3.21	0.069	2.15	2.7%	1.4%	40%	61%

[a]UV = Ultraviolet absorbance reported in units of "inverse centimeters" (APHA, 1998)

[b]SUVA (L/mg-m) = Specific ultraviolet absorbance = 100*UV (cm^{-1})/DOC (mg/L) or UV (m^{-1})/DOC (mg/L), where DOC = dissolved organic carbon, which typically = 90-95% TOC (used TOC values in calculating SUVA) (e.g., UV = 0.184/cm = 0.184/(0.01 m) = 18.4/m, DOC = 6.72 mg/L, SUVA = (18.4 m^{-1})/(6.72 mg/L) = 2.74 L/mg-m)

Table 7 shows the values of miscellaneous other water quality parameters in the raw waters at the two EPA Region 6 plants.

Table 7. Miscellaneous water quality parameters in raw water at the EPA Region 6 plants

Plant 11

Date	Bromide (mg/L)	Alkalinity (mg/L)	Ammonia (mg/L as N)
03/26/2001	0.18	121	ND
09/10/2001	0.21	117	0.15
11/5/2001	0.16	133	ND
02/11/2002	0.18	153	ND

Plant 12

Date	Bromide (mg/L)	Alkalinity (mg/L)	Ammonia (mg/L as N)
03/26/2001	0.25	123	ND
09/10/2001	0.02	54	0.04
11/15/2001	0.15	70	ND
02/12/2002[a]	0.33	111	ND

[a]Bromide sampled at pre-treatment sample location in February 2002

Both EPA Region 6 plants treated waters high in TOC, bromide, and alkalinity in March 2001, November 2001, and February 2002 (Tables 5-7, Figure 4). However, in September 2001, the water qualities were quite different (Table 5-7, Figure 5): the TOC at plant 11 was lower, whereas the bromide and alkalinity at plant 12 was lower.

Figure 4

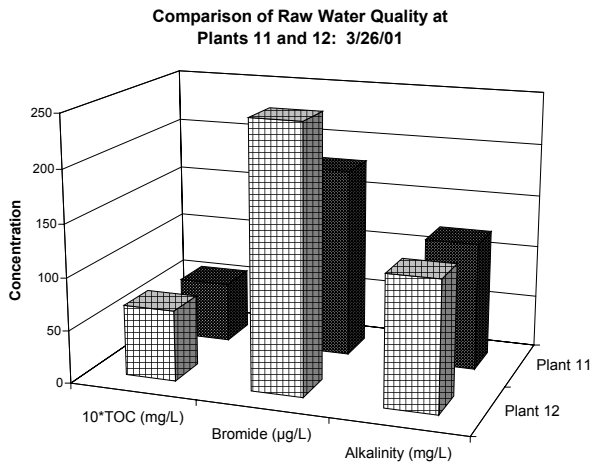
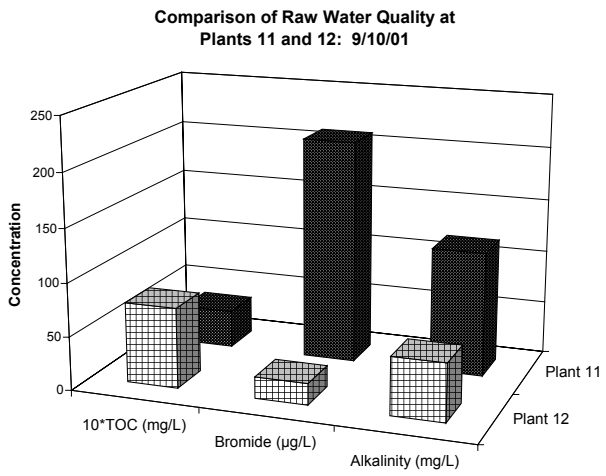


Figure 5



At plant 12, the bromide and alkalinity on September 10, 2001 were significantly lower than on March 26, 2001, whereas the TOC was only slightly higher. This could either reflect a different blend of source waters on the two sampling dates or some seasonal variation in water quality. For example, a storm event can result in an increase in TOC due to runoff and a dilution of inorganic parameters such as bromide and alkalinity.

DBPs

Oxyhalides. Tables 8-9 show the formation of oxyhalides at the two plants. Chlorine dioxide will typically not react with bromide to form bromate, as was observed at plant 11 (Table 8) and plant 12 in February 2002 (Table 9).

Table 8. Oxyhalide formation at plant 11

Location	Bromate[a] (µg/L)	Chlorite[a] (µg/L)	Chlorate[a] (µg/L)	ClO_2^-/ClO_2[b] %
03/26/2001				
Filter Eff.	ND	ND	ND	---
Clearwell Eff.	ND	639	244	85%
09/10/2001				
Clearwell Inf.	ND	399	94	47%
Clearwell Eff.	ND	406	160	48%
11/5/2001				
Filter Inf.	ND	238	47	68%
Clearwell Inf.	ND	202	47	58%
Plant Eff.	ND	478	159	56%
02/11/2002				
Filter Inf.	ND	135	36	54%
Clearwell Inf.	ND	212	289	28%
Plant Eff.	ND	420	167	56%

[a]Reporting detection level for bromate = 3 µg/L and for chlorate and chlorite = 5 µg/L

[b]Chlorine dioxide dose in March 2001 = 0.75 mg/L
Chlorine dioxide dose in September 2001 = 0.35 mg/L at clarifier and 0.5 mg/L at post
Chlorine dioxide dose in November 2001 = 0.35 mg/L before clarifier and 0.5 mg/L at post
Chlorine dioxide dose in February 2002 = 0.25 mg/L at clarifier and 0.5 mg/L at post

Table 9. Oxyhalide formation at plant 12

Location	Bromate (µg/L)	Chlorite (µg/L)	Chlorate (µg/L)	ClO_2^-/ClO_2[a] %
03/26/2001				
After Pre-Treat.	ND	ND	8.6	---
Filter Inf.	ND	ND	30	---
Filter Eff.	ND	ND	32	---
09/10/2001				
After Pre-Treat.	ND	ND	ND	---
Filter Inf.	ND	ND	ND	---
Filter Eff.	ND	ND	ND	---
11/15/2001				
After Pre-Treat.	ND	ND	ND	---
Filter Inf.	ND	ND	ND	---
Filter Eff.	ND	ND	ND	---
02/12/2002				
After Pre-Treat.	ND	900	94	90%
Filter Inf.	ND	648	182	65%
Filter Eff.	ND	634	169	63%

[a]Chlorine dioxide dose in February 2002 = 1.0 mg/L

It has been reported that during water treatment, approximately 50-70 % of the chlorine dioxide (ClO_2) reacted will immediately appear as chlorite (ClO_2^-) and the remainder as chloride (Aieta and Berg, 1986). At plant 11, a similar percentage was observed in November 2001 and for most of the samples collected in February 2002, whereas a somewhat higher amount of chlorite was detected in March 2001 and a somewhat lower level was detected in September 2001 (Table 8). Likewise, a similar percentage to that reported by Aieta and Berg (1986) was observed for most of the samples collected in February 2002 at plant 12 (Table 9).

Because chlorine dioxide was not used at plant 12 on March 26, 2001, September 10, 2001, or November 15, 2001, no chlorite was detected (Table 9). However, a very low amount of chlorate was found in the water in March 2001, even before the addition of chlorine (Table 9). In other research, low levels of chlorate have been detected in raw water samples (Bolyard et al., 1992).

Organic DBPs. Tables 10 and 11 (3/26/01), Tables 13 and 14 (9/10/01), Tables 19 and 20 (11/5/01 and 11/15/01), and Tables 22 and 23 (2/11/02 and 2/12/02) show results for the halogenated organic DBPs that were analyzed by MWDSC. Table 12 (3/26/01 [plant 11] and Table 21 (11/15/01 [plant 12]) shows results from broadscreen DBP analyses conducted at the U.S. Environmental Protection Agency (USEPA). Tables 15 and 16 (9/10/01), and Tables 24 and 25 (2/11/02 and 2/12/02) show results for additional target DBPs that were analyzed for at the University of North Carolina (UNC). Tables 17 and 18 (9/10/01), and Tables 26 and 27 (2/11/02 and 2/12/02) show results for halogenated furanones that were analyzed at UNC.

Summary of tables for organic DBPs

DBP Analyses (Laboratory)	3/26/01	9/10/01	11/5/01 and 11/15/01	2/11/02 and 2/12/02
Halogenated organic DBPs (MWDSC)	Tables 10-11	Tables 13-14	Tables 19-20	Tables 22-23
Additional target DBPs (UNC)		Tables 15-16		Tables 24-25
Halogenated furanones (UNC)		Tables 17-18		Table 26-27
Broadscreen analysis (USEPA)	Table 12[a]		Table 21[b]	

[a]Plant 11
[b]Plant 12

Table 10. DBP results at plant 11 (3/26/01)

03/26/2001	MRL[a]	Plant 11[b]							
Compound	µg/L	Raw	Filt Eff	Clearwell	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes									
Chloromethane	0.15	ND[c]		ND	ND	ND		0.35	
Bromomethane	0.20	ND		ND	ND	ND		ND	
Bromochloromethane	0.14	ND		ND	ND	ND		ND	
Dibromomethane	0.11	ND		ND	ND	ND		ND	
Chloroform[d]	0.1	ND	0.2	8	6	6	6	7	7
Bromodichloromethane[d]	0.1	ND	0.4	19	15	15	17	17	17
Dibromochloromethane[d]	0.10	ND	0.4	23	19	18	21	20	20
Bromoform[d]	0.12	ND	ND	7	6	6	5	6	6
THM4[e]		ND	1.0	57	46	45	49	50	50
Dichloroiodomethane	0.2	ND	ND	0.3	ND	0.2	ND	ND	ND
Bromochloroiodomethane	0.20	ND	ND	0.3	ND	0.2	ND	0.2	ND
Dibromoiodomethane	0.60	ND	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.51	ND	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.56	ND	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.54	ND	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.06	ND		0.2	0.15	ND		ND	
Tribromochloromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids									
Monochloroacetic acid[d]	2		ND	ND	ND	ND		2.7	
Monobromoacetic acid[d]	1		ND	ND	ND	ND		ND	
Dichloroacetic acid[d]	1		ND	10	9.7	11		12	
Bromochloroacetic acid[d]	1		ND	12	11	13		13	
Dibromoacetic acid[d]	1		ND	8.7	8.1	8.9		9.2	
Trichloroacetic acid[d]	1		ND	4.5	3.8	5.1		5.4	
Bromodichloroacetic acid	1		ND	10	9.0	11		11	
Dibromochloroacetic acid	1		ND	8.8	7.5	8.9		9.2	
Tribromoacetic acid	2		ND	ND	ND	ND		ND	
HAA5[f]			ND	23	22	25		29	
HAA9[g]			ND	54	49	58		63	
DXAA[h]			ND	31	29	33		34	
TXAA[i]			ND	23	20	25		26	
Haloacetonitriles									
Chloroacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[d]	0.10	ND	ND	0.3	2	2	2	2	2
Bromochloroacetonitrile[d]	0.1	ND	ND	0.4	3	3	3	3	3
Dibromoacetonitrile[d]	0.17	ND	ND	0.6	3	4	4	4	4
Trichloroacetonitrile[d]	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetaldehydes									
Dichloroacetaldehyde	0.16	ND	ND	1	0.4	0.8	1	0.8	1
Bromochloroacetaldehyde	0.1	0.1	ND	0.6	0.3	0.4	0.8	0.4	0.4
Chloral hydrate[d]	0.1	0.2	ND	0.3	0.5	0.6	1	0.7	0.6
Tribromoacetaldehyde	0.1	ND	ND	ND	ND	ND	0.5	ND	ND

Table 10 (continued)

03/26/2001	MRL[a]	Plant 11[b]							
Compound	µg/L	Raw	Filt Eff	Clearwell	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloketones									
Chloropropanone	0.5	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloropropanone[d]	0.11	ND	ND	1	0.3	0.4	0.3	0.4	0.5
1,3-Dichloropropanone	0.10	ND	ND	ND	ND	ND	0.5	ND	ND
1,1-Dibromopropanone	3	ND		ND	ND	ND		ND	
1,3-Dibromopropanone	3	ND		ND	ND	ND		ND	
1,1,1-Trichloropropanone[d]	0.10	ND	ND	ND	0.8	0.4	1	0.6	0.4
1,1,3-Trichloropropanone	0.11	ND	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	3	ND		ND	<1[j]	ND		ND	
1,1,1-Tribromopropanone	3	ND		ND	ND	ND		ND	
1,1,3-Tribromopropanone	3	ND		ND	ND	ND		ND	
1,1,3,3-Tetrachloropropanone	0.12	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	3	ND		ND	ND	ND		ND	
1,1,3,3-Tetrabromopropanone	0.5	ND	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes									
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	3	ND		ND	<1	<1		<1	
Bromochloronitromethane	3	ND		ND	<1	<1		<1	
Dibromonitromethane	0.12	ND	ND	0.2	0.4	ND	0.2	ND	ND
Chloropicrin[d]	0.1	ND	ND	ND	ND	0.4	0.1	0.2	0.4
Miscellaneous Compounds									
Methyl ethyl ketone	1.90	ND		ND	ND	ND		ND	
Methyl *tertiary* butyl ether	0.16	ND		ND	ND	ND		ND	
Benzyl chloride	2	ND	ND	ND	ND	ND	ND	ND	ND

[a]MRL = Minimum reporting level, which equals method detection limit (MDL) or lowest calibration standard or concentration of blank

[b]Plant 11 sampled at (1) raw water, (2) filter effluent, (3) clearwell effluent, (4) plant effluent, distribution system (DS) at (5) average and (6) maximum detention times, and SDS testing of plant effluent at (7) average and (8) maximum detention times

[c]ND = Not detected at or above MRL

[d]DBP in the Information Collection Rule (ICR) (note: some utilities collected data for all 9 haloacetic acids for the ICR, but monitoring for only 6 haloacetic acids was required)

[e]THM4 = Sum of 4 THMs (chloroform, bromodichloromethane, dibromochloromethane, bromoform)

[f]HAA5 = Sum of 5 haloacetic acids (monochloro-, monobromo-, dichloro-, dibromo-, trichloroacetic acid)

[g]HAA9 = Sum of 9 haloacetic acids

[h]DXAA = Sum of dihaloacetic acids (dichloro-, bromochloro-, dibromoacetic acid)

[i]TXAA = Sum of trihaloacetic acids (trichloro-, bromodichloro-, dibromochoro-, tribromoacetic acid)

[j]<1: Concentration less than lowest calibration standard (i.e., 1 µg/L)

Table 11. DBP results at plant 12 (3/26/01)

03/26/2001	MRL[a]	Plant 12[k]								
Compound	µg/L	Raw	Pre-Treat	Filt Inf	Filt Eff	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes										
Chloromethane	0.15	ND[c]		ND		ND	ND		ND	
Bromomethane	0.20	ND		ND		ND	ND		ND	
Bromochloromethane	0.14	ND		ND		ND	ND		ND	
Dibromomethane	0.11	ND		ND		ND	ND		ND	
Chloroform[d]	0.1	ND	0.2	6	5	5	6	6	5	7
Bromodichloromethane[d]	0.1	ND	ND	11	10	11	14	17	12	15
Dibromochloromethane[d]	0.10	ND	0.4	8	8	10	18	30	12	16
Bromoform[d]	0.12	ND	ND	5	7	8	14	31	9	11
THM4[e]		ND	0.6	30	30	34	52	84	38	49
Dichloroiodomethane	0.2	ND	ND	3	NR[l]	4	4	NR	4	NR
Bromochloroiodomethane	0.20	ND	ND	3	NR	3	6	NR	3	2
Dibromoiodomethane	0.60	ND	ND	2	2	3	7	0.8	4	4
Chlorodiiodomethane	0.51	ND	ND	2	1	2	3	ND	3	2
Bromodiiodomethane	0.56	ND	ND	ND	ND	0.3	1	ND	0.4	ND
Iodoform	0.54	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.06	ND		ND		ND	ND		ND	
Tribromochloromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids										
Monochloroacetic acid[d]	2		ND	ND	ND	ND	ND		2.0	
Monobromoacetic acid[d]	1		ND	ND	ND	ND	ND		ND	
Dichloroacetic acid[d]	1		ND	11	12	14	12		14	
Bromochloroacetic acid[d]	1		ND	10	12	15	15		14	
Dibromoacetic acid[d]	1		ND	6.9	7.7	12	14		12	
Trichloroacetic acid[d]	1		ND	2.4	4.1	5.1	3.5		5.1	
Bromodichloroacetic acid	1		ND	2.1	4.8	6.0	5.2		5.8	
Dibromochloroacetic acid	1		ND	1.5	3.4	3.9	4.1		3.7	
Tribromoacetic acid	2		ND	ND	ND	ND	ND		ND	
HAA5[f]			ND	20	24	31	30		33	
HAA9[g]			ND	34	44	56	54		57	
DXAA[h]			ND	28	32	41	41		40	
TXAA[i]			ND	6.0	12	15	13		15	
Haloacetonitriles										
Chloroacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[d]	0.10	ND	ND	0.8	0.7	1	2	1	2	2
Bromochloroacetonitrile[d]	0.1	ND	ND	1	1	2	2	3	2	2
Dibromoacetonitrile[d]	0.17	ND	ND	0.6	0.6	1	3	4	2	2
Trichloroacetonitrile[d]	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetaldehydes										
Dichloroacetaldehyde	0.16	ND	ND	1	0.5	0.6	0.6	0.3	0.7	0.8
Bromochloroacetaldehyde	0.1	ND	ND	0.9	0.4	0.6	0.9	0.6	0.8	0.9
Chloral hydrate[d]	0.1	0.1	ND	0.8	0.2	0.2	0.4	0.2	0.3	0.3
Tribromoacetaldehyde	0.1	ND	ND	0.6	ND	0.2	0.2	0.2	0.3	0.2

Table 11 (continued)

03/26/2001	MRL[a]	Plant 12[b]								
Compound	µg/L	Raw	Pre-Treat	Filt Inf	Filt Eff	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloketones										
Chloropropanone	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloropropanone[d]	0.11	ND	ND	0.4	0.3	0.3	ND	ND	0.3	0.3
1,3-Dichloropropanone	0.10	ND	ND	0.3	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	3	ND		ND		ND	ND		ND	
1,3-Dibromopropanone	3	ND		ND		ND	ND		ND	
1,1,1-Trichloropropanone[d]	0.10	ND	ND	0.3	0.2	0.3	0.2	ND	0.3	0.3
1,1,3-Trichloropropanone	0.11	ND	ND	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	3	ND		<1[j]		<1	ND		<1	
1,1,1-Tribromopropanone	3	ND		ND		ND	ND		ND	
1,1,3-Tribromopropanone	3	ND		ND		ND	ND		ND	
1,1,3,3-Tetrachloropropanone	0.12	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	3	ND		ND		ND	ND		ND	
1,1,3,3-Tetrabromopropanone	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes										
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	3	ND		<1		<1	<1		<1	
Bromochloronitromethane	3	ND		<1		<1	<1		<1	
Dibromonitromethane	0.12	ND	ND	0.1	ND	0.3	0.4	0.8	0.3	0.2
Chloropicrin[d]	0.1	ND	ND	0.1	0.1	0.2	0.2	0.1	0.2	0.4
Miscellaneous Compounds										
Methyl ethyl ketone	1.90	ND		ND		ND	ND		ND	
Methyl *tertiary* butyl ether	0.16	ND		ND		ND	ND		ND	
Benzyl chloride	2	ND	ND	ND	ND	ND	ND	ND	ND	ND

[k]Plant 12 sampled at (1) raw water, (2) after pre-treatment, (3) filter influent, (4) filter effluent, (5) plant effluent, DS at (6) average and (7) maximum detention times, and SDS testing of plant effluent at (8) average and (9) maximum detention times

[l]NR = Not reported, due to interference problem on gas chromatograph or to problem with quality assurance

Table 12. Occurrence of other DBPs[a] at plant 11: plant effluent (3/26/01)

Halomethanes *Dibromochloromethane*[b] *Bromoform* *Dichloroiodomethane* *Bromochloroiodomethane* *Dibromoiodomethane*	Haloketones 1,1-Dichloropropanone 1,1,1-Trichloropropanone 1,1,3-Trichloropropanone 1-Bromo-1,1-dichloropropanone *1,1-Dibromo-3-chloropropanone* *1,1,3-Tribromopropanone* 1-Bromo-1,3,3-trichloropropanone *1,3-Dibromo-1,3-dichloropropanone* *1,1,3-Tribromo-3-chloropropanone* *1,1,3,3-Tetrabromopropanone*
Haloacids *Dichloroacetic acid* *Bromochloroacetic acid* *Dibromoacetic acid* *Bromodichloroacetic acid* *Tribromoacetic acid* *2,2-Dibromopropanoic acid* Dibromochloropropanoic acid[c] *3,3-Dibromopropenoic acid* Bromochloro-4-oxopentanoic acid[c] *3,3-Dibromo-4-oxopentanoic acid* Bromoheptanoic acid[c] Bromochloroheptanoic acid[c] (2 isomers) Dibromoheptanoic acid[c] Bromochlorononanoic acid[c] 2-(4-Chloro-2-methylphenoxy)-propanoic acid *cis-2-Bromo-3-methylbutenedioic acid*	Haloacetonitriles *Bromochloroacetonitrile* *Dibromoacetonitrile* Dibromochloroacetonitrile *Tribromoacetonitrile* Haloaldehydes Bromochloroacetaldehyde Dibromoacetaldehyde Bromodichloroacetaldehyde 2-Bromo-2-methylpropanal Halonitromethanes *Dichloronitromethane* Non-halogenated DBPs *Octadecanoic acid*

[a]DBPs detected by broadscreen gas chromatography/mass spectrometry (GC/MS) technique.
[b]Compounds listed in italics were confirmed through the analysis of authentic standards; haloacids and non-halogenated carboxylic acids identified as their methyl esters.
[c]Exact isomer not known

Table 13. DBP results at plant 11 (9/10/01)

09/10/2001	MRL[a]	Plant 11[b]							
Compound	µg/L	Raw	Filt Eff	Clearwell	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes									
Chloromethane	0.2	ND[c]		ND	ND	ND		ND	
Bromomethane	0.2	ND		ND	ND	ND		ND	
Bromochloromethane	0.5	ND		ND	ND	ND		ND	
Dibromomethane	0.5	ND		ND	ND	ND		ND	
Chloroform[d]	0.1	ND	1	3	2	4	4	1	1
Bromodichloromethane[d]	0.1	ND	6	16	17	21	22	16	44
Dibromochloromethane[d]	0.1	ND	10	24	24	26	27	24	16
Bromoform[d]	0.1	ND	2	6	6	8	9	5	8
THM4[e]		ND	19	49	49	59	62	46	69
Dichloroiodomethane	0.5	ND	2	1	2	0.9	0.7	ND	ND
Bromochloroiodomethane	0.5	ND	ND	0.8	0.7	ND	ND	ND	ND
Dibromoiodomethane	0.25	ND	ND	0.4	0.4	ND	ND	ND	ND
Chlorodiiodomethane	0.1	ND	ND	ND	0.3	ND	ND	ND	ND
Bromodiiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.2	ND		ND	ND	ND		ND	
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids									
Monochloroacetic acid[d]	2		ND	ND	ND	ND			
Monobromoacetic acid[d]	1		ND	1.4	1.4	1.2			
Dichloroacetic acid[d]	1		3.2	4.8	4.7	5.1			
Bromochloroacetic acid[d]	1		5.1	8.0	7.8	9.4			
Dibromoacetic acid[d]	1		8.2	9.1	9.4	8.8			
Trichloroacetic acid[d]	1		ND	2.2	2.0	2.3			
Bromodichloroacetic acid	1		3.1	8.1	7.6	7.8			
Dibromochloroacetic acid	1		3.2	7.6	7.2	7.1			
Tribromoacetic acid	2		ND	2.2	2.0	2.2			
HAA5[f]			11	18	18	17			
HAA9[g]			23	43	42	44			
DXAA[h]			17	22	22	23			
TXAA[i]			6.3	20	19	19			
Haloacetonitriles									
Chloroacetonitrile	0.1	ND	ND	0.2	ND	ND	ND	ND	ND
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	0.2	ND	ND
Dichloroacetonitrile[d]	0.1	ND	0.4	0.6	0.6	0.7	0.8	0.2	0.2
Bromochloroacetonitrile[d]	0.1	ND	0.6	1	1	1	1	2	2
Dibromoacetonitrile[d]	0.1	ND	0.6	2	2	2	2	NR[l]	NR
Trichloroacetonitrile[d]	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Bromodichloroacetonitrile	0.5	ND		ND	ND				ND
Dibromochloroacetonitrile	0.5	ND		0.6	ND				ND
Tribromoacetonitrile	0.5	ND		ND	ND				ND
Haloacetaldehydes									
Dichloroacetaldehyde	0.22	ND	0.7	1	2	0.9	0.9	0.4	0.9
Bromochloroacetaldehyde	0.5	ND	0.6	1	0.8	0.9	0.9	0.3	0.4
Chloral hydrate[d]	0.1	ND	ND	1	NR	0.9	0.8	0.2	0.3
Tribromoacetaldehyde	0.1	ND	0.2	0.8	0.4	ND	ND	ND	ND

Table 13 (continued)

09/10/2001	MRL[a]	Plant 11[b]							
Compound	µg/L	Raw	Filt Eff	Clearwell	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloketones									
Chloropropanone	0.1	ND	0.1	ND	0.1	ND	0.1	ND	ND
1,1-Dichloropropanone[d]	0.10	ND	0.4	0.2	0.3	0.2	0.3	0.1	0.1
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	0.1	ND	0.4	0.2	0.2	0.2	0.2	ND	ND
1,1,1-Trichloropropanone[d]	0.1	ND	0.3	0.5	0.5	0.3	0.2	ND	ND
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	0.1	ND	0.2	0.4	0.4	ND	ND	ND	ND
1,1,1-Tribromopropanone	2.5	ND	NR	ND	ND	ND	NR	ND	NR
1,1,3-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrachloropropanone	0.1	ND	0.6	0.3	0.1	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	0.10	ND	ND	0.5	0.1	ND	ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.5	ND	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes									
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Bromochloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Dibromonitromethane	0.10	ND	ND	0.2	0.2	0.1	ND	ND	ND
Chloropicrin[d]	0.1	ND	ND	ND	ND	ND	0.1	ND	ND
Bromodichloronitromethane	0.5	ND		ND	ND				0.6
Dibromochloronitromethane	0.5	ND		ND	ND				0.5
Bromopicrin	0.5	ND		ND	ND				ND
Miscellaneous Compounds									
Methyl ethyl ketone	0.5	0.6		ND	ND	0.6		0.7	
Methyl *tertiary* butyl ether	0.2	ND		ND	ND	ND		ND	
Benzyl chloride	0.25	ND	NR	ND	ND	ND	NR	ND	NR
1,1,2,2-Tetrabromo-2-chloroethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND

Table 14. DBP results at plant 12 (9/10/01)

09/10/2001	MRL[a]	Plant 12[k]						
Compound	µg/L	Raw	Pre-Treat	Filt Inf	Filt Eff	Plant Eff	DS/Ave	DS/Max
Halomethanes								
Chloromethane	0.2	ND[c]		ND		ND	ND	
Bromomethane	0.2	ND		ND		ND	ND	
Bromochloromethane	0.5	ND		ND		ND	ND	
Dibromomethane	0.5	ND		ND		ND	ND	
Chloroform[d]	0.1	ND	0.4	9	14	14	17	19
Bromodichloromethane[d]	0.2	ND	NR[l]	9	NR	13	15	NR
Dibromochloromethane[d]	0.25	ND	NR	4	NR	6	7	NR
Bromoform[d]	0.5	ND	ND	1	NR	1	2	NR
THM4[e]		ND	NR	23	NR	34	41	NR
Dichloroiodomethane	0.5	ND	NR	6	NR	7	10	NR
Bromochloroiodomethane	0.5	ND	ND	1	2	2	2	2
Dibromoiodomethane	0.52	ND	ND	0.6	0.8	1	1	ND
Chlorodiiodomethane	0.25	ND	NR	0.4	NR	0.5	2	NR
Bromodiiodomethane	0.25	ND	ND	ND	ND	0.3	0.6	ND
Iodoform	0.25	ND	NR	ND	NR	ND	0.3	NR
Carbon tetrachloride	0.2	ND		ND		ND	ND	
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids								
Monochloroacetic acid[d]	2		ND	2.8	2.8	3.0	2.1	
Monobromoacetic acid[d]	1		ND	1.0	1.2	1.3	ND	
Dichloroacetic acid[d]	1		ND	26	26	29	26	
Bromochloroacetic acid[d]	1		ND	15	16	19	14	
Dibromoacetic acid[d]	1		ND	4.8	4.9	6.7	5.9	
Trichloroacetic acid[d]	1		ND	8.0	9.8	11	9.0	
Bromodichloroacetic acid	1		ND	4.9	5.9	6.9	5.6	
Dibromochloroacetic acid	1		ND	1.1	1.3	1.8	1.3	
Tribromoacetic acid	2		ND	ND	ND	ND	ND	
HAA5[f]			ND	43	45	51	43	
HAA9[g]			ND	64	68	79	64	
DXAA[h]			ND	46	47	55	46	
TXAA[i]			ND	14	17	20	16	
Haloacetonitriles								
Chloroacetonitrile	0.1	ND	ND	ND	0.1	0.1	0.1	ND
Bromoacetonitrile	0.1	ND	ND	ND	0.2	ND	ND	ND
Dichloroacetonitrile[d]	0.1	ND	ND	1	2	3	2	3
Bromochloroacetonitrile[d]	0.1	ND	ND	0.6	0.9	1	1	1
Dibromoacetonitrile[d]	0.1	ND	ND	0.2	0.4	0.6	0.9	1
Trichloroacetonitrile[d]	0.1	ND	ND	ND	ND	ND	ND	ND
Bromodichloroacetonitrile	0.5	ND		ND		ND		
Dibromochloroacetonitrile	0.5	ND		ND		ND		
Tribromoacetonitrile	0.5	ND		ND		ND		
Haloacetaldehydes								
Dichloroacetaldehyde	0.22	1	0.7	3	5	4	6	6
Bromochloroacetaldehyde	0.5	ND	ND	1	2	2	1	1
Chloral hydrate[d]	0.1	0.5	ND	2	2	2	2	2
Tribromoacetaldehyde	0.1	0.7	0.1	0.7	0.9	0.3	0.1	ND

Table 14 (continued)

09/10/2001	MRL[a]	Plant 12[k]						
Compound	µg/L	Raw	Pre-Treat	Filt Inf	Filt Eff	Plant Eff	DS/Ave	DS/Max
Haloketones								
Chloropropanone	0.1	ND	ND	0.1	0.1	0.1	0.2	0.3
1,1-Dichloropropanone[d]	0.10	ND	0.1	0.8	1	1	0.8	0.9
1,3-Dichloropropanone	0.1	ND	ND	0.2	ND	ND	ND	ND
1,1-Dibromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloropropanone[d]	0.1	ND	ND	0.1	0.3	0.4	ND	ND
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1,1-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1,3-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrachloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	0.10	ND	0.2	0.5	0.5	0.5	0.4	0.3
1,1,3,3-Tetrabromopropanone	2	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes								
Bromonitromethane	0.1	ND	ND	ND	0.4	ND	ND	ND
Dichloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND
Bromochloronitromethane	0.1	ND	ND	ND	ND	0.2	ND	ND
Dibromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[d]	0.1	ND	ND	0.4	0.6	0.9	1	2
Bromodichloronitromethane	0.5	ND		1		2		
Dibromochloronitromethane	0.5	ND		2		2		
Bromopicrin	0.5	ND		2		ND		
Miscellaneous Compounds								
Methyl ethyl ketone	0.5	ND		0.6		ND	0.6	
Methyl *tertiary* butyl ether	0.2	ND		ND		ND	ND	
Benzyl chloride	0.25	ND	NR	ND	NR	ND	ND	NR
1,1,2,2-Tetrabromo-2-chloroethane	0.5	ND	NR	ND	NR	ND	ND	NR

Table 15. Additional target DBP results (µg/L) at plant 11 (9/10/01)

9/10/01	Plant 11[a]						
Compound	Raw	FI	CWI	CWE	PE	DS	SDS
Monochloroacetaldehyde	0	0	0.2	0	0	0	0
Dichloroacetaldehyde	0	0	1.4	1.2	3.2	2.8	3.5
Bromochloroacetaldehyde	0	0	1.0	1.5	2.8	2.6	1.8
3,3-Dichloropropenoic acid	0	0	0.8	0.9	0.7	0.6	0.6
Bromochloromethylacetate	0	0	0	0	0	0	0
2,2-Dichloroacetamide	0	0	0	2.5	2.8	2.7	2.4
TOX (µg/L as Cl^-)	33.5	48.1	299	129	126	118	121
Cyanoformaldehyde	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
5-Keto-1-hexanal	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6-Hydroxy-2-hexanone	<0.1	0.8	<0.1	<0.1	<0.1	<0.1	<0.1
Dimethylglyoxal	<0.1	<0.1	1.1	1.5	1.2	0.8	1.5
trans-2-Hexenal	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

[a]Plant 11 sampled at (1) raw water, (2) filter influent (FI), (3) clearwell influent (CWI), (4) clearwell effluent (CWE), (5) finished water at plant effluent (PE), (6) distribution system (DS) at average detention time, and (6) SDS at maximum detection time.

Table 16. Additional target DBP results (µg/L) at plant 12 (9/10/01)

9/10/01	Plant 12[b]						
Compound	Raw	PT	FI	FE	PE	DS	SDS
Monochloroacetaldehyde	0	0.3			1.2		1.8
Dichloroacetaldehyde	0	0.4	4.2	6.2	5.8	6.5	6.8
Bromochloroacetaldehyde	0	2.1	2.4	3.1	3.0	2.5	2.1
3,3-Dichloropropenoic acid	0	0	0.5	0	0	0	0
Bromochloromethylacetate	0	0	0	0	0	0	0
2,2-Dichloroacetamide	0	0	4.5	4.4	5.6	5.1	5.5
TOX (µg/L as Cl^-)	6.6	35.0	196	223	260	245	165
Cyanoformaldehyde	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
5-Keto-1-hexanal	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6-Hydroxy-2-hexanone	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Dimethylglyoxal	<0.1	<0.1	2.4	3.1	2.5	2.0	2.9
Trans-2-Hexenal	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

[b]Plant 12 sampled at (1) raw water, (2) pre-treated water (PT), (3) filter influent (FI), (4) filter effluent (FE), (5) finished water at plant effluent (PE), (6) distribution system (DS) at average detention time, and (7) SDS at maximum detection time.

Table 17. Halogenated furanone results (µg/L) at plant 11 (9/10/01)

Compound	FI	FE	CWE	PE	DS/ave	SDS/max
BMX-1	<0.02	0.05	0.12	0.17	0.14	0.21
BEMX-1	0.02	<0.02	<0.02 (0.01)	<0.02	<0.02 (0.01)	<0.02
BMX-2	<0.02	<0.02 (0.011)	<0.02 (0.011)	<0.02 (0.016)	<0.02 (0.015)	<0.02 (0.013)
BEMX-2	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
BMX-3	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
BEMX-3	<0.02	0.37	0.31	0.20	<0.02	0.49
MX	<0.02	<0.02	0.02	0.02	0.85	NA
EMX	<0.02	<0.02	<0.02	<0.02	<0.02	NA
ZMX	<0.02	<0.02	0.09	<0.02	<0.02	NA
Mucochloric acid (ring)	<0.02	<0.02	<0.02	<0.02	<0.02	NA
Mucochloric acid (open)	<0.02	<0.02	<0.02	<0.02	<0.02	NA

Table 18. Halogenated furanone results (µg/L) at plant 12 (9/10/01)

Compound	Raw	PT	FI	FE	PE	DS/ave	SDS/max
BMX-1	<0.02	<0.02	<0.02	<0.02	0.09	0.08	0.03
BEMX-1	0.03	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
BMX-2	<0.02	<0.02	<0.02	<0.02	0.03	0.02	<0.02 (0.017)
BEMX-2	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
BMX-3	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
BEMX-3	<0.02	<0.02	<0.02	<0.02	<0.02	0.04	<0.02
MX	<0.02	<0.02	<0.02	0.08	<0.02 (0.014)	NA	NA
EMX	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA
ZMX	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA
Mucochloric acid (ring)	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA
Mucochloric acid (open)	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA

Table 19. DBP results at plant 11 (11/5/01)

11/05/2001	MRL[a]	Plant 11[m]							
Compound	µg/L	Raw	Filt Inf	Clearwell	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes									
Chloromethane	0.2	ND[c]		ND	ND	ND		ND	
Bromomethane	0.2	ND		ND	ND	ND		ND	
Bromochloromethane	0.5	ND		ND	ND	ND		ND	
Dibromomethane	0.5	ND		ND	ND	ND		ND	
Chloroform[d]	0.5	ND	ND	ND	5	7	8	8	9
Bromodichloromethane[d]	0.1	ND	0.1	0.4	14	17	17	18	20
Dibromochloromethane[d]	0.1	ND	ND	0.3	15	16	18	18	19
Bromoform[d]	0.11	ND	ND	ND	3	3	4	3	3
THM4[e]		ND	0.1	0.7	37	43	47	47	51
Dichloroiodomethane	0.5	ND	ND	ND	1	2	NR[l]	2	NR
Bromochloroiodomethane	0.25	ND		ND	0.4	0.3		0.4	
Dibromoiodomethane	0.52	ND	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.5	ND	NR	ND	ND	ND	NR	ND	NR
Bromodiiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND
Iodoform	2	ND	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.2	ND		ND	ND	ND		ND	
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids									
Monochloroacetic acid[d]	2		ND	ND	ND	ND		ND	
Monobromoacetic acid[d]	1		ND	ND	1.1	1.1		1.1	
Dichloroacetic acid[d]	1		ND	ND	8.8	11		11	
Bromochloroacetic acid[d]	1		ND	ND	10	11		11	
Dibromoacetic acid[d]	1		ND	ND	7.9	8.0		8.0	
Trichloroacetic acid[d]	1		ND	ND	4.7	5.3		4.5	
Bromodichloroacetic acid	1		ND	ND	9.6	11		10	
Dibromochloroacetic acid	1		ND	ND	6.2	6.9		5.9	
Tribromoacetic acid	2		ND	ND	ND	ND		ND	
HAA5[f]			ND	ND	23	25		25	
HAA9[g]			ND	ND	48	54		52	
DXAA[h]			ND	ND	27	30		30	
TXAA[i]			ND	ND	21	23		20	
Haloacetonitriles									
Chloroacetonitrile	0.1	ND	ND	ND	ND	0.3	ND	0.4	ND
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[d]	0.10	ND	ND	ND	1	1	2	2	2
Bromochloroacetonitrile[d]	0.1	ND	ND	ND	NR	NR	2	2	2
Dibromoacetonitrile[d]	0.14	ND	ND	ND	2	2	1	2	2
Trichloroacetonitrile[d]	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Bromodichloroacetonitrile	0.5	ND		ND	ND				ND
Dibromochloroacetonitrile	0.5	ND		ND	0.6				0.5
Tribromoacetonitrile	0.90	ND		ND	ND				ND
Haloacetaldehydes									
Dichloroacetaldehyde	1.1	ND	ND	ND	1	2	3	3	3
Bromochloroacetaldehyde	0.5	ND	ND	ND	1	1	1	1	1
Chloral hydrate[d]	0.1	ND	ND	0.1	1	1	1	2	2
Tribromoacetaldehyde	0.5	ND	ND	ND	<0.5[n]	ND	ND	ND	ND

Table 19 (continued)

11/05/2001	MRL[a]	Plant 11[m]							
Compound	µg/L	Raw	Filt Inf	Clearwell	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloketones									
Chloropropanone	0.1	ND	ND	ND	0.2	0.1	0.3	ND	ND
1,1-Dichloropropanone[d]	0.10	ND	0.2	0.1	0.5	0.6	0.7	0.8	0.8
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloropropanone[d]	0.1	ND	ND	ND	0.8	0.7	0.7	0.5	0.4
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	1.0	ND	NR	ND	ND	ND	NR	ND	ND
1,1,1-Tribromopropanone	0.29	ND	ND	ND	ND	ND	ND	ND	NR
1,1,3-Tribromopropanone	0.14	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.5	ND	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes									
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	0.1	ND	ND	ND	0.2	0.3	0.3	0.4	0.4
Bromochloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Dibromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[d]	0.1	ND	ND	ND	0.1	0.2	0.5	1	1
Bromodichloronitromethane	0.5	ND		ND	0.7				1
Dibromochloronitromethane	2	ND		ND	ND				ND
Bromopicrin	2	ND		ND	ND				ND
Miscellaneous Compounds									
Methyl ethyl ketone	0.5	2		ND	0.8	0.7		0.9	
Methyl *tertiary* butyl ether	0.2	ND		ND	ND	ND		ND	
Benzyl chloride	0.5	ND	ND	ND	ND	ND	ND	ND	ND
1,1,2,2-Tetrabromo-2-chloroethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND

[m] Plant 11 sampled at (1) raw water, (2) filter influent, (3) clearwell influent, (4) plant effluent, DS at (5) average and (6) maximum detention times, and SDS testing of plant effluent at (7) average and (8) maximum detention times

[n] <0.5: Concentration less than MRL (i.e., 0.5 µg/L)

Table 20. DBP results at plant 12 (11/15/01)

11/15/2001	MRL[a]	Plant 12[k]								
Compound	µg/L	Raw	Pre-Treat	Filt Inf	Filt Eff	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes										
Chloromethane	0.2	ND[c]		ND		ND	ND		ND	
Bromomethane	0.2	ND		ND		ND	ND		ND	
Bromochloromethane	0.5	ND		ND		ND	ND		ND	
Dibromomethane	0.5	ND		ND		ND	ND		ND	
Chloroform[d]	0.1	ND	0.3	7	5	5	11	13	11	11
Bromodichloromethane[d]	0.1	ND	0.3	11	8	10	21	25	20	19
Dibromochloromethane[d]	0.1	ND	ND	6	5	6	15	18	14	14
Bromoform[d]	0.11	ND	ND	2	1	2	9	9	7	8
THM4[e]		ND	0.6	26	19	23	56	65	52	52
Dichloroiodomethane	0.5	ND	NR[l]	11	NR	11	15	NR	14	NR
Bromochloroiodomethane	0.25	ND		3	2	3	5	4	4	3
Dibromoiodomethane	0.52	ND	ND	1	NR	2	3	3	3	NR
Chlorodiiodomethane	0.5	ND	NR	0.6	NR	2	1	NR	1	NR
Bromodiiodomethane	0.5	ND	ND	ND	ND	0.7	0.7	0.7	ND	ND
Iodoform	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.2	ND		ND		ND	ND		ND	
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids										
Monochloroacetic acid[d]	2		ND	3.7	3.3	5.5	2.1		2.8	
Monobromoacetic acid[d]	1		ND	ND	ND	ND	1.0		2.7	
Dichloroacetic acid[d]	1		1.1	19	18	22	17		27	
Bromochloroacetic acid[d]	1		ND	21	21	18	18		21	
Dibromoacetic acid[d]	1		ND	8.6	8.6	11	8.2		15	
Trichloroacetic acid[d]	1		ND	4.5	4.2	5.7	7.2		7.1	
Bromodichloroacetic acid	1		ND	3.8	3.9	5.7	5.4		6.7	
Dibromochloroacetic acid	1		ND	1.8	1.7	2.8	2.2		2.8	
Tribromoacetic acid	2		ND	ND	ND	ND	ND		ND	
HAA5[f]			1.1	36	34	44	36		55	
HAA9[g]			1.1	62	61	71	61		85	
DXAA[h]			1.1	49	48	51	43		63	
TXAA[i]			ND	10	10	14	15		17	
Haloacetonitriles										
Chloroacetonitrile	0.1	ND	ND	ND	ND	0.4	ND	ND	ND	ND
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[d]	0.10	ND	ND	1	0.7	2	2	2	2	2
Bromochloroacetonitrile[d]	0.1	ND	ND	0.7	0.4	1	3	2	3	2
Dibromoacetonitrile[d]	0.14	ND	ND	0.5	0.2	0.9	2	0.9	2	1
Trichloroacetonitrile[d]	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodichloroacetonitrile	0.5	ND		ND		ND				ND
Dibromochloroacetonitrile	0.5	ND		ND		ND				ND
Tribromoacetonitrile	0.90	ND		ND		ND				ND
Haloacetaldehydes										
Dichloroacetaldehyde	0.22	ND	ND	3	2	3	4	4	5	5
Bromochloroacetaldehyde	0.5	ND	ND	1	0.5	2	4	4	3	4
Chloral hydrate[d]	0.1	ND	0.2	1	1	1	2	2	1	2
Tribromoacetaldehyde	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table 20 (continued)

11/15/2001	MRL[a]	Plant 12[k]								
Compound	µg/L	Raw	Pre-Treat	Filt Inf	Filt Eff	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloketones										
Chloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	0.6	ND
1,1-Dichloropropanone[d]	0.10	ND	0.2	0.7	0.8	0.8	0.8	0.8	0.9	0.7
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	0.10	ND	ND	ND	ND	ND	0.1	0.1	ND	ND
1,1,1-Trichloropropanone[d]	0.1	ND	ND	0.2	ND	0.3	0.4	0.3	0.1	0.1
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1-Tribromopropanone	2.5	ND	NR	ND	NR	ND	ND	NR	ND	NR
1,1,3-Tribromopropanone	0.14	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	0.10	ND	ND	0.1	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes										
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	0.1	ND	ND	0.3	0.3	0.4	0.6	0.9	ND	0.4
Bromochloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[d]	0.1	ND	ND	0.3	0.2	0.7	1	0.9	2	1
Bromodichloronitromethane	0.5	ND		1		1				ND
Dibromochloronitromethane	0.5	ND		2		1				1
Bromopicrin	0.5	ND		2		2				0.7
Miscellaneous Compounds										
Methyl ethyl ketone	0.5	1		ND		0.7	0.8		1	
Methyl *tertiary* butyl ether	0.2	ND		ND		ND	ND		0.3	
Benzyl chloride	0.5	ND	ND	ND	ND	ND	ND	ND	ND	NR
1,1,2,2-Tetrabromo-2-chloroethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table 21. Occurrence of other DBPs[a] at plant 12: plant effluent (11/15/01)

Halomethanes
Bromodichloromethane[b]
Dibromochloromethane
Bromoform
Dichloroiodomethane
Bromochloroiodomethane
Dibromoiodomethane
Chlorodiiodomethane
Bromodiiodomethane
Haloacids
Iodoacetic acid
Dichloroacetic acid
Bromochloroacetic acid
Dibromoacetic acid
Iodobromoacetic acid
Tribromoacetic acid
3,3-Dichloropropenoic acid
3,3-Dibromopropenoic acid
Iodobromopropenoic acid[c] (2 isomers)
cis-2-Bromo-butenedioic acid
2-Iodo-3-methylbutenedioic acid
Haloacetonitriles
Bromochloroacetonitrile
Dibromoacetonitrile
Haloaldehydes
2-Bromo-2-methylpropanal

Haloketones
1,1-Dibromo-3,3-dichloropropanone
1,3-Dibromo-1,3-dichloropropanone
1,1,3-Tribromo-3-chloropropanone
1,1,3,3-Tetrabromopropanone
Pentachloropropanone
Miscellaneous Halogenated DBPs
Dibromoaniline
Dibromodichloroaniline
Tribromochloroaniline
Non-halogenated DBPs
Acetone
Glyoxal
Hexanoic acid
Heptanoic acid
Octanoic acid
Nonanoic acid
Decanoic acid
Dodecanoic acid
Tetradecanoic acid
Hexanedioic acid
Decanedioic acid
Undecanedioic acid

[a]DBPs detected by broadscreen gas chromatography/mass spectrometry (GC/MS) technique.
[b]Compounds listed in italics were confirmed through the analysis of authentic standards; haloacids and non-halogenated carboxylic acids identified as their methyl esters.
[c]Exact isomer not known

Table 22. DBP results at plant 11 (2/11/02)

02/11/2002	MRL[a]	Plant 11[m]							
Compound	µg/L	Raw	Filt Inf	Clearwell	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes									
Chloromethane	0.2	ND[c]		ND	ND	ND		ND	
Bromomethane	0.2	ND		ND	ND	ND		ND	
Bromochloromethane	0.5	ND		ND	ND	ND		ND	
Dibromomethane	0.5	ND		ND	ND	ND		ND	
Chloroform[d]	0.2	ND	NR[l]	4	5	7	NR	6	NR
Bromodichloromethane[d]	0.5	ND	NR	4	9	10	NR	11	NR
Dibromochloromethane[d]	0.25	ND	NR	5	10	11	NR	12	NR
Bromoform[d]	0.5	ND	NR	2	4	4	NR	4	NR
THM4[e]		ND	NR	15	28	32	NR	33	NR
Dichloroiodomethane	1.0	ND	NR	<1[o]	<1	<1	NR	<1	NR
Bromochloroiodomethane	0.5	ND	ND	<0.5[n]	<0.5	<0.5	ND	0.7	ND
Dibromoiodomethane	0.53	ND	ND	ND	ND	0.6	ND	ND	ND
Chlorodiiodomethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.52	ND	ND	ND	ND	ND	ND	ND	ND
Iodoform	2.2	ND	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.2	ND		ND	ND	ND		ND	
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids									
Monochloroacetic acid[d]	2		ND	3.0	2.8	2.8		3.2	
Monobromoacetic acid[d]	1		ND	1.0	1.4	1.5		1.6	
Dichloroacetic acid[d]	1		4.8	6.6	6.7	9.2		8.0	
Bromochloroacetic acid[d]	1		ND	5.0	6.3	6.3		6.2	
Dibromoacetic acid[d]	1		ND	5.7	6.1	5.5		5.3	
Trichloroacetic acid[d]	1		2.0	3.4	4.4	4.7		4.0	
Bromodichloroacetic acid	1		ND	6.6	9.0	8.8		8.6	
Dibromochloroacetic acid	1		ND	6.2	9.1	8.7		8.5	
Tribromoacetic acid	2		ND	ND	ND	4.6		ND	
HAA5[f]			6.8	20	21	24		22	
HAA9[g]			6.8	38	46	52		45	
DXAA[h]			4.8	17	19	21		20	
TXAA[i]			2.0	16	23	27		21	
Haloacetonitriles									
Chloroacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[d]	2.5	ND	NR	<1	<1	<1	NR	<1	NR
Bromochloroacetonitrile[d]	0.5	ND	ND	0.5	2	2	NR	2	NR
Dibromoacetonitrile[d]	1.0	ND	ND	<1	2	2	NR	2	NR
Trichloroacetonitrile[d]	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Bromodichloroacetonitrile	0.5	ND		ND	ND				ND
Dibromochloroacetonitrile	0.5	ND		ND	ND				ND
Tribromoacetonitrile	0.90	ND		ND	ND				ND
Haloacetaldehydes									
Dichloroacetaldehyde	0.98	ND	ND	ND	ND	ND	ND	ND	ND
Bromochloroacetaldehyde	0.5	ND	ND	ND	0.6	0.7	0.7	0.8	0.8
Chloral hydrate[d]	0.1	0.5	0.2	0.2	0.3	0.3	0.3	0.5	0.4
Tribromoacetaldehyde	0.1	ND	ND	ND	ND	ND	ND	ND	ND

Table 22 (continued)

02/11/2002	MRL[a]	Plant 11[m]							
Compound	µg/L	Raw	Filt Inf	Clearwell	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloketones									
Chloropropanone	0.1	ND	0.1	1	1	1	0.5	1	1
1,1-Dichloropropanone[d]	1.0	ND	1	1	<1	<1	<1	<1	<1
1,3-Dichloropropanone	0.1	0.2	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	0.1	ND	ND	0.4	0.3	0.4	0.2	0.2	0.2
1,1,1-Trichloropropanone[d]	0.5	ND	<0.5	0.9	0.8	0.8	0.9	0.7	0.9
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	0.1	ND	ND	0.2	0.4	ND	ND	0.1	ND
1,1,1-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.5	ND	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes									
Chloronitromethane	NA	ND		ND	ND	ND		ND	
Bromonitromethane	0.1	ND	ND	ND	ND	0.1	ND	ND	ND
Dichloronitromethane	0.10	ND	ND	ND	ND	ND	ND	ND	ND
Bromochloronitromethane	0.1	ND	ND	0.1	0.1	0.1	0.2	0.2	0.2
Dibromonitromethane	0.10	ND	ND	ND	ND	0.1	ND	0.1	ND
Chloropicrin[d]	0.1	ND	ND	0.3	0.4	0.2	0.4	0.4	0.7
Bromodichloronitromethane	2	ND		ND	ND				ND
Dibromochloronitromethane	2	ND		ND	ND				ND
Bromopicrin	0.5	ND		ND	1				ND
Miscellaneous Compounds									
Methyl ethyl ketone	0.5	ND		ND	ND	ND		ND	
Methyl *tertiary* butyl ether	0.2	ND		ND	ND	ND		ND	
Benzyl chloride	0.5	ND	NR	ND	ND	ND	NR	ND	NR
1,1,2,2-Tetrabromo-2-chloroethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND

[o]<1.0: Concentration less than MRL (e.g., 1.0 µg/L)

Table 23. DBP results at plant 12 (2/12/02)

02/12/2002	MRL[a]	Plant 12[k]								
Compound	µg/L	Raw	Pre-Treat	Filt Inf	Filt Eff	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes										
Chloromethane	0.2		ND[c]	ND		ND	ND		ND	
Bromomethane	0.2		ND	ND		ND	ND		ND	
Bromochloromethane	0.5		ND	ND		ND	ND		ND	
Dibromomethane	0.5		ND	ND		ND	ND		ND	
Chloroform[d]	0.2	ND	0.4	3	NR[l]	3	3	NR	3	NR
Bromodichloromethane[d]	0.5	ND	0.8	12	NR	14	15	NR	12	NR
Dibromochloromethane[d]	0.25	ND	1	19	NR	21	23	NR	19	NR
Bromoform[d]	0.5	ND	0.5	17	NR	19	19	NR	16	NR
THM4[e]		ND	3	51	NR	57	60	NR	50	NR
Dichloroiodomethane	1.0	ND	NR	<1[o]	NR	<1	<1	NR	<1	NR
Bromochloroiodomethane	0.5	ND	ND	2	NR	2	3	NR	2	NR
Dibromoiodomethane	0.53	ND	ND	3	NR	4	4	NR	3	NR
Chlorodiiodomethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.52	ND	ND	ND	ND	<0.5[n]	<0.5	<0.5	ND	ND
Iodoform	2.2	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.2		ND	ND		ND	ND		ND	
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids										
Monochloroacetic acid[d]	2		3.9	3.2	3.2	3.0	2.1		2.6	
Monobromoacetic acid[d]	1		1.3	2.2	2.2	2.1	2.5		2.0	
Dichloroacetic acid[d]	1		7.8	11	11	10	18		9.6	
Bromochloroacetic acid[d]	1		6.9	14	13	14	22		14	
Dibromoacetic acid[d]	1		6.6	16	14	18	22		16	
Trichloroacetic acid[d]	1		ND	2.4	2.2	3.1	3.8		2.7	
Bromodichloroacetic acid	1		4.7	6.5	8.0	9.0	9.7		9.1	
Dibromochloroacetic acid	1		1.2	6.3	5.9	8.1	8.8		7.5	
Tribromoacetic acid	2		ND	ND	ND	ND	ND		ND	
HAA5[f]			20	35	33	36	48		33	
HAA9[g]			32	62	60	67	89		64	
DXAA[h]			21	41	38	42	62		40	
TXAA[i]			5.9	15	16	20	22		19	
Haloacetonitriles										
Chloroacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[d]	2.5	ND	ND	<1	NR	<1	<1	NR	<1	<1
Bromochloroacetonitrile[d]	0.5	ND	NR	1	NR	2	2	NR	2	NR
Dibromoacetonitrile[d]	1.0	ND	NR	1	NR	2	2	NR	2	NR
Trichloroacetonitrile[d]	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodichloroacetonitrile	0.5		ND	ND		ND				ND
Dibromochloroacetonitrile	0.5		ND	ND		ND				ND
Tribromoacetonitrile	0.90		ND	ND		ND				ND
Haloacetaldehydes										
Dichloroacetaldehyde	0.98	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromochloroacetaldehyde	0.5	ND	ND	2	2	2	2	2	2	2
Chloral hydrate[d]	0.1	0.6	ND	0.7	0.5	0.7	0.9	1	0.8	0.7
Tribromoacetaldehyde	0.1	ND	ND	2	1	2	1	0.6	2	2

Table 23 (continued)

02/12/2002	MRL[a]	Plant 12[k]								
Compound	µg/L	Raw	Pre-Treat	Filt Inf	Filt Eff	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloketones										
Chloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloropropanone[d]	1.0	ND	<1	<1	<1	<1	<1	<1	<1	<1
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	0.1	ND	0.3	0.4	0.3	0.4	0.2	0.2	0.4	0.4
1,1,1-Trichloropropanone[d]	0.5	ND	<0.5	0.6	<0.5	0.6	<0.5	<0.5	0.6	0.6
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	0.1	ND	ND	0.5	0.1	0.5	0.1	ND	0.6	0.2
1,1,1-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes										
Chloronitromethane	NA		ND	ND		ND	ND		ND	
Bromonitromethane	0.1	ND	ND	ND	0.1	0.2	ND	ND	ND	ND
Dichloronitromethane	0.10	ND	ND	0.3	0.2	0.3	0.3	0.3	0.2	0.2
Bromochloronitromethane	0.1	ND	0.2	0.7	0.7	0.7	0.9	0.9	0.8	0.8
Dibromonitromethane	0.10	ND	ND	0.5	0.4	0.5	0.4	0.4	0.5	0.6
Chloropicrin[d]	0.1	ND	ND	0.4	0.4	0.4	0.7	1	0.4	0.4
Bromodichloronitromethane	2		ND	ND		ND				ND
Dibromochloronitromethane	2		ND	3		3				3
Bromopicrin	0.5		ND	4		5				5
Miscellaneous Compounds										
Methyl ethyl ketone	0.5		ND	ND		ND	ND		ND	
Methyl *tertiary* butyl ether	0.2		ND	ND		ND	ND		ND	
Benzyl chloride	1.0	ND	NR	ND	NR	ND	ND	NR	ND	NR
1,1,2,2-Tetrabromo-2-chloroethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table 24. Additional target DBP results (µg/L) at plant 11 (2/11/02)

2/11/02	Plant 11[c]		
Compound	FI	PE	DS
Monochloroacetaldehyde	0	0.2	1.6
Dichloroacetaldehyde	0	1.8	6.7
Bromochloroacetaldehyde	0	2.0	3.1
3,3-Dichloropropenoic acid	0	0	0
Bromochloromethylacetate	0	0	0
Monochloroacetamide	0	0.4	0.6
Monobromoacetamide	0	0.8	1.0
2,2-Dichloroacetamide	0	1.4	1.0
Dibromoacetamide	0	1.8	1.5
Trichloroacetamide	0	1.1	0.8
TOX (µg/L as Cl^-)	57.0	151	139
TOBr (µg/L as Br^-)	59.3	79.0	83.0
TOCl (µg/L as Cl^-)	14.6	105	102
Cyanoformaldehyde	<0.1	<0.1	<0.1
5-Keto-1-hexanal	<0.1	<0.1	<0.1
6-Hydroxy-2-hexanone	<0.1	<0.1	<0.1
Dimethylglyoxal	<0.1	1.4	1.1
trans-2-Hexenal	<0.1	<0.1	<0.1

[c]Plant 11 sampled at (1) FI, (2) PE, and (3) DS at maximum detention time.

Table 25. Additional target DBP results (µg/L) at plant 12 (2/12/02)

2/12/02	Plant 12[d]			
Compound	FI	FE	PE	DS
Monochloroacetaldehyde	0.5	0.5	0.1	0.4
Dichloroacetaldehyde	2.1	2.1	1.3	2.4
Bromochloroacetaldehyde	2.1	2.1	4.0	4.0
3,3-Dichloropropenoic acid	0		0	0
Bromochloromethylacetate	0		0	0
Monochloroacetamide	1.0		0.5	0.8
Monobromoacetamide	1.5		1.1	1.0
2,2-Dichloroacetamide	2.4		2.0	1.5
Dibromoacetamide	2.5		2.8	2.2
Trichloroacetamide	0.9		1.0	1.1
TOX (µg/L as Cl^-)	236		211	212
TOBr (µg/L as Br^-)	250		229	212
TOCl (µg/L as Cl^-)	108		145	139
Cyanoformaldehyde	<0.1		<0.1	<0.1
5-Keto-1-hexanal	<0.1		<0.1	<0.1
6-Hydroxy-2-hexanone	<0.1		<0.1	<0.1
Dimethylglyoxal	3.2		1.5	1.9
trans-2-Hexenal	<0.1		<0.1	<0.1

[d]Plant 12 sampled at (1) FI, (2) FE, (3) PE, and (4) DS at maximum detention time.

Table 26. Halogenated furanone results (µg/L) at plant 11 (2/11/02)

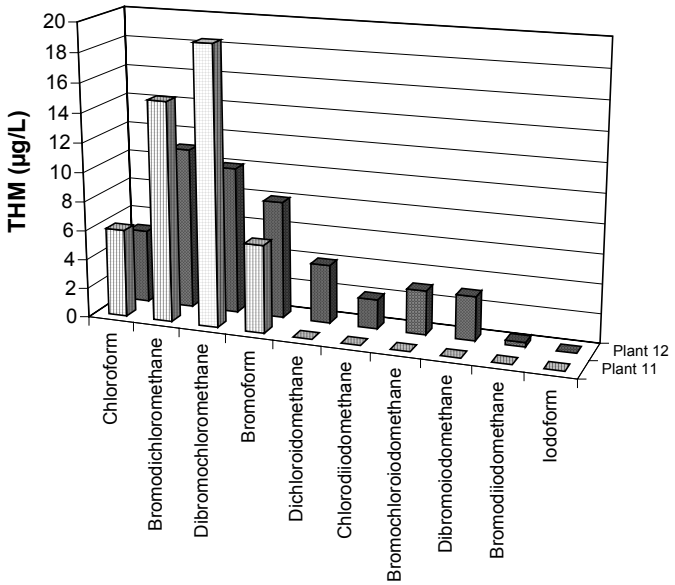
Compound	FI	PE	DS/max
BMX-1	<0.02	0.08	<0.02
BEMX-1	<0.02	<0.02	<0.02
BMX-2	<0.02	<0.02	<0.02
BEMX-2	<0.02	<0.02	<0.02
BMX-3	<0.02	<0.02	<0.02
BEMX-3	<0.02	<0.02	<0.02
MX	<0.02	<0.02	0.03
EMX	<0.02	<0.02	<0.02
ZMX	<0.02	<0.02	<0.02
Ox-MX	<0.02	<0.02	<0.02
Mucochloric acid (*ring*)	0.02	0.04	0.06
Mucochloric acid (*open*)	<0.02 (0.01)	0.02	0.02

Table 27. Halogenated furanone results (µg/L) at plant 12 (2/12/02)

Compound	FI	PE	DS/max
BMX-1	<0.02	0.06	<0.02
BEMX-1	<0.02	<0.02	<0.02
BMX-2	<0.02	<0.02	<0.02
BEMX-2	<0.02	<0.02	<0.02
BMX-3	<0.02	<0.02	<0.02
BEMX-3	<0.02	<0.02	<0.02
MX	<0.02 (0.01)	0.03	<0.02 (0.01)
EMX	<0.02	<0.02	<0.02
ZMX	<0.02	<0.02	<0.02
Ox-MX	<0.02	<0.02	<0.02
Mucochloric acid (*ring*)	0.13	0.08	0.06
Mucochloric acid (*open*)	<0.02	<0.02	<0.02

Figure 6. March 26, 2001

Effect of Bromide and Iodide and Disinfection Scheme on THM Speciation in Plant Effluents at Plant 11 (Chlorine Dioxide/ Chlorine/Chloramines) and Plant 12 (Chloramines Only)



Halomethanes. Chlorine dioxide/chlorine/chloramine disinfection at plant 11 resulted in the formation of 28-49 µg/L of the four regulated trihalomethanes (THM4) in the plant effluent in March 2001, September 2001, November 2001, and February 2002. Chloramine disinfection at plant 12 resulted in the formation of 23-57 µg/L of THM4 in the plant effluent in March 2001, September 2001, November 2001, and February 2002. Even with chloramines only, a fair amount of THMs was formed at plant 12. Because of the relatively high amount of TOC and/or bromide in these EPA Region 6 waters, THM formation potentials were probably high; thus, alternative disinfectants were used to minimize THM formation.

In March 2001, because of the high level of bromide in these waters, the major THMs formed were mixed bromochloro species (Figure 6). In addition, sub-µg/L levels of two iodinated THMs were detected in selected samples at plant 11, whereas µg/L levels of five iodinated THMs were detected at plant 12 (Figure 6). In addition to bromide in the source water, there was iodide as well. In other research, the formation of iodinated THMs was favored by chloramination, especially if the ammonia was added first, whereas the addition of chlorine first was found to favor the formation of the bromochloro species (Bichsel and von Gunten, 2000). Although the source water concentration of iodide was not measured in this study, the level of bromide in both source waters was comparable in March 2001. The difference in the formation of iodinated THMs at these two utilities may have been due to the order of addition of the chlorine and ammonia (chlorine first at plant 11, chlorine and ammonia together at plant 12).

At plant 11, there was no significant seasonal variation in THM speciation (Figure 7). However, the formation of THM4 was highest in September 2001 when the water temperature

was the warmest (25ºC) and was the lowest in February 2002 when the water temperature was the coldest (11ºC). Likewise, there was a similar seasonal variation in iodinated THM formation (Figure 8), with more formation in September 2001 and less in March 2001 (18ºC) and in February 2002.

Figure 7. Seasonal formation and speciation of THMs at plant 11 effluent

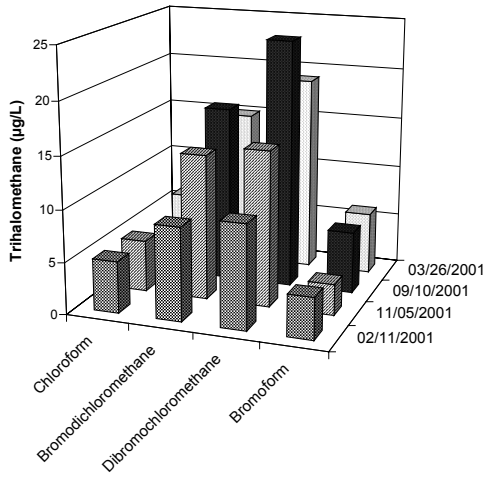
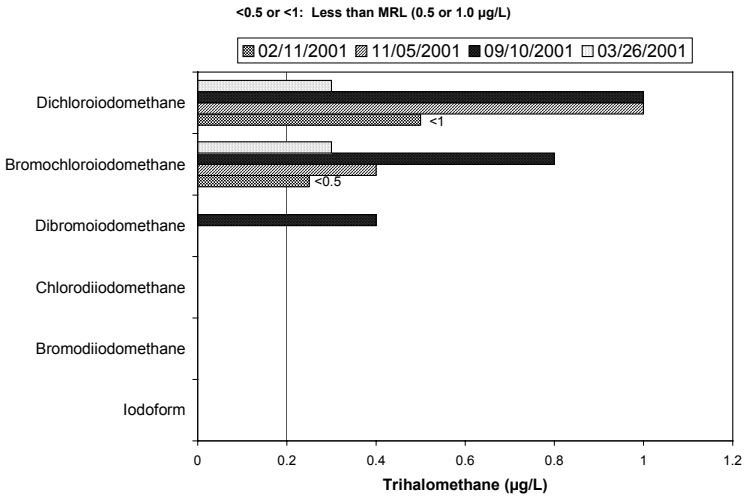


Figure 8. Seasonal variations in iodinated THM formation at plant 11 clearwell or plant effluent



At plant 12, because of the high level of bromide in this water in March 2001 (0.25 mg/L) and February 2002 (0.33 mg/L), the major THMs formed were brominated species (Figure 9). Alternatively, in September 2001 the low level of bromide (0.02 mg/L) resulted in a shift to more highly chlorinated THMs (Figure 9). In addition, µg/L levels of five of the iodinated THMs were detected in these samples (Figure 10). The sixth iodinated THM, iodoform, was detected in only one sample (in the distribution system) in September 2001. The iodinated THMs formed included various combinations of chlorine, bromine, and iodide atoms. Similar to the THM4 speciation (Figure 9), as the level of bromide increased, the formation of dibromoiodomethane increased (from 1 to 4 µg/L), whereas the formation of dichloroiodomethane decreased (from 7-11 down to <1 µg/L) (Figure 10).

Figure 9. Impact of bromide on THM speciation at plant 12 effluent

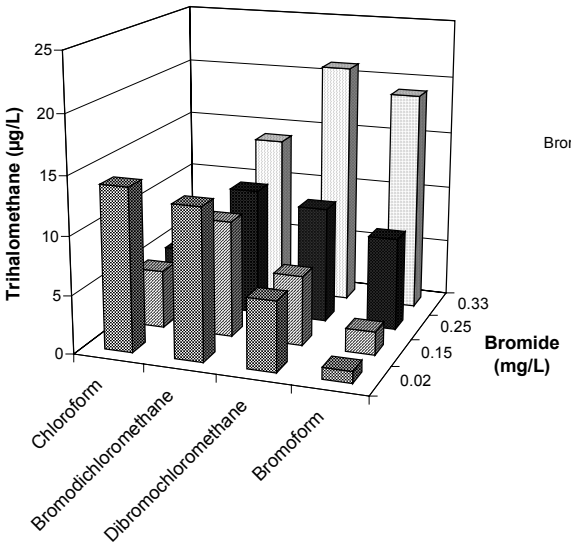
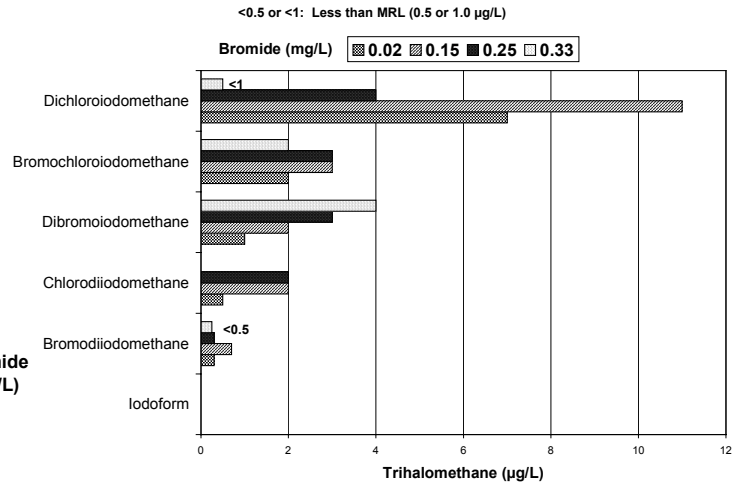


Figure 10. Seasonal variations in iodinated THM speciation at plant 12 effluent



Haloacids. Chlorine dioxide/chlorine/chloramine disinfection at plant 11 resulted in the formation of 18-23 µg/L of the five regulated haloacetic acids (HAA5) in the plant effluent in March 2001, September 2001, November 2001, and February 2002. In addition, all nine HAAs (HAA9) were measured, which included all of the brominated HAA species. The levels of HAA9 in the plant effluents in March 2001, September 2001, November 2001, and February 2002 at plant 11 were 42-49 µg/L. In March 2001, September 2001, November 2001, and February 2002, (chlorine dioxide and) chloramine disinfection at plant 12 resulted in the formation of 31-51 and 56-79 µg/L of HAA5 and HAA9, respectively, in the plant effluents. At these two plants, variations in bromide and disinfection practices impacted HAA formation and speciation (see discussion below).

Because of the high level of bromide in these waters in March 2001, a major portion of the HAAs formed in the plant effluent and distribution system were the mixed bromochloro species (i.e., bromochloro-, bromodichloro-, and dibromochloroacetic acid) (Figure 11). At plant 11 in March 2001, the formation of dihalogenated HAAs (DXAAs) was somewhat higher than the formation of the trihalogenated species (TXAAs) (Figure 12). The monohalogenated HAAs (MXAAs) were formed to a very low extent (as is found in other waters [Krasner et al., 1989]). A different pattern was observed at plant 12 in March 2001. At plant 12, the formation of DXAAs was significantly higher than the formation of TXAAs (Figure 12).

Figure 11. March 26, 2001

Effect of Bromide on HAA Speciation at Plants 11 and 12 in Simulated Distribution System Samples/Average Detention Time

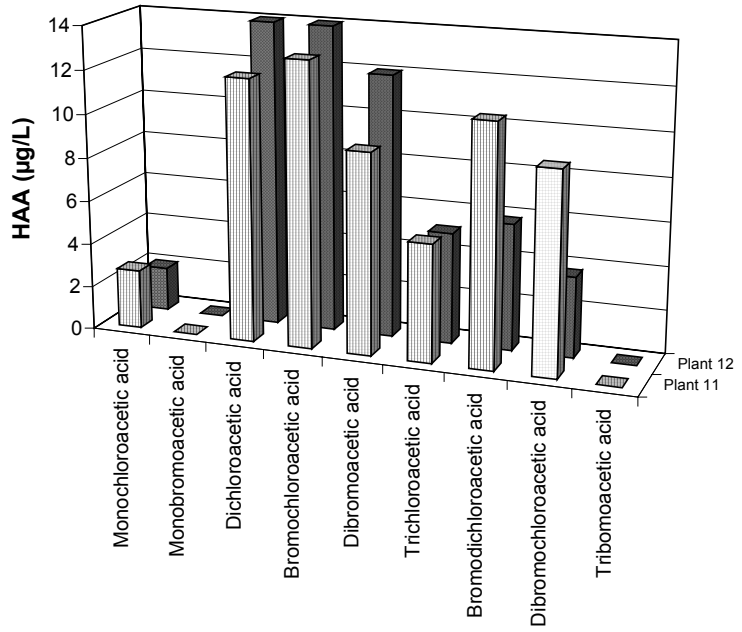
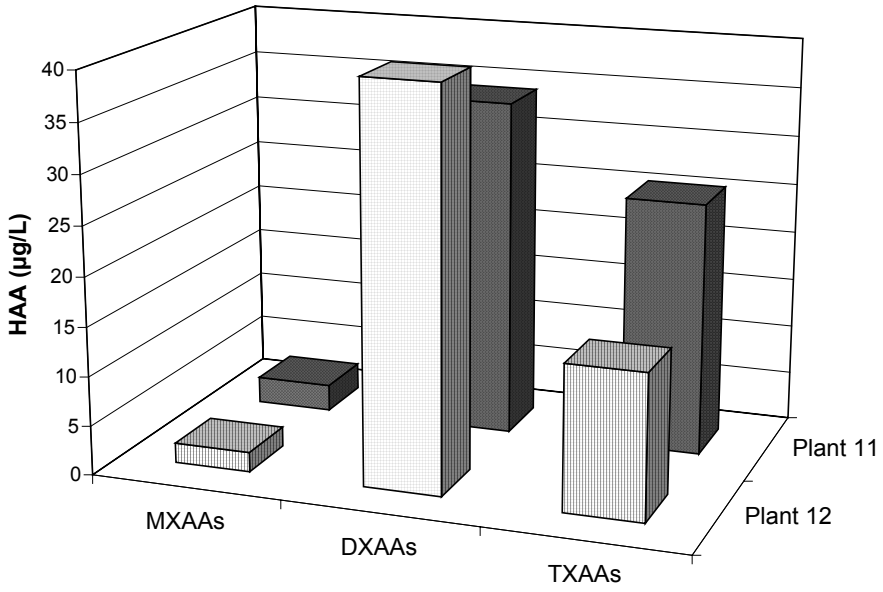


Figure 12. March 26, 2001

Effect of Disinfection Scheme on HAA Speciation in Plant Effluents at Plant 11 (Chlorine Dioxide/Chlorine/Chloramines) and Plant 12 (Chloramines Only)



In other research, chlorine dioxide (Zhang et al., 2000) and chloramines (Krasner et al., 1996) have both been shown to produce little or no TXAAs, whereas DXAAs have been formed. The use of chloramines only at plant 12 did minimize TXAA formation much more than DXAA formation, whereas the formation of both types of HAAs at plant 11 was probably due to the presence of free chlorine in the clearwell. Because of the presence of a significant amount of THMs at plant 11, it is likely that most of the THMs and HAAs formed at this plant is due to the free chlorine usage. In other research, waters with relatively low levels of specific UV absorbance (SUVA) have formed more DXAAs than TXAAs (Hwang et al., 2000). The SUVA of the water at plant 11, especially at the point of disinfectant addition (i.e., 2.1 L/mg-m in March 2001), was relatively low. It is likely that a combination of the disinfection scheme and natural organic matter of the water resulted in a higher formation of DXAAs than TXAAs at plant 11.

Because of the higher level of bromide at plant 11 as compared to plant 12 in September 2001, there was a greater shift to the formation of brominated HAAs at plant 11 than at plant 12 (Figure 13). At both plants, there was 19-20 µg/L of TXAAs in the plant effluent (Figure 14), with the major difference for this DBP subclass being the bromine speciation (Figure 13). Alternatively, there was much more formation of DXAAs in the plant effluent at plant 12 than at plant 11 (55 versus 23 µg/L) (Figure 14). The change in bromide levels at plant 12—between March and September 2001—resulted in a shift in HAA speciation between chlorinated and brominated species (Figures 11 and 13). However, the relative formation of DXAAs and TXAAs was comparable in March and September 2001 at plant 12 (Figures 12 and 14), which was due to the use of chloramines only.

Figure 13. 9/10/01 (plant 11 Br^- = 0.21 mg/L, plant 12 Br^- = 0.02 mg/L)

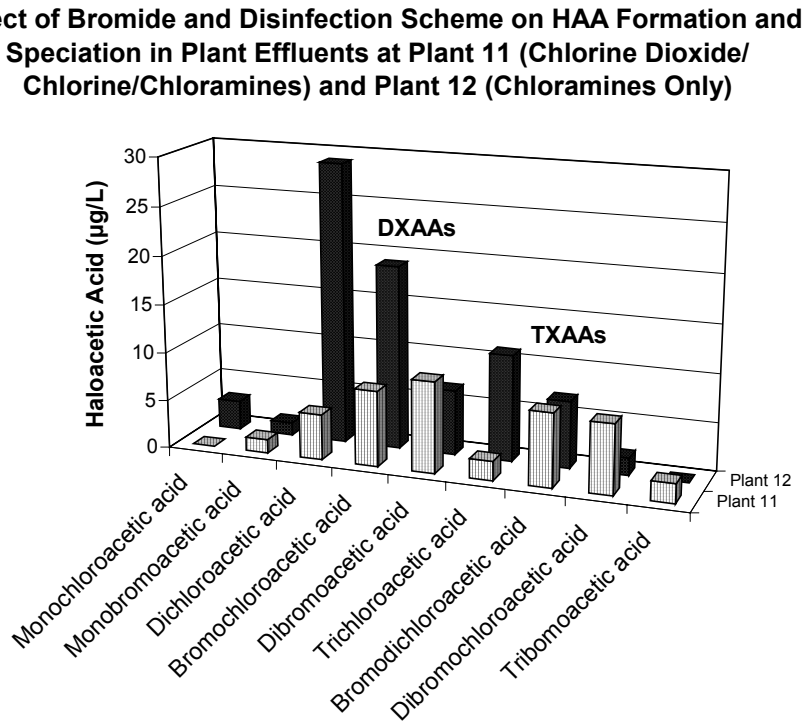
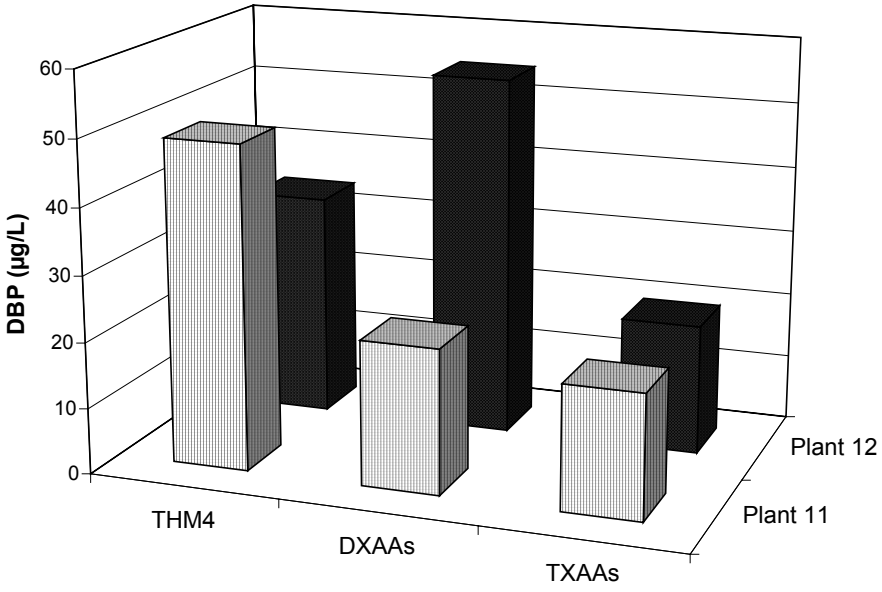


Figure 14. September 10, 2001

Effect of Disinfection Scheme on THM and HAA Formation and Speciation in Plant Effluents at Plant 11 (Chlorine Dioxide/ Chlorine/Chloramines) and Plant 12 (Chloramines Only)



At plant 11 in November 2001, chlorine dioxide was initially dosed before the clarifier. No HAAs and essentially no THMs were detected from pre-disinfection with chlorine dioxide. At plant 11 in February 2002, chlorine dioxide was initially dosed at the clarifier. HAAs (5 and 2 µg/L of dichloro- and trichloroacetic acid, respectively) were detected from pre-disinfection with chlorine dioxide. THM data for the filter influent sample were not reported due to quality control problems. However, the primary THM detected at that sample site was chloroform. At plant 11 in February 2002, after the addition of chlorine, significantly more THMs and HAAs were detected, which included the brominated species. It is possible that there was some DBP formation during the preparation of the chlorine dioxide solution, when the chlorine dioxide gas was dissolved in water.

At plant 12 in February 2002, a significant level of HAA9 (32 µg/L) was produced during pre-treatment with chlorine dioxide disinfection, whereas very little THMs (3 µg/L) were formed. The majority of the HAAs produced were DXAAs (21 µg/L). These results are consistent with that of Zhang and colleagues (2000), in which chlorine dioxide was found to form very little THMs or TXAAs, but did form a significant amount of DXAAs.

In addition to the target HAAs, several new brominated acids were identified by the broadscreen gas chromatography/mass spectrometry (GC/MS) methods (Tables 12 and 21). For example, 2,2-dibromopropanoic acid, dibromochloropropanoic acid, 3,3-dibromopropenoic acid, bromochloro-4-oxo-pentanoic acid, 3,3-dibromo-4-oxopentanoic acid, bromoheptanoic acid, bromochloroheptanoic acid, bromochlorononanoic acid, dibromoheptanoic acid, and cis-2-bromo-3-methylbutenedioic acid were identified (Table 12). Several of these bromo-acids were

also seen in finished waters from plant 1 (EPA Region 9), and also in drinking waters from Israel that had been treated with chlorine or chlorine dioxide-chloramine (Richardson et al., submitted).

At plant 12, in addition to the detection of brominated acids, five iodinated acids were detected (Table 21; mass spectra included in the Appendix). This represents the first time an iodo-acid has been identified as a DBP in drinking water. The identification of iodoacetic acid was confirmed through the analysis of an authentic standard (match of retention time and mass spectrum). Other identifications should be considered tentative until authentic chemical standards can be obtained to confirm them. However, high resolution mass spectrometry confirmed the presence of iodine in their structures, as well as their overall empirical formulas. In the case of iodobromoacetic acid, this assignment is very confident, due to only one isomer being possible. An attempt is currently being made to synthesize chemical standards for the remaining compounds to confirm their identities.

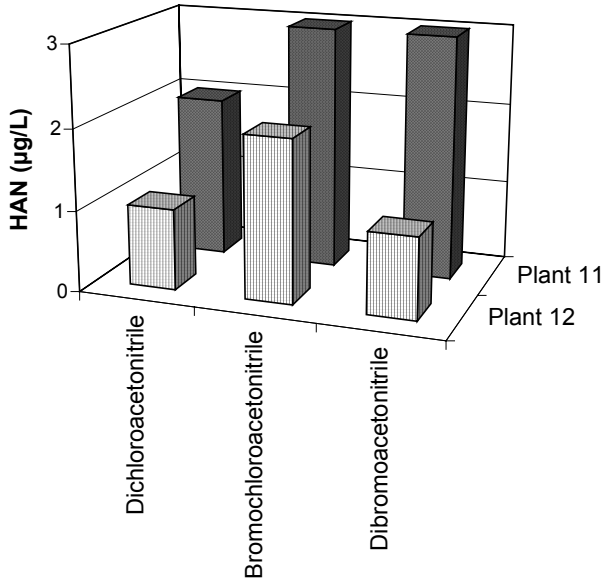
Finally, target analysis carried out by UNC revealed the presence of 3,3-dichloropropenoic acid in finished water from plant 11 in September 2001 (Table 15). It was present at 0.7 µg/L in the finished water and remained stable in the distribution system. 3,3-Dichloropropenoic acid was also formed at plant 12 in September 2001 but was not detected in downstream locations (Table 16).

Haloacetonitriles. In other DBP research, haloacetonitriles (HANs) have been found to be produced at approximately one-tenth the level (10 %) of the THMs (Oliver, 1983). A somewhat higher amount (on a relative basis) was detected in the plant 11 samples in March 2001, and a somewhat lower amount was detected in September 2001. A somewhat higher amount (12 and 14 % in March and September 2001, respectively) was detected in the plant 12 samples.

Because of the high level of bromide in these waters in March 2001, brominated HANs predominated (Figure 15). Although plant 12 had somewhat more raw-water bromide than plant 11 in March 2001, the shift in speciation to the more brominated HANs was greater in the plant 11 samples. This may have been due, in part, to differences in the formation of brominated DBPs in the presence of chlorine (i.e., at plant 11) and in the presence of chloramines (i.e., at plant 12). In the presence of chlorine, bromide is oxidized to hypobromous acid, which is a very powerful halogenation agent. In the presence of chloramines, bromide can be converted to bromamines, which will not produce as much brominated DBPs as hypobromous acid.

Figure 15. March 26, 2001

Effect of Bromide and Disinfection Scheme on HAN Speciation in Plants Effluents at Plant 11 (Chlorine Dioxide/Chlorine/Chloramines) and Plant 12 (Chloramines Only)



Because of the higher level of bromide at plant 11 than plant 12 in September 2001, there was a significantly greater shift to the formation of brominated HANs at plant 11 than at plant 12 that month (Figure 16). In addition to the formation of more of the brominated HANs in the Information Collection Rule (ICR) (e.g., dibromoacetonitrile) at plant 11, the target HAN dibromochloroacetonitrile was detected at plant 11 but not at plant 12 in September and November 2001.

Chloroacetonitrile, another target HAN, was detected at both plants in September 2001 (Figure 16) and November 2001. In addition, bromoacetonitrile was detected in one sample site per plant in September 2001. Dibromochloro- and tribromoacetonitrile—both brominated analogues of the ICR HAN trichloroacetonitrile—were detected at plant 11 in March 2001 by the broadscreen GC/MS methods (Table 12).

Haloketones. In addition to the formation of low levels of haloketone (HK) compounds from the ICR (i.e., 1,1-dichloro- and 1,1,1-trichloropropanone), low levels of some of the target study HKs were detected in selected samples from plant 11 and plant 12 (Figure 17). In addition to the formation of the two chlorinated HKs in the ICR, brominated analogues of these two HKs (i.e., 1,1-dibromo- and 1-bromo-1,1-dichloropropanone, respectively) were detected in September 2001 at plant 11, but were not detected at plant 12. In contrast, more of the 1,1,1,3-tetrachloropropanone was formed in September 2001 at plant 12.

Figure 16. September 10, 2001

Effect of Bromide on HAN Speciation at
Plant 11 (Br^- = 0.21 mg/L) and Plant 12 (Br^- = 0.02 mg/L)

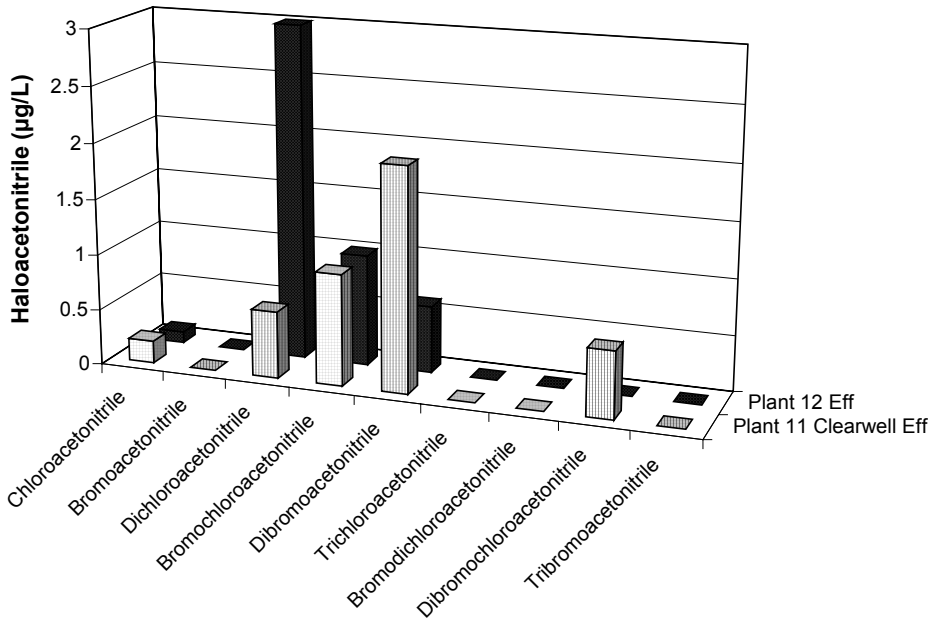


Figure 17. September 10, 2001

Effect of Bromide on HK Speciation in Plant Effluents at
Plant 11 (Br^- = 0.21 mg/L) and Plant 12 (Br^- = 0.02 mg/L)

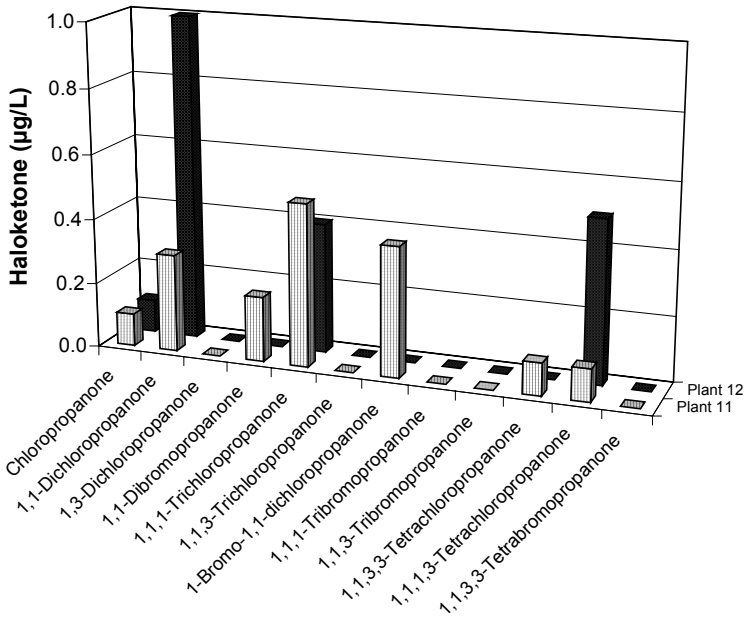
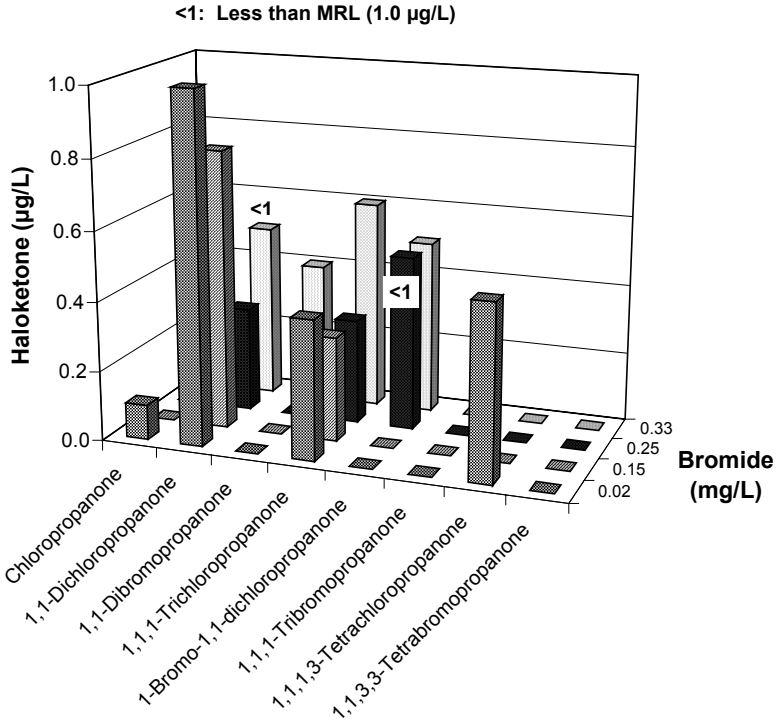


Figure 18 shows the impact of bromide on HK speciation at plant 12. In September 2001, when the bromide level was low (0.02 mg/L), two chlorinated HKs (chloro- and 1,1,1,3-tetrachloropropanone) were detected that were not found in March 2001, November 2001, or February 2002. In March 2001 and February 2002, when the bromide level was high (0.25 and 0.3 mg/L, respectively), two brominated HKs (1,1-bromopropanone [February 2002 only] and 1-bromo-1,1-dichloropropanone) were detected that were not found in September and November 2001 (November bromide = 0.15 mg/L).

Figure 18. Impact of bromide on HK speciation at plant 12 effluent



In addition to the target HKs, other HKs were detected by the broadscreen GC/MS methods (Tables 12 and 21). Some of these HKs were analogous to the tri- and tetrahalogenated HKs analyzed by MWDSC, except they were mixed bromochloro species. In addition, another HK that was detected by the broadscreen GC/MS methods at plant 12 was pentachloropropanone (PCP). MWDSC analysts had attempted to include PCP in its target compound list, but it degraded immediately and completely in water under all conditions they evaluated (Gonzalez et al., 2000).

Haloaldehydes. In addition to the formation of low levels of chloral hydrate (trichloroacetaldehyde), low levels of target haloacetaldehydes were detected (Figure 19). Both chlorinated and brominated species were formed. In March 2001, the level of chloral hydrate was higher at plant 11. In other research, chloramines were found to minimize the formation of chloral hydrate, whereas certain dihalogenated DBPs were formed to greater extents (Young et al., 1995). Consistent with that research, the formation of dihalogenated acetaldehydes was favored over trihalogenated species at plant 12. Moreover, the relative formation of di- versus

trihalogenated acetaldehydes at both utilities was consistent with the DXAA versus TXAA data at these plants (Figure 20).

Figure 19. March 26, 2001

Effect of Bromide and Disinfection Scheme on Haloacetaldehyde Speciation at Plant 11 (Chlorine Dioxide/Chlorine/Chloramines) and Plant 12 (Chloramines Only) in Distribution System Sample/Maximum Detention Time

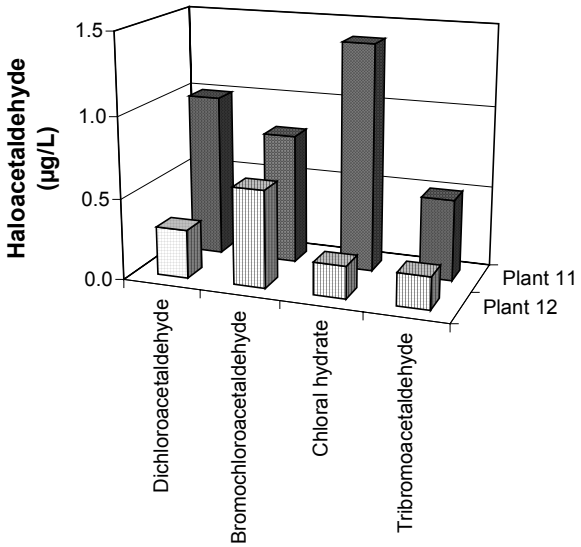


Figure 20. March 26, 2001

Effect of Disinfection Scheme on HAA and Haloacetaldehyde Speciation in Plant Effluents at Plant 11 (Chlorine Dioxide/ Chlorine/Chloramines) and Plant 12 (Chloramines Only)

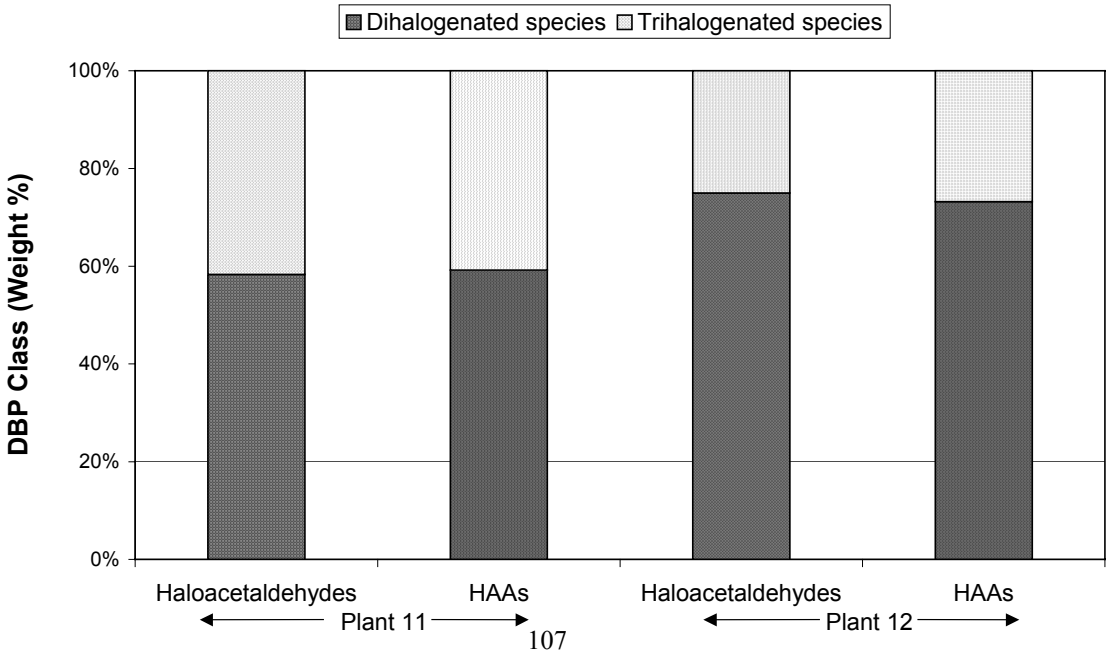


Figure 21 shows seasonal variations in the formation and speciation of haloacetaldehydes at plant 11. In September 2001, there was more of a shift to the brominated species. Also, because of the warmer water temperature in September 2001, there was the greatest haloacetaldehyde formation that month. Because of the colder water temperature in February 2002, there was the lowest halaocetaldehyde formation that month.

Figure 21. Seasonal formation and speciation of haloacetaldehydes at plant 11 clearwell or plant effluent

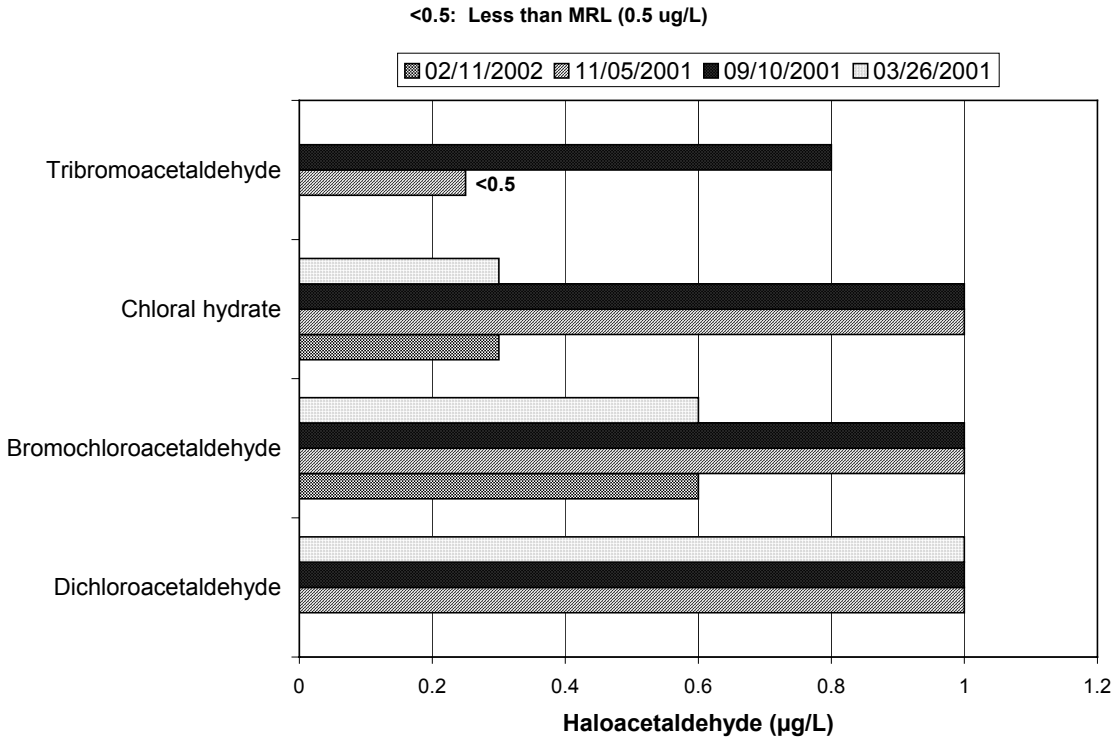


Figure 22 shows the impact of bromide on the formation and speciation of haloacetaldehydes at plant 12. In February 2002, when the level of bromide was the highest (0.33 mg/L), no dichloroacetaldehyde was detected, whereas there was bromochloroacetaldehyde formation. In addition, the formation of chloral hydrate (trichloroacetaldehyde) was low, whereas the formation of tribromoacetaldehyde was high. In March 2001 when the level of bromide was also high (0.25 mg/L), the formation of dichloro- and bromochloroacetaldehyde (both dihalogenated species) were similar and the amounts of the chloral hydrate and tribromoacetaldehyde (both trihalogenated species) were the same. Alternatively, in September 2001 when the level of bromide was low (0.02) or in November 2001 when the level of bromide was moderate (0.15 mg/L), the formation of dichloroacetaldehyde was higher than that of bromochloroacetaldehyde and the formation of chloral hydrate was higher than that of tribromoacetaldehyde. Regardless of the level of bromide, the formation of dihalogenated species was typically favored over trihalogenated species (e.g., dichloroacetaldehyde versus chloral hydrate) at plant 12 (Figure 22). In February 2002 (bromide = 0.33 mg/L),

dichloroacetaldehyde was not detected with an minimum reporting level (MRL) of 0.98 µg/L. As a result, the sum of the dihalogenated species was relatively low that month. In addition, that was the only month in which chlorine dioxide was used during pre-treatment.

In addition to the target haloacetaldehydes, other haloaldehydes were detected by the broadscreen GC/MS methods (Tables 12 and 21). At plant 11, dibromo- and bromodichloroacetaldehyde—which are brominated analogues of dichloroacetaldehyde and chloral hydrate, respectively—were detected. In addition, another brominated aldehyde (2-bromo-2-methylpropanal) was detected at both plants.

Halonitromethanes. In March 2001, September 2001, November 2001, and February 2002, sub-µg/L levels of chloropicrin (trichloronitromethane) and other halonitromethanes were detected in selected samples at plant 11 (bromopicrin was detected at 1 µg/L in one sample in February 2002). This included mono-, di-, and trihalogenated species, with and without bromine. Sub-µg/L to low µg/L levels of halonitromethanes were detected at plant 12 in March 2001, September 2001, November 2001, and February 2002.

Figure 22. Impact of bromide on haloacetaldehyde speciation at plant 12 effluent

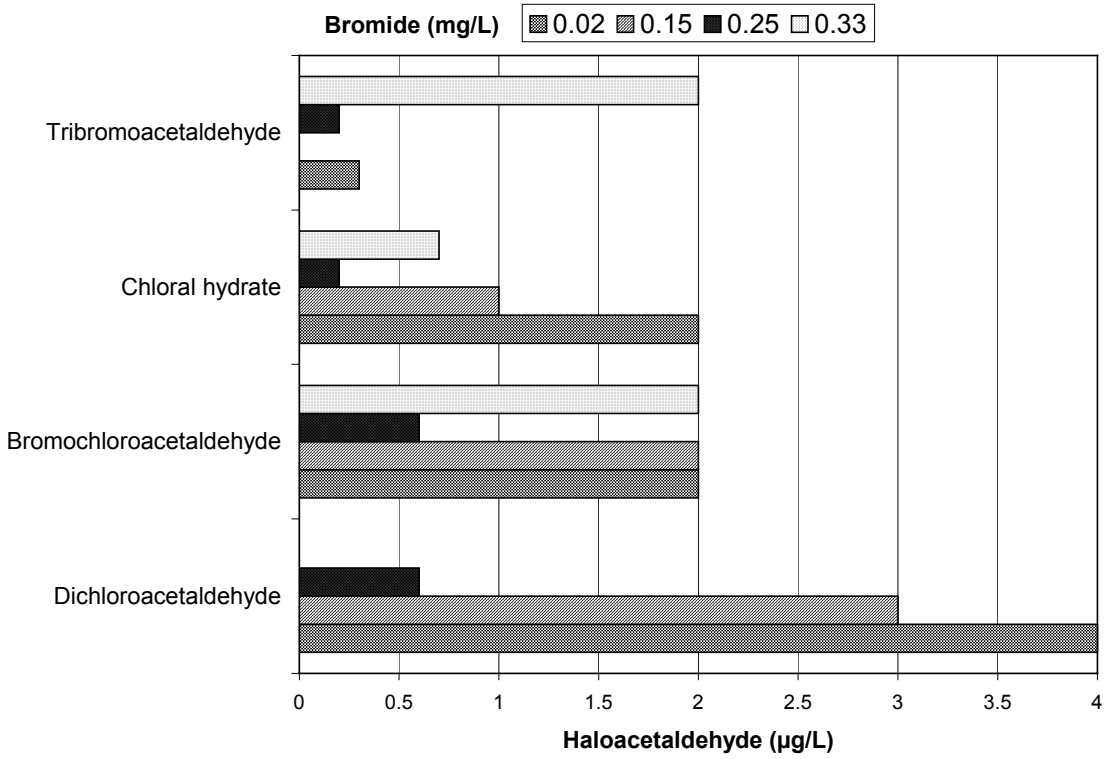


Figure 23. Haloacetaldehyde speciation at plant 12 effluent

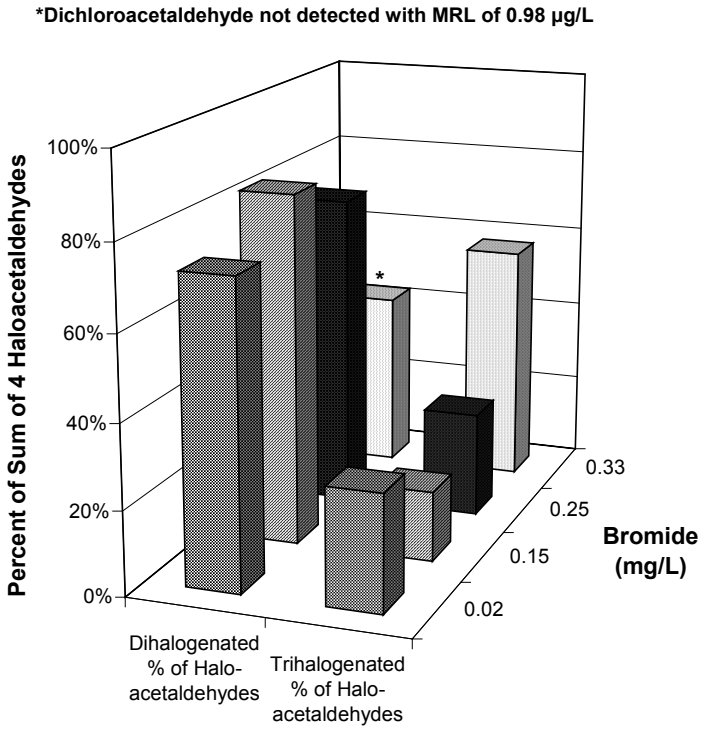
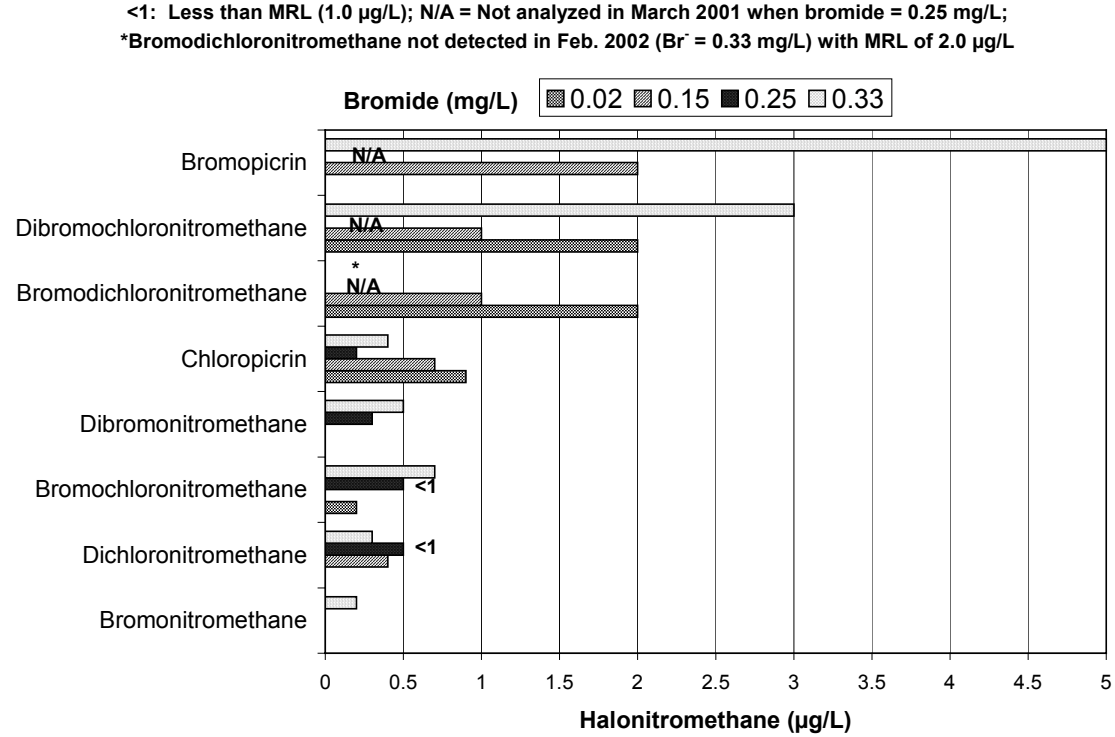


Figure 24 shows the impact of bromide on the speciation of the halonitromethanes at plant 12. As bromide increased, the formation of chloropicrin decreased (from 0.9 down to 0.2-0.4 µg/L), whereas the formation of the brominated species increased (e.g., bromochloronitromethane formation increased from not detected or 0.2 to 0.7 or <1 µg/L). In February 2002, when the level of bromide was the highest (0.33 mg/L), bromonitromethane was detected, but not in other months. In addition, dibromonitromethane was only detected in February 2002 and in March 2001 (bromide = 0.25 mg/L). In addition to the formation of chloropicrin, brominated analogues of this trihalogenated nitromethane were detected in the September 2001, November 2001, and February 2002 samples. Data for the brominated trihalogenated nitromethanes were not available (N/A) in the March 2001 samples. Bromopicrin was detected in September 2001 (bromide = 0.02 mg/L) in the filter influent sample, but was not detected in the plant effluent sample, whereas the two mixed bromochloro trihalogenated species were detected in the plant effluent. Alternatively, when bromide was higher (in November 2001 [0.15 mg/L) and February 2002), bromopicrin formation was the highest (2 and 5 µg/L, respectively).

Figure 24. Impact of bromide on halonitromethane speciation at plant 12 effluent



At plant 11 in September 2001, bromodichloro- and dibromochloronitromethane were detected at or above the MRL of 0.5 µg/L in the SDS sample held for maximum detention time. Although the SDS samples were not kept cold during the prolonged shipping period in September 2001, these results suggest that these compounds may have been present in other plant 11 samples, but at concentrations below the MRL.

Halogenated furanones. Tables 17 and 18 show the results for halogenated furanones in the September 2001 samplings for plants 11 and 12; Tables 26 and 27 show the results for the February 2002 samplings. Data are included for 3-chloro-4-(dichloromethyl)-5-hydroxy-2[5H]-furanone, otherwise known as MX; (E)-2-chloro-3-(dichloromethyl)-4-oxobutenoic acid, otherwise known as EMX; (Z)-2-chloro-3-(dichloromethyl)-4-oxobutenoic acid (ZMX); the oxidized form of MX (Ox-MX); brominated forms of MX and EMX (BMXs and BEMXs); and mucochloric acid (MCA), which can be found as a closed *ring* or in an *open* form. Results are displayed graphically in Figures 25 and 26.

Many sample points were analyzed in the EPA Region 6 plants (9/10/01), clearly showing that ClO_2 at plant 11 did not produce MX and MX-analogues at the filter influent except for 20 ng/L of BEMX-1, and that intermediate chlorination/post-chloramination at plant 11 produced more MX-analogues than chloramines at plant 12. ZMX was detected (90 ng/L) in the plant 11 clearwell effluent, but was not detected in the plant effluent, whereas MX was the same at both sample sites (20 ng/L). Predisinfection with ClO_2 at plant 11 did not appear to effectively remove precursors of MX-analogues as has been observed for predisinfection with ozone for other treatment plants in this study. A significant higher concentration of MX (853 ng/L) was detected in the plant 11 DS/average sample compared to the PE sample (20 ng/L), whereas the BEMX-3 was detected in the PE (200 ng/L) and not in the DS/average sample. The plant 11 SDS/maximum sample (490 ng/L BEMX-3) shows that BEMX-3 was stable under the conditions employed in the SDS test. These results suggest that the DS/average sample may represent a different water than the PE sample, as these samples were not collected to follow a "plug" of water over time (as the SDS test was set up to do). With a bromide concentration of 0.21 mg/L and TOC concentration of 3.5 mg/L, the raw water for plant 11 produced BMX compounds during intermediate chlorination/post-chloramination, as found in the majority of samples (11-490 ng/L) from plant 11. Due to the difference in water quality of the river basin in September 2001 (0.02 mg/L Br- and 7.5 mg/L TOC), which fed plant 12, and the difference in disinfection (chloramines only), substantially less brominated MX-analogues (17-90 ng/L) were produced relative to plant 11. At plant 11, the major production of BMX-analogues occurred in the clearwell influent after intermediate chlorination, whereas at plant 12, it occurred between the filter effluent and plant effluent samples.

In the second sampling of the EPA Region 6 plants (2/11/02 or 2/12/02) for halogenated furanones, MX and a chlorinated MX-analogue, MCA, were more predominant at plants 11 and 12 than in the earlier sampling (September 2001). One BMX analogue, BMX-1, was also formed at 80 and 60 ng/L in finished waters from plants 11 and 12, respectively, but was not detectable in the DS/maximum samples. The raw water quality of plant 11 was not that different in February 2002 (0.18 mg/L of bromide and 4.3 mg/L of TOC), whereas plant 12's was significantly different (0.33 mg/L bromide and 5.3 mg/L of TOC). In addition, plant 12 used chlorine dioxide during pretreatment in February 2002. These changes in the distribution and occurrence levels of the MX-analogues may be due to changes in raw water quality and operational (treatment/disinfection) parameters from Fall 2001 to Winter 2002.

Figure 25. Halofuranone data at EPA Region 6 plants (9/10/01)

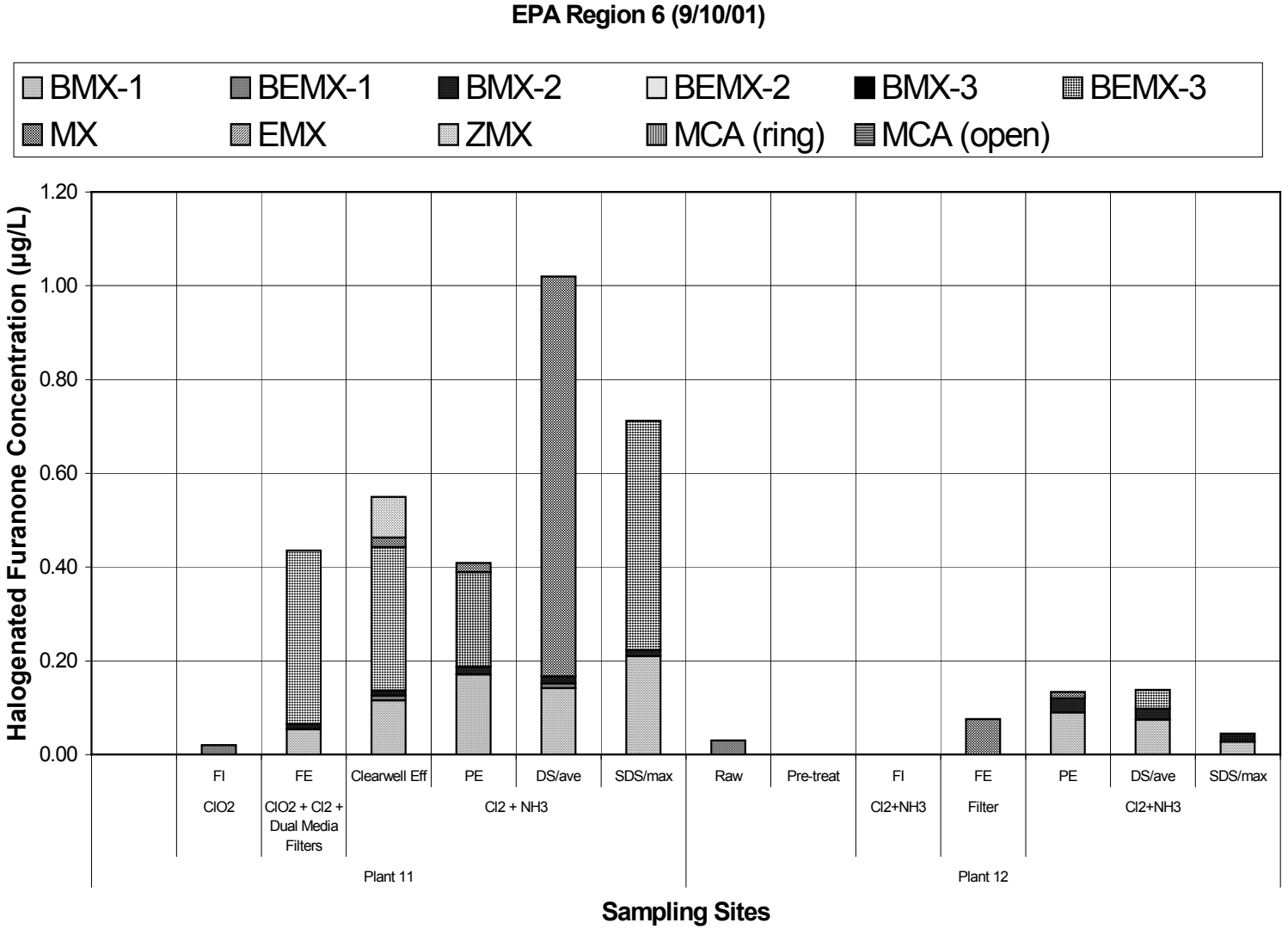
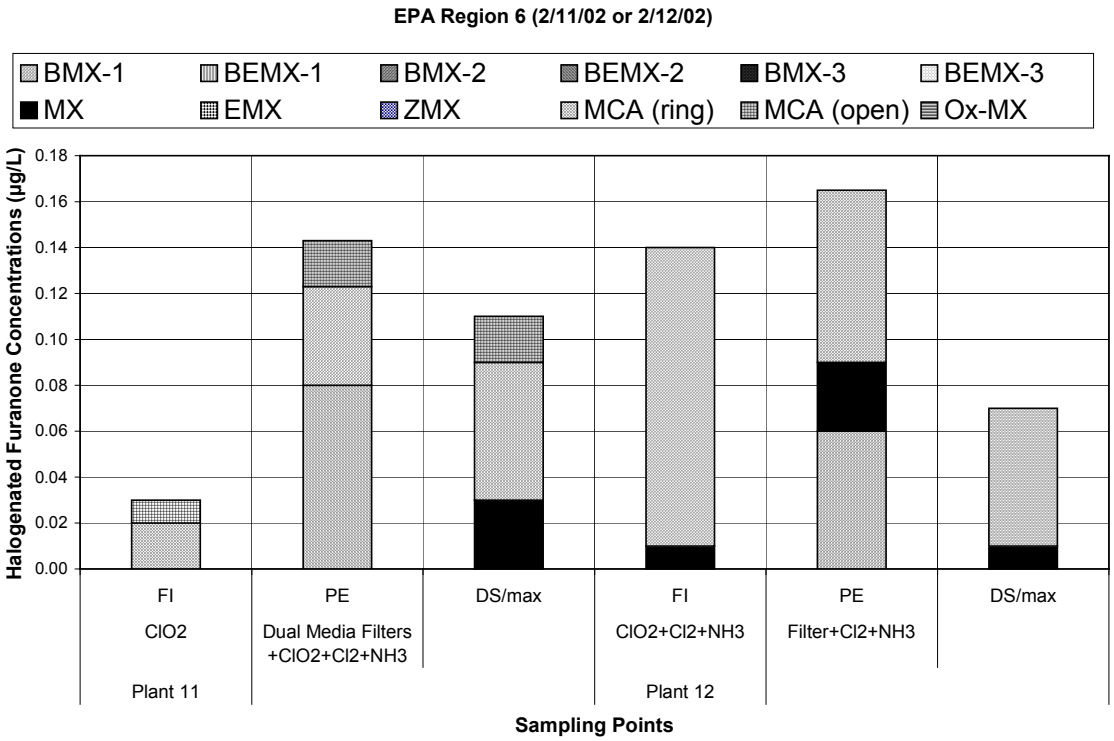


Figure 26. Halofuranone data at EPA Region 6 plants (2/11/02 or 2/12/02)



Other Halogenated DBPs. In target analyses conducted at UNC, haloamides were frequently identified in finished waters from plants 11 and 12 (Tables 15-16, 24-25). In samples taken in February 2002, all five target haloamides were identified: monochloroacetamide, monobromoacetamide, dichloroacetamide, dibromoacetamide, and trichloroacetamide. Concentrations of individual species ranged from 0.4 to 2.8 µg/L in the plant effluent and were comparable in the distribution system. In September 2001, only one haloacetamide was targeted—dichloroacetamide, which was found at 2.8 and 5.6 µg/L in finished waters from plants 11 and 12, respectively. Haloamides have not been a class of DBPs quantified in potable waters previously. Because the levels observed in these samples are similar to other DBPs that are commonly measured, this may be an important class of DBP that warrants further study.

A few additional halogenated DBPs were identified by broadscreen GC/MS analysis, including dibromoaniline, dibromodichloroaniline, and tribromochloroaniline (plant 12 finished water, November 2001). These compounds were not present in the raw, untreated water.

Volatile Organic Compounds. Carbon tetrachloride was detected in two samples at plant 11 (clearwell and plant effluent) in March 2001 at sub-µg/L levels. Carbon tetrachloride is a volatile organic compound (VOC) and a possible DBP. Carbon tetrachloride has been detected by some utilities in gaseous chlorine cylinders (EE&T, 2000). Incidents of carbon tetrachloride contamination of chlorine cylinders have been traced to either imperfections in the manufacturing process or improper cleaning procedures. Carbon tetrachloride is used to clean

out cylinders before filling with chlorine. If carbon tetrachloride is not allowed sufficient time to evaporate, it can contaminate the chlorine.

Methyl ethyl ketone (MEK) was detected in the raw water, in the distribution system, and in SDS testing at plant 11 on September 10, 2001 at a concentration of 0.6-0.7 µg/L. MEK was not detected at or above the MRL of 0.5 µg/L in the clearwell effluent or the plant effluent. MEK was detected at the filter influent and in the distribution system of plant 12 on September 10, 2001 at a concentration of 0.6 µg/L. MEK was not detected at or above the MRL in the raw water or the plant effluent. MEK is an industrial solvent and a possible DBP. At plant 11, its presence in the distribution system was most likely due to its low-level occurrence in the raw water. At plant 12, its occurrence in some samples slightly above the MRL does not allow for a determination as to its origin.

Non-Halogenated DBPs. A few non-halogenated DBPs were detected in treated waters from plants 11 and 12 (Tables 15-16, 24-25). The finding of 6-hydroxy-2-hexanone in the filter influent (at 0.8 µg/L) of plant 11 represented one of the few times this DBP was identified in this study (September 2001, Table 15). This compound was likely formed by the initial treatment with chlorine dioxide. 6-Hydroxy-2-hexanone has also been previously reported as an ozone DBP (Richardson et al., 1999). However, although it was initially formed, it was not present in the plant effluent (finished water). Because plant 11 did not use GAC or biofiltration, it was probably not removed by the filtration process. Many ketones can undergo base-catalyzed hydrolysis or can react with chlorine to form secondary by-products. Either phenomenon may be responsible for the loss of this DBP. Another DBP that is typically an ozone DBP—dimethylglyoxal—was also found in the finished water from both plants 11 and 12, generally at levels between 1 and 3 µg/L in the plant effluent. Zhang and colleagues (2000) demonstrated that other disinfectants/oxidants can form carbonyl containing compounds. Broadscreen GC/MS analysis also revealed the presence of acetone and glyoxal in finished water from plant 12 (November 2001), as well as several non-halogenated carboxylic acids in the finished waters, which were at significantly higher concentrations than in the raw, untreated water.

Distribution System Issues. Because plant 11 used chloramines in the distribution system, most of the DBPs were found to not increase significantly in concentration in SDS testing (Figure 27) or in the distribution system. Many non-THM DBPs (e.g., dichloroacetonitrile, 1,1,1-trichloropropanone, chloral hydrate) are known to degrade at high pH (Stevens et al., 1989; Croué and Reckhow, 1989). Because the distribution system and SDS testing in March 2001 was only at a pH of 7.4-7.6, most non-THM DBPs were found to be relatively stable (Figure 27).

Figure 27: March 26, 2001

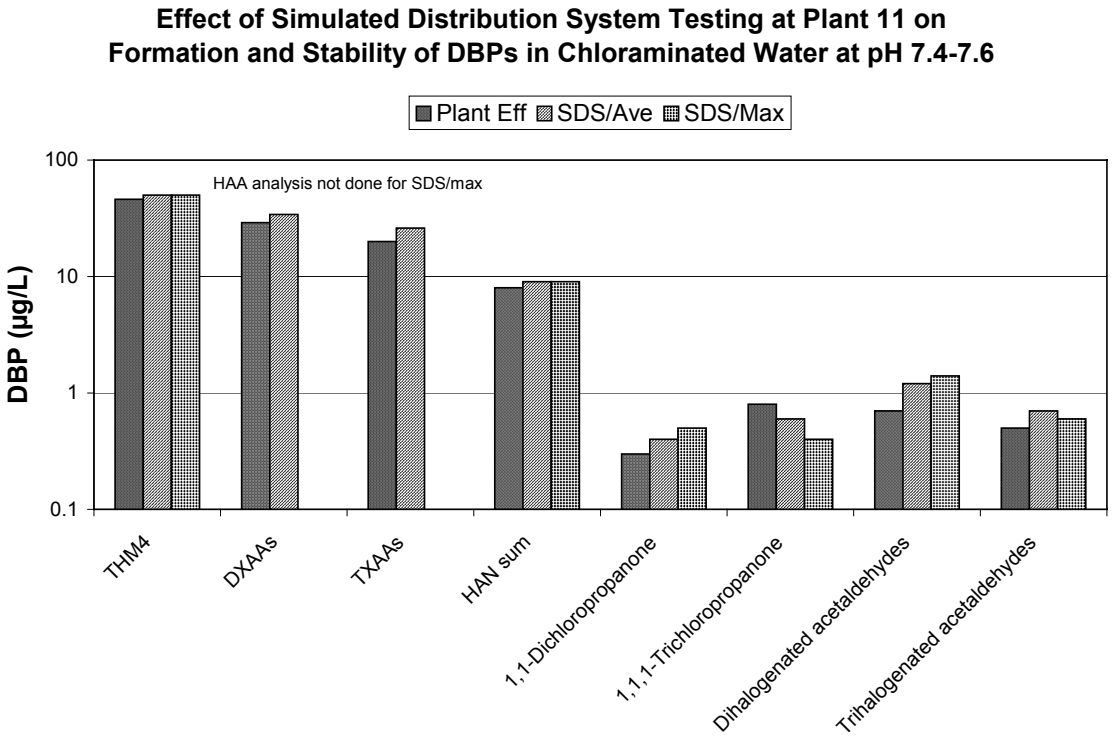
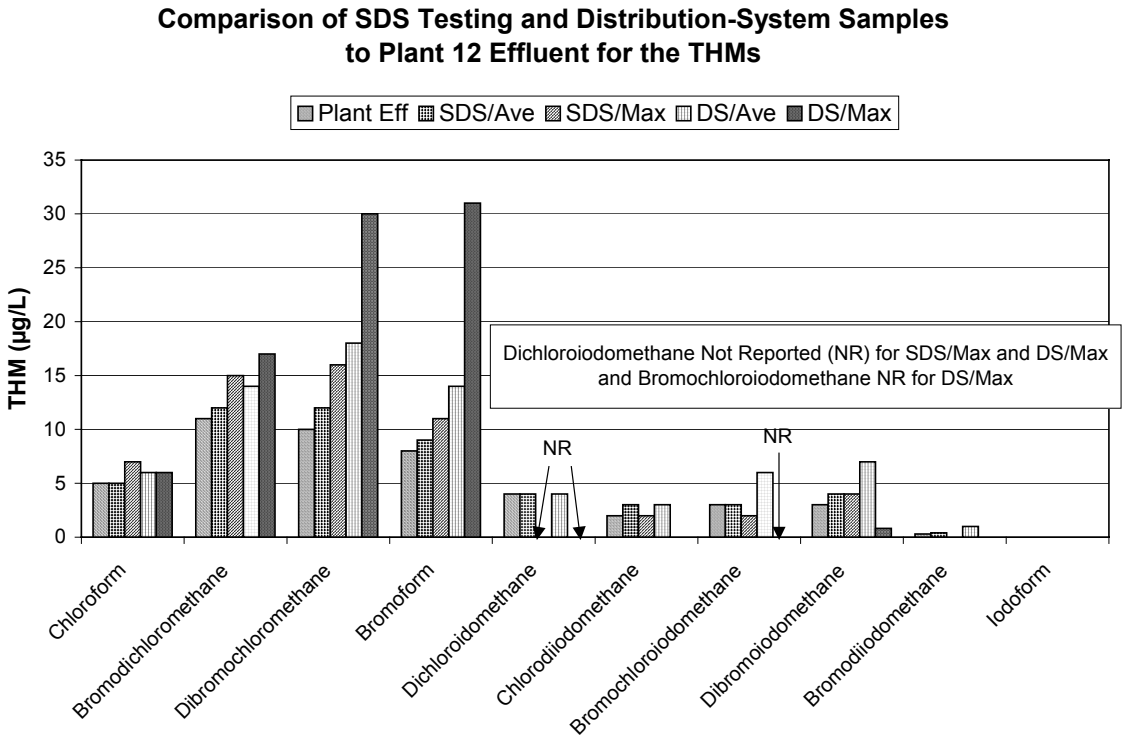


Figure 28 shows a comparison of SDS testing and distribution-systems samples to the plant effluent for the THMs for plant 12 for March 2001. Because plant 12 used chloramines, THMs would not be expected to increase significantly in concentration in the distribution system or in SDS testing. THM4 concentration did increase in the plant 12 SDS testing (from 34 µg/L in the plant effluent to 38 and 49 µg/L in the SDS samples held for average and maximum detention times, respectively). The increase in concentration in the SDS samples (especially at maximum detention time) was primarily due to the formation of the brominated THMs (Figure 28). Other research has shown that THM formation can increase in chloraminated water when an elevated level of bromide is present (Diehl et al., 2000).

Figure 28. March 26, 2001



Alternatively, THM4 was significantly higher in concentration in the plant 12 distribution-system samples in March 2001 (34 µg/L in the plant effluent versus 52 and 84 µg/L in the distribution-system samples collected at average and maximum detention times, respectively). The increase in concentration in the distribution-system samples (especially at maximum detention time) was primarily due to the formation of dibromochloromethane and bromoform (Figure 28). Distribution-system samples can be significantly different than the plant effluent for two reasons:

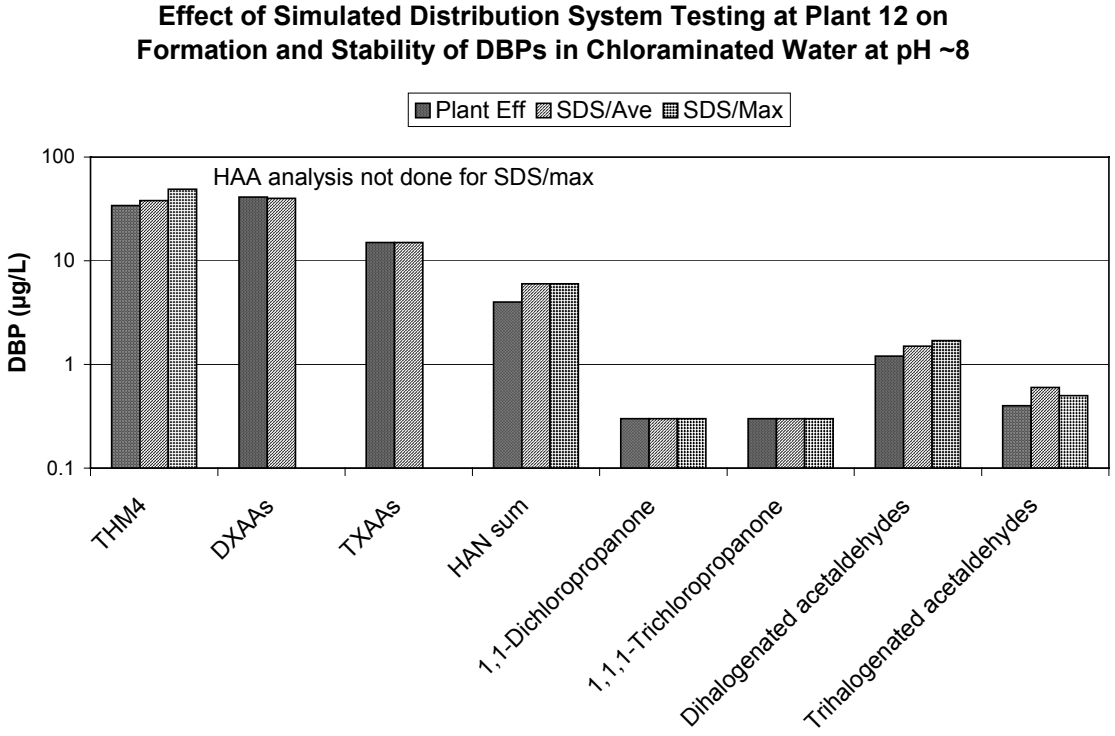
- One, grab samples for the plant and distribution system were collected on the same day (as requested) rather than following a plug of water over time--i.e., collecting the plant effluent on one day and collecting the distribution-system samples a period of time (e.g., days) later that matched the expected detention time in the system. Thus, the distribution-system samples (especially at maximum detention time) represented water produced at the plant on a different day in which the source-water quality and/or plant operations may have been different.
- Second, distribution-system samples may not always contain water only from the plant effluent if there are other sources of water that may feed the distribution system (e.g., well water).
- Thus, distribution-system samples represented the actual occurrence of DBPs, whereas SDS testing allowed for an examination of the effect of detention time on DBP formation without any of the confounding issues associated with distributed water.

In terms of the iodinated THMs at plant 12 in March 2001, SDS results were comparable to the plant effluent data. Alternatively, some of the iodinated THMs (i.e.,

bromochloroiodomethane, dibromoiodomethane, and bromodiiodomethane) were significantly higher in the distribution system at average detention time as compared to the plant effluent and one of the iodinated THMs (i.e., dibromoiodomethane) was significantly lower in the distribution system at maximum detention time (Figure 28). Because a similar increase or decrease in formation was not observed in the SDS testing, this suggests that the distribution-system samples represented a somewhat different source of water than the plant effluent collected on the same day.

Figure 29 shows the effect of SDS testing at plant 12 in March 2001 on the formation and stability of a range of DBPs. Because the SDS testing was only at a pH of ~8, most non-THM DBPs were found to be relatively stable (Figure 29).

Figure 29. March 26, 2001



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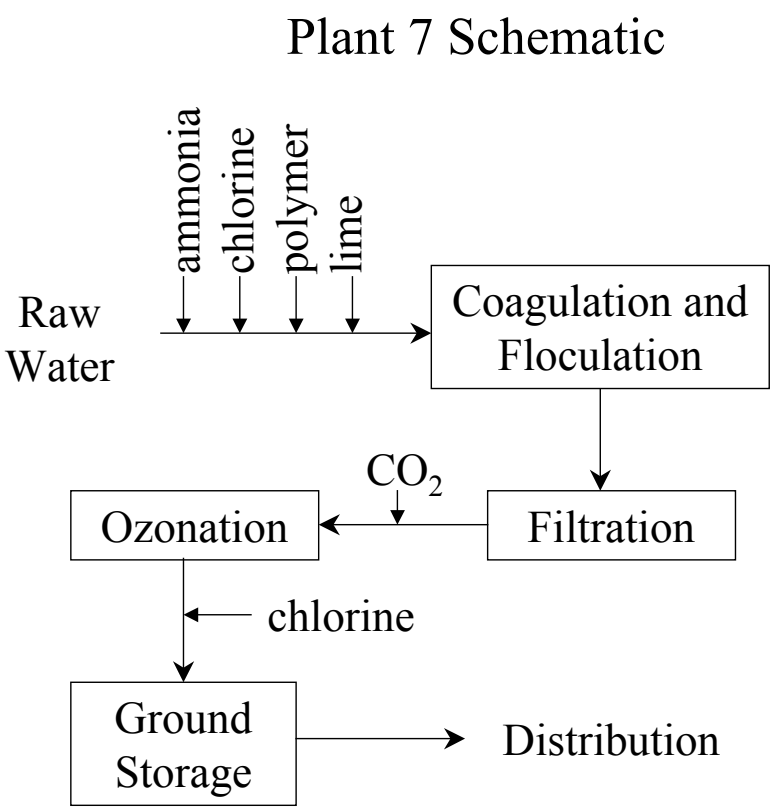
EPA REGION 4: PLANTS 7 AND 8

Plant Operations and Sampling

On December 11, 2000, March 12, 2001, September 24, 2001, and January 14-16, 2002, plants 7 and 8 (in EPA Region 4) were sampled.

Plant 7 is an ozone plant (Figure 1). The raw water was first treated with chloramines. The water was then lime-softened and filtered. The filtered water was ozonated. The ozonated water was chlorinated, stored, and distributed.

Figure 1

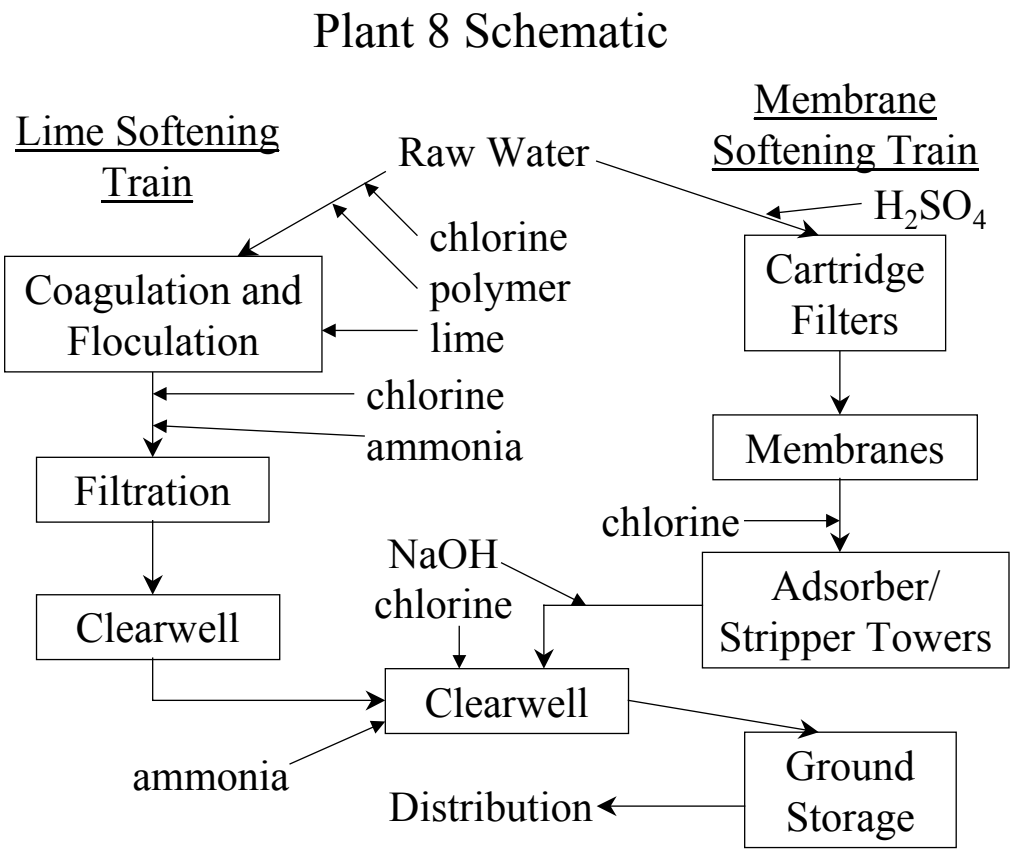


Plant 8 is a membrane plant (Figure 2). This plant consisted of two facilities operating simultaneously and parallel to one another; a portion of the water was treated with membranes:

- In the lime softening portion of the plant, the raw water was treated with chlorine. The water was then lime-softened. The softened water was chloraminated, filtered, and stored.
- In the membrane-softening portion of the plant, the pH of the raw water was adjusted with sulfuric acid. The acidified water was filtered and treated with membranes (TFC®-S polyamide, Koch Membrane Systems; softening, low pressure for brackish water treatment membrane elements). The membrane-treated water was chlorinated and passed through an adsorber and stripper towers. The pH of the water was adjusted with sodium hydroxide and mixed with the lime-softened water.

The combined treated waters were chloraminated, stored, and distributed.

Figure 2



Plant 7 was sampled at the following locations:

(1) raw water
(2) settled water
(3) filter effluent
(4) effluent of the ozone contactor
(5) the plant effluent

In addition, plant effluent was collected and simulated distribution system (SDS) testing was conducted (a 24-hr holding time was typically used [27-hr in January 2002]). Furthermore, the distribution system was sampled at a location that receives water from plant 7 and from another treatment plant.

Plant 8 was sampled at the following locations:

(1) raw water

Lime Softening

(2) settled water
(3) filter effluent

Membrane Softening

(4) membrane effluent
(5) effluent of the stripper towers

Combined Treated Waters

(6) the plant effluent

In addition, plant effluent at plant 8 was collected and SDS testing was conducted (a 24-hr holding time was typically used [22.5 h in September 2001]. Furthermore, the distribution system of plant 8 was sampled at one location.

On the day of sampling, information was collected on the operations at each plant (Tables 1-2).

Table 1. Operational information at plant 7

Parameter	12/11/00	3/12/01	9/24/01	1/14/02
Plant flow (mgd)	8.7	9.0	9.6	13.6
Total chlorine dose at plant influent (mg/L as Cl_2)	13	10	5	5.3
Chlorine dose at influent pipe or raw standpipe (mg/L as Cl_2)	3.0	7.0	2	2
Chlorine dose at treatment unit collector ring or basin effluent (mg/L as Cl_2)	7.0	3.0	3	3.3
Ammonia dose at plant influent (mg/L as NH_3-N)	1.1	1.1	0.94	1.3
Lime dosage (mg/L)	219	225	230	243
Polymer dosage (mg/L)	0.2	0.2	0.2	0.2
CO_2 dosage (mg/L)	8.3	4.0	10	3.6
Ozone dose (mg/L)	6.4	5.0	4	7.4
Hydraulic retention time in ozone contactor (min)	25	20	30	20
CT achieved from ozonation (mg/L-min)	NA[a]	NA	NA	0.37
Chlorine dose at ozone contactor eff. (mg/L as Cl_2)	3.1	3.0	6.0	6.7

[a]NA = Not available

Table 2. Operational information at plant 8

Parameter	12/11/00	3/12/01	9/24/01	1/16/02
Overall plant flow (mgd)	11.05	11.41	10.1	11.64
Plant flow for lime softening (mgd)	4.5	3.0	3.3	3.00
Plant flow for membrane softening (mgd)	6.55	8.41	6.8	8.64
Lime Softening				
Chlorine dose at lime softening inf. (mg/L as Cl_2)	6.0	6.0	8.0	8
Lime dosage (mg/L)	205	225	215	225
Polymer dosage (mg/L)	0.05	0.05	0.025	0.025
Chlorine dose at filter influent (mg/L as Cl_2)	12	12	12	12
Ammonia dose at filter influent (mg/L as NH_3-N)	1.0	1.0	1.0	1
Membrane Softening				
H_2SO_4 dose at membrane softening inf. (mg/L)	180	180	134	182
Operating pressure (psi)	118	118	118	118
Chlorine dose at membrane effluent (mg/L as Cl_2)	2.6	2.6	2.6	1.8
NaOH dose at stripper tower effluent (mg/L)	16.6	62	16	26
Chlorine dose at stripper tower eff. (mg/L as Cl_2)	7.1	7.1	7.5	6.5
Combined Treated Waters				
Ammonia dose at plant effluent (mg/L as NH_3-N)	1.0	1.0	1.0	NA

Water Quality

On the day of sampling, information was also collected on water quality at each plant (Tables 3-4). Data were collected for total organic carbon (TOC) and ultraviolet (UV) absorbance for plant 7 and plant 8 (Table 5). Plants 7 and 8 treated a groundwater that was high in TOC (12-13 mg/L) and in color. Lime softening at plant 7 and plant 8 removed 21-35 % of the TOC and reduced the UV by 38-48 %. Filtration removed another 3-9 % of the TOC. At plant 7, ozonation did not significantly effect the level of TOC, whereas the UV was reduced by another 13-37 %. The overall (cumulative) removal of TOC at plant 7 (due to lime softening, filtration, and ozonation) was 27-33 % and the UV was reduced by 52-61 %. The overall (cumulative) removal of TOC at plant 8 in the lime-softening portion of the plant was 29-39 % and the UV was reduced by 43-54 %. At plant 8, the membrane process reduced both the TOC and the UV by 97-98 %. At plant 8, the plant effluent TOC was 2.5-3.6 mg/L, which approximately matched the relative contributions of TOC from each of the two portions of the plant. The concentration of TOC (2.6-3.5 mg/L) in the distribution system of plant 8 confirmed that this location was receiving membrane treated water.

Table 6 shows the values of miscellaneous other water quality parameters in the raw water of plants 7 and 8. The raw water at each plant contained a moderate or high amount of bromide (the bromide concentrations at plant 7 and plant 8 were 0.12-0.14 and 0.25-0.33 mg/L, respectively). At plant 8, a significant percentage (60-67 %) of the raw-water bromide was rejected by the membrane process.

The raw water also contained a moderate amount of ammonia (0.5-0.7 mg/L as N). It takes 7.6 mg/L of chlorine to breakpoint chlorinate 1.0 mg/L of ammonia-nitrogen. Ground-waters that are high in ammonia are often high in hydrogen sulfide (Krasner et al., 1996), which also exerts a high chlorine demand. When chlorine is added to such groundwaters, typically chloramines are formed, since not all of the ammonia will be breakpoint chlorinated. At plant 8, chloramines were formed during the chlorination of the raw water at the lime-softening portion of the plant and during the chlorination of the membrane effluent (Table 4).

DBPs

Oxyhalides. At plant 7, ozonation did not result in the formation of bromate at or above the minimum reporting level (MRL) of 3 µg/L. Ammonia addition is a method of controlling bromate formation, because the ammonia may be able to tie up the bromide as bromamines (Krasner et al., 1993). At plant 7, 0.9-1.3 mg/L of ammonia-nitrogen was added to the raw water in addition to the 0.6-0.7 mg/L that was naturally present. Ozonation of a water with a free chlorine residual can result in the formation of chlorate. Chlorate was not detected at plant 7, since the free chlorine was converted to chloramines by the ammonia present prior to the addition of ozone.

Table 3. Water quality information at plant 7

	pH				Temperature (ºC)				Disinfectant Residual[a] (mg/L)			
Location	12/11/00	3/12/01	9/24/01	1/14/02	12/11/00	3/12/01	9/24/01	1/14/02	12/11/00	3/12/01	9/24/01	1/14/02
Raw water	7.1	7.35	7.3	7.30	25	25	25	25	---	---	---	---
Settled	9.75	9.59	10.1	10.09	25	25	25	25	2.5	---	0.6	ND[b]
Filter eff.	9.60	9.51	9.8	9.96	25	25	25	25	1.4	3.6	0.4	0.9
Ozone eff.	9.23	9.24	9.4	9.55	25	25	25	25	>0.9	2.7	trace	1.0
Plant eff.	8.95	8.91	9.0	9.07	25	25	25	25	5.0	4.8	4.9	4.7
Dist. syst.	8.98	8.95	9.0	9.08	25	25	25	25	4.4	3.6	4.6	4.1
SDS	NA	NA	NA	9.07	NA	NA	NA	25	NA	NA	NA	4.7

[a]Chloramine residuals
[b]ND = Not detected

Table 4. Water quality information at plant 8

	pH				Temperature (ºC)				Disinfectant Residual[a] (mg/L)			
Location	12/11/00	3/12/01	9/24/01	1/14/02	12/11/00	3/12/01	9/24/01	1/14/02	12/11/00	3/12/01	9/24/01	1/14/02
Raw water	7.05	7.02	7.2	7.19	24.8	24.8	24.6	24.2	---	---	---	---
Lime Softening												
Settled	9.7	10.4	NA	10.52	24.4	25.0	NA	23.9	1.1	0.4	NA	1.6
Filter eff.	9.2	10.0	10.2	10.16	25.6	25.3	24.8	23.9	5.0	3.5+	5.9	3.5+
Membrane Softening												
Memb. eff	5.5	5.38	5.4	5.55	25.0	25.4	23.8	24.4	---	---	---	---
Stripper tower eff.	8.1	7.30	9.1	6.81	25.0	25.2	24.2	25.1	5.5	3.5+	4.7	3.5+
Combined Treated Waters												
Plant eff.	8.8	8.93	9.0	8.75	25.0	26.7	24.3	25.1	4.1	3.5+	4.6	3.5+
Dist. syst.	8.8	8.90	9.0	8.95	25.0	25.5	24.9	25.0	4.1	4.0	4.5	4.2
SDS	8.7	NA	8.8	8.8	23.5	NA	23.0	24.2	3.7	NA	4.3	4.0

[a]Chloramine residuals

Table 5. TOC and UV removal at plants 7 and 8

Location	TOC (mg/L)	UV[a] (cm^{-1})	SUVA[b] (L/mg-m)	Removal/Unit (%)		Removal/Cumulative (%)		Flow (mgd)
				TOC	UV	TOC	UV	
12/11/2000								
Plant 7 Raw	12.7	0.470	3.70	---	---	---	---	
Plant 7 Settled	9.21	0.277	3.01	27%	41%	27%	41%	
Plant 7 Filter Eff.	8.85	0.282	3.19	3.9%	-1.8%	30%	40%	
Plant 7 Ozone Eff.	8.55	0.211	2.47	3.4%	25%	33%	55%	
Plant 7 Dist. Syst.	7.87							
Plant 8 Raw	13.4	0.505	3.77	---	---	---	---	
Plant 8 Settled	8.7	0.262	3.01	35%	48%	35%	48%	
Plant 8 Filter Eff.	8.13	0.233	2.87	6.6%	11%	39%	54%	4.5
Plant 8 Membrane Eff.	0.42	0.01	2.38	97%	98%	97%	98%	6.55
Plant 8 Plant Eff./Measured	3.55							11.05
Plant 8 Plant Eff./Predicted[c]	3.56							
Plant 8 Dist. Syst.	3.47							
3/12/2001								
Plant 7 Raw	12.3	0.458	3.72	---	---	---	---	
Plant 7 Settled	9.28	0.283	3.05	25%	38%	25%	38%	
Plant 7 Filter Eff.	8.96	0.283	3.16	3.4%	0%	27%	38%	
Plant 7 Ozone Eff.	8.52	0.179	2.10	4.9%	37%	31%	61%	
Plant 7 Dist. Syst.	8.42							
Plant 8 Raw	12.8	0.494	3.86	---	---	---	---	
Plant 8 Settled	8.84	0.267	3.02	31%	46%	31%	46%	
Plant 8 Filter Eff.	8.44	0.248	2.94	4.5%	7.1%	34%	50%	3.00
Plant 8 Membrane Eff.	0.3	0.013	4.33	98%	97%	98%	97%	8.41
Plant 8 Plant Eff./Measured	2.9							11.41
Plant 8 Plant Eff./Predicted	2.44							
Plant 8 Dist. Syst.	2.82							
9/24/2001								
Plant 7 Raw	12.7	0.465	3.66	---	---	---	---	
Plant 7 Settled	10.0	0.287	2.86	21%	38%	21%	38%	
Plant 7 Filter Eff.	9.3	0.277	2.97	6.9%	3.5%	27%	40%	
Plant 7 Ozone Eff.	9.2	0.224	2.44	1.6%	19%	28%	52%	
Plant 8 Raw	12.4	0.454	3.67	---	---	---	---	
Plant 8 Settled	9.4	0.268	2.85	24%	41%	24%	41%	
Plant 8 Filter Eff.	8.7	0.257	2.96	7.7%	4.1%	30%	43%	3.3
Plant 8 Membrane Eff.	0.39	0.012	3.08	97%	97%	97%	97%	6.8
Plant 8 Plant Eff./Measured	3.5							10.1
Plant 8 Plant Eff./Predicted	3.1							
Plant 8 Dist. Syst.	3.3							
01/14-16/2002								
Plant 7 Raw	12.6	0.454	3.60	---	---	---	---	
Plant 7 Settled	9.5	0.262	2.76	25%	42%	25%	42%	
Plant 7 Filter Eff.	9.3	0.248	2.68	2.2%	5.3%	26%	45%	
Plant 7 Ozone Eff.	9.2	0.213	2.32	0.9%	13%	27%	53%	
Plant 7 Dist. Syst.	8.8							
Plant 8 Raw	11.3	0.414	3.66	---	---	---	---	
Plant 8 Settled	8.8	0.248	2.82	22%	40%	22%	40%	
Plant 8 Filter Eff.	8.0	0.233	2.90	8.6%	6.0%	29%	44%	3.0
Plant 8 Membrane Eff.	0.28	0.01	3.57	98%	98%	98%	98%	8.6
Plant 8 Plant Eff./Measured	2.5							11.6
Plant 8 Plant Eff./Predicted	2.3							
Plant 8 Dist. Syst.	2.6							

[a]UV = Ultraviolet absorbance reported in units of "inverse centimeters" (APHA, 1998)

[b]SUVA (L/mg-m) = Specific ultraviolet absorbance = 100*UV (cm^{-1})/DOC (mg/L) or UV (m^{-1})/DOC (mg/L),
where DOC = dissolved organic carbon, which typically = 90-95% TOC (used TOC values in calculating SUVA)
(e.g., UV = 0.470/cm = 0.470/(0.01 m) = 47.0/m, DOC = 12.7 mg/L, SUVA = (47.0 m^{-1})/(12.7 mg/L) = 3.70 L/mg-m)

[c](lime softening flow)*(filter effluent TOC) + (membrane softening flow)*(membrane effluent TOC) = plant effluent TOC

Table 6. Miscellaneous water quality parameters at plants 7 and 8

Location	Bromide (mg/L)	Alkalinity (mg/L)	Ammonia (mg/L as N)	Chlorine Demand[a] (mg/L)
12/11/2000				
Plant 7 Raw	0.12	265	0.73	5.5
Plant 8 Raw	0.33	249	0.62	4.7
Plant 8 Membrane Eff.	0.11			
Plant 8 Bromide Rejection (%)	66%			
3/12/2001				
Plant 7 raw water	0.14	265	0.69	5.2
Plant 8 raw water	0.3	250	0.62	4.7
Plant 8 membrane effluent	0.1			
Plant 8 bromide rejection (%)	67%			
9/24/2001				
Plant 7 Raw	0.14	264	0.62	4.7
Plant 8 Raw	0.25	236	0.48	3.6
Plant 8 Membrane Eff.	0.1			
Plant 8 Bromide Rejection (%)	60%			
01/14-16/2002				
Plant 7 Raw	0.14	130	0.67	5.1
Plant 8 Raw	0.27	236	0.46	3.5
Plant 8 Membrane Eff.	0.1			
Plant 8 Bromide Rejection (%)	63%			

[a]Chlorine demand from ammonia = 7.6 x ammonia (mg/L as N)

Biodegradable Organic Matter. Ozone can convert natural organic matter in water to carboxylic acids (Kuo et al., 1996) and other assimilable organic carbon (AOC) (van der Koiij et al., 1982). Table 7 shows the carboxylic acid and AOC data for all four sampling dates at plant 7. In addition, Figure 3 shows the AOC results for the December 2000, March 2001, and September 2001 samplings. Low concentrations of AOC and certain carboxylic acids were detected in the raw water at plant 7. Those levels increased somewhat after chloramination and increased significantly after ozonation (except for the AOC in September 2001).

Because AOC data are expressed in units of micrograms of carbon per liter (µg C/L), the carboxylic acid data were converted to the same units. A portion of the molecular weight (MW) of each carboxylic acid is due to carbon atoms (i.e., 27-49 %) and the remainder is due to oxygen and hydrogen atoms. The sums of the five carboxylic acids (on a µg C/L basis) were compared to the AOC data. On a median basis for each sample date, 23-30 % of the AOC was accounted for by the carboxylic acids. The amount of AOC that was accounted for by carboxylic acids in the ozone contactor effluent was typically greater than the percentage accounted for in the chloraminated water. Although carboxylic acids have been shown to be ozone by-products, they have not been shown to be by-products of chloramines. However, in other research (Jacangelo et

Table 7. Formation and removal of carboxylic acids and AOC at plant 7

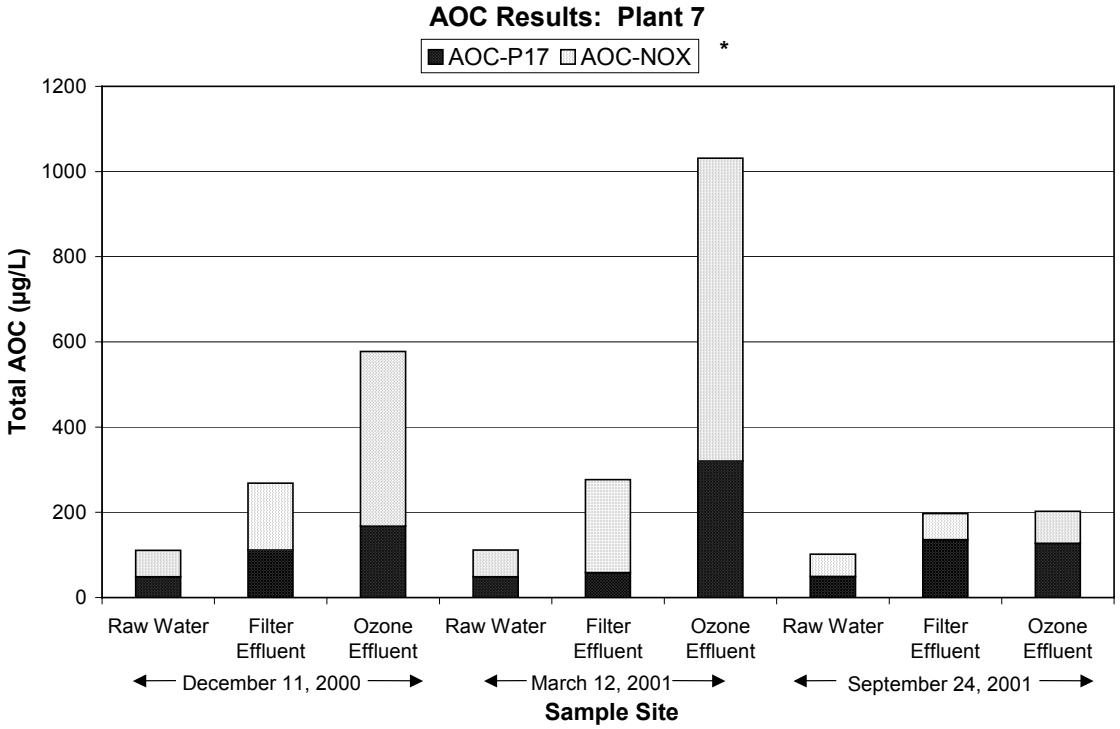
Location	Concentration[a] (µg/L)					Concentration (µg C/L)							Sum/ AOC
	Acetate	Propionate	Formate	Pyruvate	Oxalate	Acetate	Propionate	Formate	Pyruvate	Oxalate	Sum	AOC	
12/11/2000													
Plant 7 Raw	35	ND[b]	37	NR[c]	21	14	ND	9.8	NR	5.8	30	111	27%
Plant 7 Filter Eff.	50	ND	50	NR	54	20	ND	13	NR	15	48	269	18%
Plant 7 Ozone Eff.	150	ND	247	NR	324	61	ND	66	NR	88	215	577	37%
												median	27%
3/12/2001													
Plant 7 Raw	ND	ND	23	ND	ND	ND	ND	6.1	ND	ND	6.1	112	5%
Plant 7 Filter Eff.	41	ND	59	44	60	17	ND	16	18	16	67	277	24%
Plant 7 Ozone Eff.	223	ND	369	52	657	91	ND	98	22	179	390	1031	38%
												median	24%
9/24/2001													
Plant 7 Raw	*7.1*	ND	*8.5*	ND	*5.7*	*2.9*	ND	*2.3*	ND	*1.6*	6.7	102	7%
Plant 7 Filter Eff.	37	ND	37	17	35	15	ND	10	7.0	10	41	197	21%
Plant 7 Ozone Eff.	102	*5.2*	177	24	235	41	*2.6*	47	10	64	165	203	81%
												median	23%
1/14/2002													
Plant 7 Raw	*11*	ND	73	ND	19	*4.6*	ND	19	ND	5.1	29	98	30%
Plant 7 Filter Eff.	28	ND	122	27	37	11	ND	33	11	10	65	147	44%
Plant 7 Ozone Eff.	102	ND	223	40	279	41	ND	59	16	76	194	657	29%
												median	30%
Formula	$CH3COO^-$	$CH_3CH_2COO^-$	$HCOO^-$	CH_3COCOO^-	$C_2O_4^{2-}$								
MW (gm/mole)	59	73	45	87	88								
C portion (gm/mole)	24	36	12	36	24								
C% of MW	41%	49%	27%	41%	27%								

[a]Method detection limit (MDL) = 3 µg/L; reporting detection level (RDL) = 15 µg/L
Values > MDL but < RDL shown in italics

[b]ND = Not detected, value is < RDL

[c]NR = Not reported, quality control problem

Figure 3



*AOC evaluated with two test bacteria: *Pseudomonas fluorescens* P-17 and *Spirillum* NOX

al., 1989), chloramines have been shown to be capable of producing aldehydes—other ozone by-products—at lower levels than that produced during ozonation.

Halogenated Organic and Other Nonhalogenated Organic DBPs. Tables 8 and 9 (12/11/00), Tables 11 and 12 (3/12/01), Tables 14 and 15 (9/24/01), and Tables 17 and 18 (1/14-16/02) show results for the halogenated organic DBPs that were analyzed at Metropolitan Water District of Southern California (MWDSC). Table 10 (12/11/00 [plant 7] and Table 16 (9/24/01 [plant 8]) show results from broadscreen DBP analyses conducted at the U.S. Environmental Protection Agency (USEPA). Table 13 (3/12/01) and Table 19 (1/14-16/02) show results for additional target DBPs that were analyzed for at the University of North Carolina (UNC). Tables 20-21 (1/14-16/02) show results for halogenated furanones that were analyzed at UNC.

Summary of tables for halogenated organic and other nonhalogenated organic DBPs

DBP Analyses (Laboratory)	12/11/00	3/12/01	9/24/01	1/14-16/02
Halogenated organic DBPs (MWDSC)	Tables 8-9	Tables 11-12	Tables 14-15	Tables 17-18
Additional target DBPs (UNC)		Table 13		Table 19
Halogenated furanones (UNC)				Tables 20-21
Broadscreen analysis (USEPA)	Table 10[a]		Table 16[b]	

[a]Plant 7
[b]Plant 8

Table 8. DBP results at plant 7 (12/11/00)

12/11/2000	MRL[a]	Plant 7[b]						
Compound	µg/L	Raw	Settled	Filt Eff	O3 Eff	Plant Eff	DS	SDS
Halomethanes								
Chloromethane	0.15	ND[d]		ND		ND	ND	ND
Bromomethane	0.20	ND		ND		ND	ND	ND
Bromochloromethane	0.14	ND		ND		ND	ND	ND
Dibromomethane	0.11	ND		ND		ND	ND	ND
Chloroform[e]	0.10	ND	10	17	16	17	16	17
Bromodichloromethane[e]	0.10	ND	1	1	NR[f]	1	1	1
Dibromochloromethane[e]	0.12	ND	ND	0.1	NR	0.1	0.1	0.1
Bromoform[e]	0.12	ND	ND	ND	ND	ND	ND	0.3
THM4[g]		ND	11	18	NR	18	17	18
Dichloroiodomethane	0.10	ND	ND	ND	ND	0.3	ND	0.2
Bromochloroiodomethane	3	ND	NR	ND	NR	ND	ND	<1[h]
Dibromoiodomethane	0.64	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.10	ND	ND	0.2	ND	ND	ND	0.2
Bromodiiodomethane	0.12	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.14	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.06	ND		ND		ND	0.07	ND
Haloacetic acids								
Monochloroacetic acid[e]	2		ND	ND		2.2	ND	2.6
Monobromoacetic acid[e]	1		1.2	1.3		1.6	1.4	1.5
Dichloroacetic acid[e]	1		6.5	12		20	22	27
Bromochloroacetic acid[e]	1		ND	1.1		1.7	1.7	2.0
Dibromoacetic acid[e]	1		ND	ND		ND	1.0	ND
Trichloroacetic acid[e]	1		1.1	3.2		3.4	3.0	3.3
Bromodichloroacetic acid	1		ND	ND		ND	ND	ND
Dibromochloroacetic acid	1		ND	ND		ND	ND	ND
Tribromoacetic acid	2		ND	ND		ND	ND	ND
HAA5[i]			8.8	16		27	27	34
HAA9[j]			8.8	17		29	29	36
DXAA[k]			6.5	13		22	24	29
TXAA[l]			1.1	3.2		3.4	3.0	3.3
Haloacetonitriles								
Chloroacetonitrile	0.10	ND	ND	ND	ND	ND	ND	ND
Bromoacetonitrile	0.10	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[e]	0.10	ND	ND	ND	0.2	0.3	ND	ND
Bromochloroacetonitrile[e]	0.10	ND	ND	ND	ND	ND	ND	ND
Dibromoacetonitrile[e]	0.10	ND	ND	ND	ND	ND	ND	ND
Trichloroacetonitrile[e]	0.10	ND	ND	ND	ND	ND	ND	ND
Haloacetaldehydes								
Dichloroacetaldehyde	0.16	ND	1	3	12	14	15	16
Bromochloroacetaldehyde[m]								
Chloral hydrate[e]	0.20	ND	ND	ND	0.3	0.5	0.5	0.5
Tribromoacetaldehyde	0.10	ND	ND	ND	ND	ND	ND	ND

Table 8 (continued)

12/11/2000	MRL[a]	Plant 7[b]						
Compound	µg/L	Raw	Settled	Filt Eff	O3 Eff	Plant Eff	DS	SDS
Haloketones								
Chloropropanone	0.10	ND	ND	0.3	0.6	2	1	2
1,1-Dichloropropanone[e]	0.10	ND	ND	0.3	0.5	2	ND	ND
1,3-Dichloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	3	ND		ND		ND	ND	ND
1,1,1-Trichloropropanone[e]	0.10	ND	ND	ND	ND	ND	ND	ND
1,1,3-Trichloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	3	ND		ND		ND	ND	ND
1,1,1-Tribromopropanone	3	ND		ND		ND	ND	ND
1,1,3-Tribromopropanone	3	ND		ND		ND	ND	ND
1,1,3,3-Tetrachloropropanone	0.10	ND	ND	0.1	ND	ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.10	ND	0.2	0.2	0.1	0.1	ND	ND
Halonitromethanes								
Bromonitromethane	0.10	ND	ND	ND	ND	ND	ND	0.1
Dichloronitromethane	3	NR		NR		NR	NR	NR
Dibromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[e]	0.10	ND	ND	ND	ND	ND	ND	ND
Miscellaneous Compounds								
Methyl ethyl ketone	1.90	ND		ND		ND	ND	ND
Methyl *tertiary* butyl ether	0.16	ND		ND		ND	ND	ND
Benzyl chloride	0.50	ND	NR	ND	NR	ND	ND	ND

[a]MRL = Minimum reporting level, which equals method detection limit (MDL) or lowest calibration standard or concentration of blank

[b]Plant 7 sampled at (1) raw water, (2) settled water, (3) filter effluent (FE), (4) effluent of ozone contactor, (5) plant effluent (PE), (6) distribution system (DS), and (7) SDS testing of plant effluent

[c]Plant 8 sampled at (1) raw water; lime softening portion of plant at (2) settled water, (3) filter effluent; membrane softening portion of plant at (4) effluent of stripper towers; combined treated waters at (5) plant effluent, (6) DS, and (7) SDS testing of plant effluent

[d]ND = Not detected at or above MRL

[e]DBP in the Information Collection Rule (ICR) (note: some utilities collected data for all 9 haloacetic acids for the ICR, but monitoring for only 6 haloacetic acids was required)

[f]NR = Not reported, due to interference problem on gas chromatograph or to problem with quality assurance

[g]THM4 = Sum of 4 THMs (chloroform, bromodichloromethane, dibromochloromethane, bromoform)

[h]<1: Concentration less than lowest calibration standard (i.e., 1 µg/L)

[i]HAA5 = Sum of 5 haloacetic acids (monochloro-, monobromo-, dichloro-, dibromo-, trichloroacetic acid)

[j]HAA9 = Sum of 9 haloacetic acids

[k]DXAA = Sum of dihaloacetic acids (dichloro-, bromochloro-, dibromoacetic acid)

[l]TXAA = Sum of trihaloacetic acids (trichloro-, bromodichloro-, dibromochoro-, tribromoacetic acid)

[m]Bromochloroacetaldehyde and chloral hydrate co-eulte; result = sum of 2 DBPs

Table 9. DBP results at plant 8 (12/11/00)

12/11/2000	MRL[a]	Plant 8[c]						
Compound	µg/L	Raw	Settled	Filt Eff	Tower Eff	Plant Eff	DS	SDS
Halomethanes								
Chloromethane	0.15			0.2	ND	ND	ND	ND
Bromomethane	0.20			ND	ND	ND	ND	ND
Bromochloromethane	0.14			ND	ND	ND	ND	ND
Dibromomethane	0.11			ND	ND	ND	ND	ND
Chloroform[e]	0.10	0.6	15	90	1	57	61	61
Bromodichloromethane[e]	0.10	ND	NR	22	1	9	9	9
Dibromochloromethane[e]	0.12	ND	NR	3	0.5	1	1	1
Bromoform[e]	0.12	ND	ND	0.4	0.5	0.8	0.9	0.8
THM4[g]		0.6	NR	115	3	68	72	72
Dichloroiodomethane	0.10	ND	ND	2	0.8	1	1	1
Bromochloroiodomethane	3	ND	NR	<1	<1	<1	<1	<1
Dibromoiodomethane	0.64	ND	ND	<1	<1	<1	<1	<1
Chlorodiiodomethane	0.10	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.12	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.14	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.06			ND	ND	ND	ND	ND
Haloacetic acids								
Monochloroacetic acid[e]	2		ND	ND	ND	ND	ND	ND
Monobromoacetic acid[e]	1		1.3	1.7	1.3	1.5	1.4	1.4
Dichloroacetic acid[e]	1		7.6	35	1.7	21	20	24
Bromochloroacetic acid[e]	1		1.0	6.3	ND	3.2	2.7	4.4
Dibromoacetic acid[e]	1		ND	1.0	1.1	ND	1.0	1.2
Trichloroacetic acid[e]	1		1.8	15	ND	5.8	5.0	6.4
Bromodichloroacetic acid	1		ND	3.2	ND	1.1	1.1	1.3
Dibromochloroacetic acid	1		ND	1.0	ND	ND	ND	ND
Tribromoacetic acid	2		ND	ND	ND	ND	ND	ND
HAA5[i]			11	53	4.1	28	27	33
HAA9[j]			12	64	4.1	33	31	38
DXAA[k]			8.6	42	2.8	24	23	29
TXAA[l]			1.8	19	ND	6.9	6.1	7.7
Haloacetonitriles								
Chloroacetonitrile	0.10	ND	ND	ND	ND	ND	ND	ND
Bromoacetonitrile	0.10	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[e]	0.10	ND	ND	8	0.2	0.6	0.6	0.2
Bromochloroacetonitrile[e]	0.10	ND	ND	2	0.2	0.4	0.4	0.2
Dibromoacetonitrile[e]	0.10	ND	ND	0.2	0.2	0.2	0.2	0.1
Trichloroacetonitrile[e]	0.10	ND	ND	ND	ND	ND	ND	ND
Haloacetaldehydes								
Dichloroacetaldehyde	0.16	ND	1	3	ND	2	1	3
Bromochloroacetaldehyde[m]								
Chloral hydrate[e]	0.20	ND	ND	13	0.2	1.6	1.5	0.2
Tribromoacetaldehyde	0.10	ND	ND	ND	ND	ND	ND	ND

Table 9 (continued)

12/11/2000	MRL[a]	Plant 8[c]						
Compound	µg/L	Raw	Settled	Filt Eff	Tower Eff	Plant Eff	DS	SDS
Haloketones								
Chloropropanone	0.10	ND	ND	0.3	ND	0.3	0.2	0.3
1,1-Dichloropropanone[e]	0.10	ND	ND	0.4	ND	0.2	0.2	0.2
1,3-Dichloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	3			ND	ND	ND	ND	ND
1,1,1-Trichloropropanone[e]	0.10	ND	ND	0.9	0.1	ND	ND	ND
1,1,3-Trichloropropanone	0.10	ND	0.2	0.2	ND	0.1	0.1	ND
1-Bromo-1,1-dichloropropanone	3			ND	ND	ND	ND	ND
1,1,1-Tribromopropanone	3			ND	ND	ND	ND	ND
1,1,3-Tribromopropanone	3			ND	ND	ND	ND	ND
1,1,3,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.10	0.1	ND	0.1	ND	0.1	ND	0.1
Halonitromethanes								
Bromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	3			NR	NR	NR	NR	NR
Dibromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[e]	0.10	ND	ND	0.4	ND	0.4	0.4	0.4
Miscellaneous Compounds								
Methyl ethyl ketone	1.90			ND	ND	ND	ND	ND
Methyl *tertiary* butyl ether	0.16			ND	ND	ND	ND	ND
Benzyl chloride	0.50	ND	NR	ND	ND	ND	ND	ND

Table 10. Occurrence of other DBPs[a] at plant 7 (12/11/00)

Compound	FE	PE
Halomethanes		
Bromodichloromethane[b]	x	x
Dibromochloromethane	x	x
Bromoform	x	x
Dichloroiodomethane	x	x
Bromochloroiodomethane	x	x
Diiodochloromethane	x	x
Haloacids		
Dichloroacetic acid	x	x
Bromochloroacetic acid	x	x
Dibromoacetic acid	x	x
Trichloroacetic acid	x	x
Haloacetonitriles		
Bromochloroacetonitrile	x	x
Dibromoacetonitrile	x	x
Haloaldehydes		
Dibromoacetaldehyde	-	x
2-Bromo-2-methylpropanal	x	x
Halonitromethanes		
Dichloronitromethane	x	x
Bromochloronitromethane	-	x

Compound	FE	PE
Haloketones		
1,1-Dichloropropanone	x	x
1-Bromo-1-chloropropanone	x	x
1,1,1-Trichloropropanone	x	x
1,1,3-Trichloropropanone	x	x
1-Bromo-1,1-dichloropropanone	x	x
1,1,3-Tribromopropanone	x	x
1,1,3,3-Tetrachloropropanone	x	x
1-Bromo-1,3,3-trichloropropanone	x	x
1,1-Dibromo-3,3-dichloropropanone	x	x
1,3-Dibromo-1,3-dichloropropanone	-	x
1,1,3-Tribromo-3-chloropropanone	-	x
1,1,3,3-Tetrabromopropanone	-	x
Pentachloropropanone	x	x
Miscellaneous Halogenated DBPs		
Hexachlorocyclopentadiene	x	x
Bromopentachlorocyclopentadiene	x	x
Non-halogenated DBPs		
Formaldehyde	-	x
Acetone	-	x
Glyoxal	-	x
Methyl glyoxal	-	x

[a]DBPs detected by broadscreen gas chromatography/mass spectrometry (GC/MS) technique
[b]Compounds listed in italics were confirmed through the analysis of authentic standards; haloacids and non-halogenated carboxylic acids identified as their methyl esters.

Table 11. DBP results at plant 7 (3/12/01)

03/12/2001	MRL[a]	Plant 7[b]						
Compound	µg/L	Raw	Settled	Filt Eff	O3 Eff	Plant Eff	DS	SDS
Halomethanes								
Chloromethane	0.15	ND[d]		ND		ND	ND	ND
Bromomethane	0.20	ND		ND		ND	ND	ND
Bromochloromethane	0.14	ND		ND		ND	ND	ND
Dibromomethane	0.11	ND		ND		ND	ND	ND
Chloroform[e]	0.1	ND	8	15	14	13	21	24
Bromodichloromethane[e]	0.1	ND	0.8	3	3	2	3	4
Dibromochloromethane[e]	0.10	ND	ND	ND	ND	ND	ND	0.2
Bromoform[e]	0.12	ND	ND	ND	ND	ND	ND	ND
THM4[g]		ND	9	18	17	15	24	27
Dichloroiodomethane	0.25	ND	NR[f]	ND	NR	ND	ND	ND
Bromochloroiodomethane	3	ND	NR	ND	NR	ND	ND	ND
Dibromoiodomethane	0.60	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.51	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.56	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.54	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.06	ND		0.2		0.4	0.5	0.4
Tribromochloromethane	0.1	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids								
Monochloroacetic acid[e]	2		ND	ND		2.8	2.6	3.6
Monobromoacetic acid[e]	1		ND	ND		ND	ND	ND
Dichloroacetic acid[e]	1		7.4	12		22	20	32
Bromochloroacetic acid[e]	1		ND	1.0		1.7	1.5	2.1
Dibromoacetic acid[e]	1		ND	ND		ND	ND	ND
Trichloroacetic acid[e]	1		1.2	4.0		5.1	3.5	5.6
Bromodichloroacetic acid	1		ND	ND		ND	ND	ND
Dibromochloroacetic acid	1		ND	ND		ND	ND	ND
Tribromoacetic acid	2		ND	ND		ND	ND	ND
HAA5[i]			8.6	16		30	26	41
HAA9[j]			8.6	17		32	28	43
DXAA[k]			7.4	13		24	22	34
TXAA[l]			1.2	4.0		5.1	3.5	5.6
Haloacetonitriles								
Chloroacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[e]	0.10	ND	ND	0.2	0.2	0.5	0.2	0.3
Bromochloroacetonitrile[e]	0.1	ND	ND	ND	ND	ND	ND	ND
Dibromoacetonitrile[e]	0.17	ND	ND	ND	ND	ND	ND	ND
Trichloroacetonitrile[e]	0.1	ND	ND	ND	ND	ND	ND	ND
Haloacetaldehydes								
Dichloroacetaldehyde	0.16	ND	0.8	3	6	9	9	10
Bromochloroacetaldehyde	0.1	ND	ND	0.2	ND	0.1	ND	ND
Chloral hydrate[e]	0.1	ND	ND	0.1	ND	0.7	0.5	0.6
Tribromoacetaldehyde	0.1	ND	ND	ND	ND	ND	ND	ND

Table 11 (continued)

03/12/2001	MRL[a]	Plant 7[b]						
Compound	µg/L	Raw	Settled	Filt Eff	O3 Eff	Plant Eff	DS	SDS
Haloketones								
Chloropropanone	0.5	ND	ND	ND	ND	0.7	ND	ND
1,1-Dichloropropanone[e]	0.11	ND	ND	0.2	0.5	1	0.5	0.8
1,3-Dichloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	3	ND		ND		ND	ND	ND
1,3-Dibromopropanone	3	ND		ND		ND	ND	ND
1,1,1-Trichloropropanone[e]	0.10	ND	ND	ND	ND	ND	ND	ND
1,1,3-Trichloropropanone	0.11	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	3	ND		ND		ND	ND	ND
1,1,1-Tribromopropanone	3	ND		ND		ND	ND	ND
1,1,3-Tribromopropanone	3	ND		ND		ND	ND	ND
1,1,3,3-Tetrachloropropanone	0.12	ND	ND	ND	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	3	ND		ND		ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.5	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes								
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	3	ND		ND		ND	ND	ND
Bromochloronitromethane	3	ND		ND		ND	ND	ND
Dibromonitromethane	0.12	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[e]	0.1	ND	ND	ND	ND	ND	ND	ND
Miscellaneous Compounds								
Methyl ethyl ketone	1.90	ND		ND		ND	ND	ND
Methyl *tertiary* butyl ether	0.16	ND		ND		ND	ND	ND
Benzyl chloride	2	ND	ND	ND	ND	ND	ND	ND

Table 12. DBP results at plant 8 (3/12/01)

03/12/2001	MRL[a]	Plant 8[c]						
Compound	µg/L	Raw	Settled	Filt Eff	Tower Eff	Plant Eff	DS	SDS
Halomethanes								
Chloromethane	0.15			ND	ND	ND	ND	ND
Bromomethane	0.20			ND	ND	ND	ND	ND
Bromochloromethane	0.14			ND	ND	ND	ND	ND
Dibromomethane	0.11			ND	ND	ND	ND	ND
Chloroform[e]	0.1	ND	14	81	1	41	42	42
Bromodichloromethane[e]	0.1	ND	3	15	0.6	7	7	7
Dibromochloromethane[e]	0.10	ND	0.2	2	0.2	2	2	2
Bromoform[e]	0.12	ND	ND	ND	ND	ND	ND	ND
THM4[g]		ND	17	98	2	50	51	50
Dichloroiodomethane	0.25	NR	NR	2	ND	0.7	0.6	0.7
Bromochloroiodomethane	3	NR	NR	<1[h]	ND	<1	<1	<1
Dibromoiodomethane	0.60	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.51	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.56	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.54	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.06			0.7	ND	0.5	0.5	0.4
Tribromochloromethane	0.1	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids								
Monochloroacetic acid[e]	2		ND	ND	2.4	ND	2.2	ND
Monobromoacetic acid[e]	1		ND	ND	ND	ND	ND	ND
Dichloroacetic acid[e]	1		6.3	36	1.0	14	14	15
Bromochloroacetic acid[e]	1		1.0	3.8	ND	2.0	2.2	2.3
Dibromoacetic acid[e]	1		ND	ND	ND	ND	ND	ND
Trichloroacetic acid[e]	1		1.3	9.1	ND	2.5	2.4	2.5
Bromodichloroacetic acid	1		ND	1.6	ND	ND	ND	ND
Dibromochloroacetic acid	1		ND	ND	ND	ND	ND	ND
Tribromoacetic acid	2		ND	ND	ND	ND	ND	ND
HAA5[i]			7.6	45	3.4	17	19	18
HAA9[j]			8.6	51	3.4	19	21	20
DXAA[k]			7.3	40	1.0	16	16	17
TXAA[l]			1.3	11	ND	2.5	2.4	2.5
Haloacetonitriles								
Chloroacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[e]	0.10	ND	ND	3	0.1	0.5	0.5	0.2
Bromochloroacetonitrile[e]	0.1	ND	ND	ND	ND	ND	ND	ND
Dibromoacetonitrile[e]	0.17	ND	ND	ND	ND	ND	ND	ND
Trichloroacetonitrile[e]	0.1	ND	ND	ND	ND	ND	ND	ND
Haloacetaldehydes								
Dichloroacetaldehyde	0.16	0.2	0.3	0.8	ND	0.7	0.7	1
Bromochloroacetaldehyde	0.1	ND	ND	ND	ND	ND	ND	ND
Chloral hydrate[e]	0.1	ND	ND	5.7	0.5	0.4	0.4	0.3
Tribromoacetaldehyde	0.1	ND	ND	ND	ND	ND	ND	ND

Table 12 (continued)

03/12/2001	MRL[a]	Plant 8[c]						
Compound	µg/L	Raw	Settled	Filt Eff	Tower Eff	Plant Eff	DS	SDS
Haloketones								
Chloropropanone	0.5	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloropropanone[e]	0.11	ND	ND	0.3	ND	0.1	0.1	0.1
1,3-Dichloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	3			ND	ND	ND	ND	ND
1,3-Dibromopropanone	3			ND	ND	ND	ND	ND
1,1,1-Trichloropropanone[e]	0.10	ND	ND	0.2	ND	ND	ND	ND
1,1,3-Trichloropropanone	0.11	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	3			ND	ND	ND	ND	ND
1,1,1-Tribromopropanone	3			ND	ND	ND	ND	ND
1,1,3-Tribromopropanone	3			ND	ND	ND	ND	ND
1,1,3,3-Tetrachloropropanone	0.12	ND	ND	ND	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	3			ND	ND	ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.5	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes								
Bromonitromethane	0.1	ND	ND	ND	ND	0.3	0.3	0.1
Dichloronitromethane	3			ND	ND	ND	ND	ND
Bromochloronitromethane	3			ND	ND	ND	ND	ND
Dibromonitromethane	0.12	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[e]	0.1	ND	ND	0.2	ND	0.1	0.1	0.2
Miscellaneous Compounds								
Methyl ethyl ketone	1.90			ND	ND	ND	ND	ND
Methyl *tertiary* butyl ether	0.16			0.9	ND	ND	ND	ND
Benzyl chloride	2	ND	ND	ND	ND	ND	ND	ND

Table 13. Additional target DBP results (µg/L) at plants 7 and 8 (3/12/01)

3/12/01	Plant 7[a]						Plant 8[a]					
Compound	Raw	FE	OE	PE	DS	SDS	Raw	FE	STE	PE	DS	SDS
Monochloroacetaldehyde	0	0.2	1.2	0.7	0.5	0.5	0	0	0	0	0	0
Dichloroacetaldehyde	0	2.4	4.4	6.8	7.6	8.6	0.1	0.7	0	0.5	0.6	0.6
Bromochloroacetaldehyde												
3,3-Dichloropropenoic acid	0.6				0.4		0				0	
Bromochloromethylacetate	0				0		0				0	
2,2-Dichloroacetamide	0	0.2	0.1	1.8	2.5	3.0	0	4.0	0	2.1	2.2	3.4
TOX (µg/L as Cl^-)	24.2	205	127	203	121	207	33.0	459	41	142	157	130
Cyanoformaldehyde	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
5-Keto-1-hexanal	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6-Hydroxy-2-hexanone	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Dimethylglyoxal	0.4	0.2	4.0	3.5	1.4	1.9	0.3	<0.1	<0.1	<0.1	<0.1	<0.1
trans-2-Hexenal	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

[a]Plant 7 or plant 8 sampled at (1) raw water, (2) filter effluent (FE), (3) ozone contactor effluent (OE) or stripper tower effluent (STE), (4) finished water at plant effluent (PE), (5) distribution system (DS) at average detention time, and (6) SDS sample.

Table 14. DBP results at plant 7 (9/24/01)

09/24/2001	MRL[a]	Plant 7[b]						
Compound	µg/L	Raw	Settled	Filt Eff	O3 Eff	Plant Eff	DS	SDS
Halomethanes								
Chloromethane	0.2	ND[d]		ND		ND	0.2	ND
Bromomethane	0.2	ND		ND		ND	ND	ND
Bromochloromethane	0.5	ND		ND		ND	ND	ND
Dibromomethane	0.5	ND		ND		ND	ND	ND
Chloroform[e]	0.1	ND	3	3	3	7	11	12
Bromodichloromethane[e]	0.1	ND	0.3	0.3	0.4	1	1	1
Dibromochloromethane[e]	0.1	ND	ND	ND	ND	0.1	0.1	0.2
Bromoform[e]	0.1	ND	ND	ND	ND	ND	ND	ND
THM4[g]		ND	3	3	3	8	12	13
Dichloroiodomethane	0.5	ND	NR[f]	ND	NR	ND	0.6	0.6
Bromochloroiodomethane	0.25	ND	NR	ND	NR	ND	ND	ND
Dibromoiodomethane	0.52	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.1	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.1	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.2	ND		ND		ND	ND	ND
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids								
Monochloroacetic acid[e]	2		ND	ND		4.2	3.7	4.4
Monobromoacetic acid[e]	1		ND	ND		ND	ND	ND
Dichloroacetic acid[e]	1		4.7	4.2		16	16	20
Bromochloroacetic acid[e]	1		ND	ND		1.9	1.6	1.8
Dibromoacetic acid[e]	1		ND	ND		ND	ND	ND
Trichloroacetic acid[e]	1		1.1	1.1		2.0	2.5	2.3
Bromodichloroacetic acid	1		ND	ND		ND	ND	ND
Dibromochloroacetic acid	1		ND	ND		ND	ND	ND
Tribromoacetic acid	2		ND	ND		ND	ND	ND
HAA5[i]			5.8	5.3		22	22	27
HAA9[j]			5.8	5.3		24	24	29
DXAA[k]			4.7	4.2		18	18	22
TXAA[l]			1.1	1.1		2.0	2.5	2.3
Haloacetonitriles								
Chloroacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[e]	0.1	ND	0.3	0.1	0.2	0.6	0.6	0.3
Bromochloroacetonitrile[e]	0.1	ND	ND	ND	ND	ND	ND	ND
Dibromoacetonitrile[e]	0.1	ND	ND	ND	ND	ND	ND	ND
Trichloroacetonitrile[e]	0.1	ND	ND	ND	ND	ND	ND	ND
Bromodichloroacetonitrile	0.5	ND		ND	ND	ND		
Dibromochloroacetonitrile	0.5	ND		ND	ND	ND		
Tribromoacetonitrile	0.90	ND		ND	ND	ND		
Haloacetaldehydes								
Dichloroacetaldehyde	0.22	ND	0.9	1	2	14	14	15
Bromochloroacetaldehyde	0.5	ND	ND	ND	ND	ND	ND	ND
Chloral hydrate[e]	0.1	0.6	0.6	0.6	0.4	0.6	0.4	0.3
Tribromoacetaldehyde	0.1	ND	ND	ND	ND	ND	ND	ND

Table 14 (continued)

09/24/2001	MRL[a]	Plant 7[b]						
Compound	µg/L	Raw	Settled	Filt Eff	O3 Eff	Plant Eff	DS	SDS
Haloketones								
Chloropropanone	0.1	ND	0.1	0.1	0.4	0.8	0.8	0.8
1,1-Dichloropropanone[e]	0.10	ND	0.3	0.2	0.2	1	1	0.5
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloropropanone[e]	0.1	ND	ND	ND	ND	ND	ND	ND
1,1,3-Trichloropropanone	0.1	ND	ND	0.4	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1,1-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1,3-Tribromopropanone	0.5	ND	ND	0.6	ND	ND	ND	ND
1,1,3,3-Tetrachloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	0.10	ND	ND	0.4	0.1	ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.5	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes								
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	0.1	ND	ND	ND	ND	0.3	0.2	0.3
Bromochloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND
Dibromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[e]	0.1	ND	ND	ND	ND	ND	ND	ND
Bromodichloronitromethane	0.5	ND		ND	ND	1		
Dibromochloronitromethane	0.5	ND		ND	ND	0.8		
Bromopicrin	0.5	ND		ND	ND	ND		
Miscellaneous Compounds								
Methyl ethyl ketone	0.5	ND		ND		1	ND	0.9
Methyl *tertiary* butyl ether	0.2	ND		ND		ND	ND	ND
Benzyl chloride	0.25	ND	NR	ND	NR	ND	ND	ND
1,1,2,2-Tetrabromo-2-chloroethane	0.5	ND	ND	ND	ND	ND	ND	ND

Table 15. DBP results at plant 8 (9/24/01)

09/24/2001	MRL[a]	Plant 8[c]						
Compound	µg/L	Raw	Settled	Filt Eff	Tower Eff	Plant Eff	DS	SDS
Halomethanes								
Chloromethane	0.2			ND	ND	ND	ND	ND
Bromomethane	0.2			ND	ND	ND	ND	ND
Bromochloromethane	0.5			ND	ND	ND	ND	ND
Dibromomethane	0.5			ND	ND	ND	ND	ND
Chloroform[e]	0.1	1	16	63	0.5	35	27	26
Bromodichloromethane[e]	0.1	0.2	2	10	0.4	5	5	5
Dibromochloromethane[e]	0.1	ND	0.2	1	0.2	0.9	1	1
Bromoform[e]	0.1	ND	ND	ND	ND	0.1	0.2	0.2
THM4[g]		1	18	74	1	41	33	32
Dichloroiodomethane	0.5	NR	NR	7	ND	3	2	4
Bromochloroiodomethane	0.25	NR	NR	ND	ND	ND	0.3	0.3
Dibromoiodomethane	0.52	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.1	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.1	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.2			ND	ND	ND	ND	ND
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids								
Monochloroacetic acid[e]	2		ND	4.1	ND	2.4	ND	2.3
Monobromoacetic acid[e]	1		ND	ND	ND	ND	ND	ND
Dichloroacetic acid[e]	1		7.0	28	1.5	18	19	19
Bromochloroacetic acid[e]	1		ND	3.0	ND	2.5	2.6	3.4
Dibromoacetic acid[e]	1		ND	ND	ND	ND	1.0	1.0
Trichloroacetic acid[e]	1		2.0	7.3	ND	3.2	3.3	3.0
Bromodichloroacetic acid	1		ND	1.6	ND	ND	ND	ND
Dibromochloroacetic acid	1		ND	ND	ND	ND	ND	ND
Tribromoacetic acid	2		ND	ND	ND	ND	ND	ND
HAA5[i]			9.0	39	1.5	24	23	25
HAA9[j]			9.0	44	1.5	26	26	29
DXAA[k]			7.0	31	1.5	21	23	23
TXAA[l]			2.0	8.9	ND	3.2	3.3	3.0
Haloacetonitriles								
Chloroacetonitrile	0.1	ND	ND	ND	ND	ND	ND	0.1
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[e]	0.1	ND	ND	2	0.2	0.5	0.8	0.3
Bromochloroacetonitrile[e]	0.1	ND	ND	0.3	0.1	0.4	0.6	0.3
Dibromoacetonitrile[e]	0.1	ND	ND	ND	ND	0.2	0.2	0.1
Trichloroacetonitrile[e]	0.1	ND	ND	ND	ND	ND	ND	ND
Bromodichloroacetonitrile	0.5		ND	ND	ND	ND		
Dibromochloroacetonitrile	0.5		ND	ND	ND	ND		
Tribromoacetonitrile	0.90		ND	ND	ND	ND		
Haloacetaldehydes								
Dichloroacetaldehyde	0.22	0.2	4	2	ND	0.9	2	2
Bromochloroacetaldehyde	0.5	ND	0.6	ND	ND	ND	ND	ND
Chloral hydrate[e]	0.1	0.7	0.9	3	0.2	0.3	0.7	0.3
Tribromoacetaldehyde	0.1	ND	ND	ND	ND	ND	ND	ND

Table 15 (continued)

09/24/2001	MRL[a]	Plant 8[c]						
Compound	µg/L	Raw	Settled	Filt Eff	Tower Eff	Plant Eff	DS	SDS
Haloketones								
Chloropropanone	0.1	ND	0.1	0.2	0.5	0.1	0.2	0.4
1,1-Dichloropropanone[e]	0.10	ND	ND	0.5	0.1	0.3	0.3	0.2
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloropropanone[e]	0.1	ND	ND	0.2	ND	0.1	ND	ND
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1,1-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1,3-Tribromopropanone	0.5	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrachloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	0.10	ND	0.5	0.2	ND	ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.5	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes								
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND
Bromochloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND
Dibromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[e]	0.1	ND	ND	0.2	ND	ND	0.1	0.2
Bromodichloronitromethane	0.5		ND	0.5	ND	0.5		
Dibromochloronitromethane	0.5		ND	ND	ND	0.6		
Bromopicrin	0.5		ND	ND	0.6	0.6		
Miscellaneous Compounds								
Methyl ethyl ketone	0.5			ND	ND	ND	ND	0.9
Methyl *tertiary* butyl ether	0.2			ND	ND	ND	ND	ND
Benzyl chloride	0.25	NR	NR	ND	ND	ND	ND	ND
1,1,2,2-Tetrabromo-2-chloroethane	0.5	ND	ND	ND	ND	ND	ND	ND

Table 16. Occurrence of other DBPs[a] at plant 8 (9/24/01)

Compound	FE	PE
Halomethanes		
Dibromomethane	x	x
Bromodichloromethane[b]	x	x
Dibromochloromethane	x	x
Bromoform	x	x
Dichloroiodomethane	x	x
Bromochloroiodomethane	x	x
Diiodochloromethane	x	x
Haloacids		
Bromoacetic acid	x	-
Dichloroacetic acid	x	x
Bromochloroacetic acid	x	x
Dibromoacetic acid	x	x
Bromodichloroacetic acid	x	x
Trichloroacetic acid	x	x
Haloacetonitriles		
Dichloroacetonitrile	x	x
Bromochloroacetonitrile	x	x
Dibromoacetonitrile	x	x
Haloaldehydes		
Dichloroacetaldehyde	x	x
Dibromoacetaldehyde	-	x
Trichloroacetaldehyde	-	x
2-Bromo-2-methylpropanal	x	x
Haloketones		
Chloropropanone	x	x
1,1-Dichloropropanone	x	x
1-Bromo-1-chloropropanone	x	x
1,1,3-Trichloropropanone	-	x
1-Bromo-1,1-dichloropropanone	-	x
1,1,3,3-Tetrachloropropanone	x	x
1-Bromo-1,3,3-trichloropropanone	x	x
1,1-Dibromo-3,3-dichloropropanone	x	x
1,3-Dibromo-1,3-dichloropropanone	x	x
1,1,3-Tribromo-3-chloropropanone	x	x
1,1,3,3-Tetrabromopropanone	x	x
Halonitromethanes		
Dichloronitromethane	x	x
Bromochloronitromethane	-	x

Compound	FE	PE
Miscellaneous Halogenated DBPs		
Hexachlorocyclopentadiene	x	x
Bromopentachlorocyclopentadiene	x	x
Non-halogenated DBPs		
Acetone	x	x
Propanal	x	x
2-Butanone	x	x
3-Hexanone	x	x
2-Hexanone	x	x
Glyoxal	x	x
Methyl glyoxal	x	x
Heptanoic acid	-	x
Octanoic acid	-	x
Nonanoic acid	-	x
Decanoic acid	-	x
Undecanoic acid	-	x
Dodecanoic acid	-	x
Tetradecanoic acid	-	x
Pentadecanoic acid	-	x
Hexadecanoic acid	-	x
Heptadecanoic acid	-	x
Octadecanoic acid	-	x
Butanedioic acid	-	x
Pentanedioic acid	-	x
Octanedioic acid	-	x
Nonanedioic acid	-	x
Decanedioic acid	-	x
Benzene-1,3-dicarboxylic acid	-	x

[a]DBPs detected by broadscreen gas chromatography/mass spectrometry (GC/MS) technique

[b]Compounds listed in italics were confirmed through the analysis of authentic standards; haloacids and non-halogenated carboxylic acids identified as their methyl esters.

Table 17. DBP results at plant 7 (1/14/02)

1/14/2002	MRL[a]	Plant 7[b]						
Compound	µg/L	Raw	Settled	Filt Eff	O3 Eff	Plant Eff	DS	SDS
Halomethanes								
Chloromethane	0.2	ND[d]		ND		ND	ND	ND
Bromomethane	0.2	ND		ND		ND	ND	ND
Bromochloromethane	0.5	ND		ND		ND	ND	ND
Dibromomethane	0.5	ND		ND		ND	ND	ND
Chloroform[e]	0.2	ND	NR[f]	3	4	6	8	8
Bromodichloromethane[e]	0.2	ND	NR	0.3	0.6	2	1	1
Dibromochloromethane[e]	0.5	ND	ND	0.5	<0.5[n]	<0.5	ND	ND
Bromoform[e]	0.1	ND	ND	ND	ND	ND	ND	ND
THM4[g]		ND	NR	4	5	8	9	9
Dichloroiodomethane	2.5	ND	NR	ND	NR	ND	ND	ND
Bromochloroiodomethane	0.5	ND	NR	ND	ND	ND	ND	ND
Dibromoiodomethane	0.53	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.1	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.52	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.22	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.2	ND		ND	ND	ND	0.2	ND
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids								
Monochloroacetic acid[e]	2		ND	ND		3.7	4.1	5.4
Monobromoacetic acid[e]	1		ND	ND		ND	ND	ND
Dichloroacetic acid[e]	1		ND	3.9		15	15	22
Bromochloroacetic acid[e]	1		ND	ND		1.6	1.6	2.0
Dibromoacetic acid[e]	1		ND	ND		ND	ND	ND
Trichloroacetic acid[e]	1		ND	ND		1.8	1.7	2.0
Bromodichloroacetic acid	1		ND	ND		ND	ND	ND
Dibromochloroacetic acid	1		ND	ND		ND	ND	ND
Tribromoacetic acid	2		ND	ND		ND	ND	ND
HAA5[i]			ND	3.9		21	21	29
HAA9[j]			ND	3.9		22	22	31
DXAA[k]			ND	3.9		17	17	24
TXAA[l]			ND	ND		1.8	1.7	2.0
Haloacetonitriles								
Chloroacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[e]	NA	ND	ND	ND	ND	0.6	NR	NR
Bromochloroacetonitrile[e]	0.5	ND	ND	ND	ND	ND	ND	ND
Dibromoacetonitrile[e]	0.25	ND	ND	ND	ND	ND	ND	ND
Trichloroacetonitrile[e]	0.1	ND	ND	ND	ND	ND	ND	ND
Bromodichloroacetonitrile	NA	ND		ND	ND	ND		
Dibromochloroacetonitrile	NA	ND		ND	ND	ND		
Tribromoacetonitrile	NA	ND		ND	ND	ND		
Haloacetaldehydes								
Dichloroacetaldehyde	0.98	ND	ND	ND	ND	8	9	11
Bromochloroacetaldehyde	0.5	ND	ND	ND	ND	ND	ND	ND
Chloral hydrate[e]	0.1	0.7	0.2	ND	0.1	0.5	0.3	0.7
Tribromoacetaldehyde	0.1	ND	ND	ND	ND	ND	ND	ND

[n]<0.5: Concentration less than MRL of 0.5 µg/L

Table 17 (continued)

1/14/2002	MRL[a]	Plant 7[b]						
Compound	µg/L	Raw	Settled	Filt Eff	O3 Eff	Plant Eff	DS	SDS
Haloketones								
Chloropropanone	0.5	ND	NR	ND	NR	1	1	ND
1,1-Dichloropropanone[e]	NA	ND	ND	ND	ND	1	NR	NR
1,3-Dichloropropanone	0.1	0.2	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloropropanone[e]	0.1	ND	ND	ND	ND	0.1	ND	ND
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1,1-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1,3-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.5	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes								
Chloronitromethane	0.5	ND		0.6	0.6	0.5	ND	ND
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	NA	ND	NR	0.4	0.5	0.7	NR	NR
Bromochloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND
Dibromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[e]	0.1	ND	ND	ND	0.1	0.4	0.2	0.4
Bromodichloronitromethane	NA	ND		ND	ND	3		
Dibromochloronitromethane	NA	ND		ND	ND	ND		
Bromopicrin	NA	ND		ND	ND	ND		
Miscellaneous Compounds								
Methyl ethyl ketone	0.5	ND		ND		0.6	0.8	0.9
Methyl *tertiary* butyl ether	0.2	ND		ND		ND	ND	ND
Benzyl chloride	0.2	ND	ND	ND	ND	ND	ND	ND
1,1,2,2-Tetrabromo-2-chloroethane	0.5	ND	ND	ND	ND	ND	ND	ND

Table 18. DBP results at plant 8 (1/16/02)

1/16/2002	MRL[a]	Plant 8[c]						
Compound	µg/L	Raw	Settled	Filt Eff	Tower Eff	Plant Eff	DS	SDS
Halomethanes								
Chloromethane	0.2			ND[d]	ND	ND	ND	ND
Bromomethane	0.2			ND	ND	ND	ND	ND
Bromochloromethane	0.5			ND	ND	ND	ND	ND
Dibromomethane	0.5			ND	ND	ND	ND	ND
Chloroform[e]	0.2	ND	14	59	0.3	25	32	28
Bromodichloromethane[e]	0.2	ND	2	6	0.9	3	3	3
Dibromochloromethane[e]	0.5	ND	0.8	0.9	0.8	0.7	0.7	0.5
Bromoform[e]	0.1	ND	ND	ND	ND	ND	ND	ND
THM4[g]		ND	17	66	2	29	36	32
Dichloroiodomethane	2.5	NR[f]	NR	3	ND	<2.5[o]	<2.5	ND
Bromochloroiodomethane	0.5	NR	ND	ND	ND	ND	ND	ND
Dibromoiodomethane	0.53	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.1	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.52	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.22	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.2		0.2	0.3	0.6	ND	ND	ND
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids								
Monochloroacetic acid[e]	2		ND	2.7	3.4	ND	ND	2.7
Monobromoacetic acid[e]	1		ND	ND	ND	ND	ND	ND
Dichloroacetic acid[e]	1		9.9	28	1.2	17	16	16
Bromochloroacetic acid[e]	1		ND	2.6	ND	1.5	1.4	1.9
Dibromoacetic acid[e]	1		ND	ND	ND	ND	ND	ND
Trichloroacetic acid[e]	1		2.1	6.8	ND	2.6	2.4	2.4
Bromodichloroacetic acid	1		ND	1.3	ND	ND	ND	2.5
Dibromochloroacetic acid	1		ND	ND	ND	ND	ND	ND
Tribromoacetic acid	2		ND	ND	ND	ND	ND	ND
HAA5[i]			12	38	4.6	20	18	21
HAA9[j]			12	41	4.6	21	20	26
DXAA[k]			10	31	1.2	19	17	18
TXAA[l]			2.1	8.1	ND	2.6	2.4	4.9
Haloacetonitriles								
Chloroacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[e]	NA	ND	ND	0.9	ND	ND	NR	NR
Bromochloroacetonitrile[e]	0.5	ND	ND	<0.5[n]	ND	<0.5	<0.5	<0.5
Dibromoacetonitrile[e]	0.25	ND	ND	ND	ND	ND	ND	ND
Trichloroacetonitrile[e]	0.1	ND	ND	ND	ND	ND	ND	ND
Bromodichloroacetonitrile	NA		ND	ND	ND	ND		
Dibromochloroacetonitrile	NA		ND	ND	ND	ND		
Tribromoacetonitrile	NA		ND	ND	ND	ND		
Haloacetaldehydes								
Dichloroacetaldehyde	0.98	1	ND	1	ND	ND	ND	1
Bromochloroacetaldehyde	0.5	ND	ND	ND	ND	ND	ND	ND
Chloral hydrate[e]	0.1	0.3	0.7	2	0.3	0.2	0.2	0.1
Tribromoacetaldehyde	0.1	ND	ND	ND	ND	ND	ND	ND

[o]<2.5: Concentration less than MRL of 2.5 µg/L

Table 18 (continued)

1/16/2002	MRL[a]	Plant 8[c]						
Compound	µg/L	Raw	Settled	Filt Eff	Tower Eff	Plant Eff	DS	SDS
Haloketones								
Chloropropanone	0.5	ND	NR	ND	ND	ND	ND	ND
1,1-Dichloropropanone[e]	NA	ND	ND	0.9	ND	ND	NR	NR
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloropropanone[e]	0.1	ND	ND	0.5	ND	ND	ND	ND
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1,1-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1,3-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.5	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes								
Chloronitromethane	0.5		2	<0.5	<0.5	ND	ND	ND
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	NA	ND	0.4	0.5	ND	ND	NR	NR
Bromochloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND
Dibromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[e]	0.1	ND	ND	0.6	ND	0.4	0.3	0.3
Bromodichloronitromethane	NA		ND	1	1	0.9		
Dibromochloronitromethane	NA		ND	ND	ND	ND		
Bromopicrin	NA		ND	ND	1	ND		
Miscellaneous Compounds								
Methyl ethyl ketone	0.5			ND	1	ND	<0.5	ND
Methyl *tertiary* butyl ether	0.2			ND	0.3	ND	ND	ND
Benzyl chloride	0.2	ND	ND	ND	ND	ND	ND	ND
1,1,2,2-Tetrabromo-2-chloroethane	0.5	ND	ND	ND	ND	ND	ND	ND

Table 19. Additional target DBP results (µg/L) at plants 7 and 8 (1/14-16/02)

1/14-16/02	Plant 7[a]						Plant 8[a]					
Compound	Raw	FE	OE	PE	DS	SDS	Raw	FE	STE	PE	DS	SDS
Monochloroacetaldehyde	0	0	3.1	1.9	1.5	2.2	0	0.2	0		0	0
Dichloroacetaldehyde	0	1.6	7.5	12.2	9.2	13.1	0	1.3	0		0.9	1.0
Bromochloroacetaldehyde	0	0.1	0.2	0.6	0.4	0.6	0	0.3	0		0.1	0.1
3,3-Dichloropropenoic acid	0	0	0	0	0	0.6	0	0.1	0	0	0	0
Bromochloromethylacetate	0	0	0	0	0	0	0	0	0	0	0	0
Monochloroacetamide	0	0	0	0	0	0	0			0	0	0
Monobromoacetamide	0	0	0	0	0	0	0			0	0	0
Dichloroacetamide	0	0.1	0.2	1.8	2.5	3.0	0			1.5	1.4	1.2
Dibromoacetamide	0	0	0	0.2	0.4	0.5	0			0.3	0.2	0.2
Trichloroacetamide	0	0	0	0.1	0.2	0.3	0			0.1	0.6	0.5
TOX (µg/L as Cl^-)	0	94.9	94.2	200	154	212	0	486	40.4	179	161	133
TOBr (µg/L as Br^-)		17.0	12.0	36.5	23.2	42.1	0	137	24.0	80.9	64.0	68.0
TOCl (µg/L as Cl^-)		83.5	85.0	206	121	185	0	450	29.7	203	189	190
Cyanoformaldehyde	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
5-Keto-1-hexanal	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6-Hydroxy-2-hexanone	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Dimethylglyoxal	<0.1	<0.1	2.4	2.8	1.9	2.5	<0.1	0.8	<0.1	<0.1	<0.1	<0.1
trans-2-Hexenal	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Table 20. Halogenated furanone results (µg/L) at plant 7 (1/14/02)

Compound	Raw	FE	OE	PE	DS	SDS
BMX-1	<0.02	<0.02	<0.02	0.03	<0.02	0.02
BEMX-1	<0.02	<0.02	0.03	<0.02	<0.02	<0.02
BMX-2	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
BEMX-2	<0.02	<0.02	<0.02	0.06	0.06	0.03
BMX-3	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
BEMX-3	0.10	0.10	0.15	0.28	0.18	0.18
MX	<0.02	<0.02	<0.02	0.17	<0.02	0.04
EMX	<0.02	<0.02	<0.02	0.05	<0.02	<0.02
ZMX	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02 (0.013)
Ox-MX	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Mucochloric acid (*ring*)	<0.02	<0.02	<0.02 (0.015)	0.02	0.05	0.02
Mucochloric acid (*open*)	<0.02	0.03	0.08	0.20	0.21	0.22

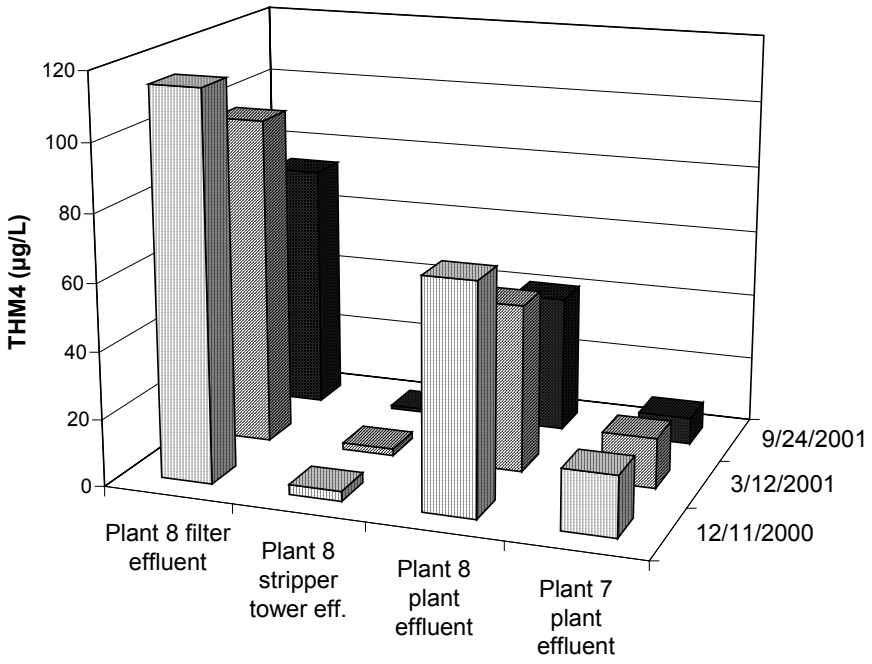
Table 21. Halogenated furanone results (µg/L) at plant 8 (1/16/02)

Compound	Raw	FE	PE	DS	SDS
BMX-1	<0.02	<0.02	0.11	0.03	0.05
BEMX-1	0.08	<0.02 (0.011)	0.72	<0.02	<0.02
BMX-2	<0.02	<0.02	<0.02 (0.014)	0.03	0.02
BEMX-2	<0.02	0.12	0.81	0.11	0.10
BMX-3	<0.02	<0.02	0.04	<0.02	<0.02
BEMX-3	<0.02	0.43	0.41	0.37	1.28
MX	<0.02	<0.02 (0.015)	0.10	0.12	0.10
EMX	<0.02	<0.02	<0.02	<0.02	<0.02
ZMX	<0.02	0.09	<0.02	<0.02	<0.02
Ox-MX	<0.02	<0.02	<0.02	<0.02	<0.02
Mucochloric acid (*ring*)	<0.02	0.02	0.02	0.02	0.02
Mucochloric acid (*open*)	<0.02	0.30	0.16	0.17	0.18

Halomethanes. Pre-chloramination at plant 7 resulted in the formation of 3-18 µg/L of the four regulated trihalomethanes (THM4) by the filter effluent sampling point. Post-ozonation did not change the concentration of the THMs. Post-chlorination at plant 7 resulted in 7-18 µg/L of THM4. Pre-chlorination and intermediate chloramination in the lime softening portion of plant 8 resulted in the formation of 66-115 µg/L of THM4, whereas only 1-3 µg/L was produced in the membrane softening portion of the plant. The combined treated waters at plant 8 after final chloramination contained 29-68 µg/L of THM4. Figure 4 shows the seasonal variation in THM4 at plant 7 and plant 8 in 2000-2001. THM formation did not vary significantly from season to season.

Figure 4

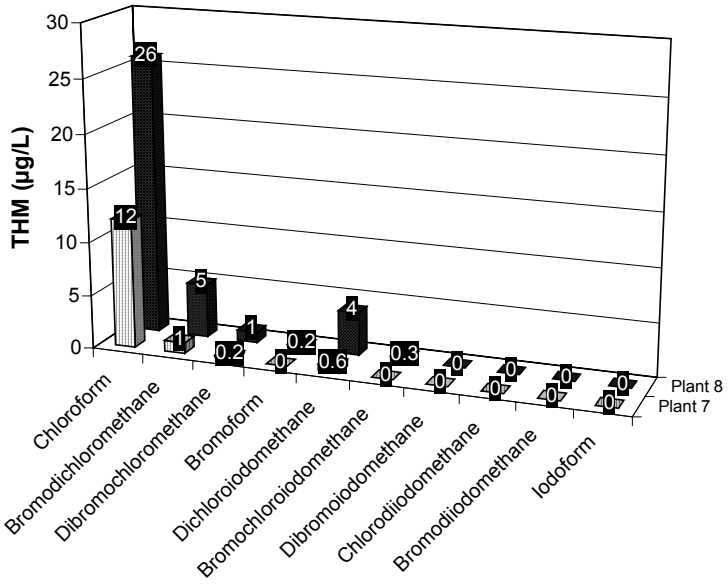
Seasonal Variation in Trihalomethanes at Plants 7 and 8



Even though the source groundwaters contained moderate to high levels of bromide (0.12 to 0.33 mg/L), chloroform was the dominant THM (e.g., 91 and 81 % of THM4 in SDS testing in September 2001 at plant 7 and plant 8, respectively) (Figure 5). In other DBP research, it has been shown that bromine speciation is effected by the bromide-to-TOC ratio and the chlorine-to-bromide ratio (Symons et al., 1993). In these samples, both the TOC (11-13 mg/L in raw water) and chlorine dosages (5-13 mg/L at plant 7 influent; 6-8 mg/L at influent to lime softening portion of plant 8) were relatively high. As a result, chlorine was able to effectively compete with bromine in forming halogenated DBPs. In addition, low levels of some of the iodinated THMs were detected (Figure 5; Tables 10, 16, and 18). Because the concentration of bromide was higher at plant 8, this resulted in somewhat more bromine incorporation in the THMs, including the formation of a bromine-containing iodinated THM (Figure 5).

Figure 5

Effect of Bromide and Treatment/Disinfection Process on Trihalomethane Formation and Speciation in Simulated Distribution System Testing (September 24, 2001): Plant 7 Br^- = 0.14 mg/L, Plant 8 Br^- = 0.25 mg/L



Haloacids. Chloramination and ozonation at plant 7 resulted in the formation of 21-30 µg/L of the five regulated haloacetic acids (HAA5). Pre-chlorination and intermediate chloramination in the lime softening portion of plant 8 resulted in the formation of 38-53 µg/L of HAA5, whereas only 2-5 µg/L were produced in the membrane softening portion of the plant. The combined treated waters at plant 8 after final chloramination contained 17-28 µg/L of HAA5.

In addition, all nine HAAs (HAA9) were measured, which includes all of the brominated HAA species. However, HAA9 values were not significantly higher than the levels of HAA5. This reflects the relatively low bromine substitution that occurred in these waters. Figure 6 shows the seasonal variation in HAA9 at plant 7 and plant 8 in 2000-2001. HAA formation did not vary significantly from season to season.

At both plants, the sum of the dihalogenated HAAs (DXAAs) was much higher than the sum of the trihalogenated HAAs (TXAAs) (Figure 7). In other DBP research, chloramination has been shown to control TXAA formation much better than DXAA formation (Krasner et al., 1996). In addition, ozonation has been shown to be able to destroy trichloroacetic acid (TCAA) precursors better than dichloroacetic acid (DCAA) precursors (Reckhow and Singer, 1984). Furthermore, other research has shown that THM formation—in the presence of free chlorine—was higher with increasing pH (Stevens et al., 1989). In this same research, pH (in the range of 5 to 9.4) had no significant effect on DCAA formation, whereas TCAA formation was lower at pH 9.4 than at the lower pH levels (Stevens et al., 1989). Because chlorine (and chloramines) was applied to lime-softened water at plants 7 and 8, pH was a factor in determining which DBPs

Figure 6

Seasonal Variation in Haloacetic Acids at Plants 7 and 8

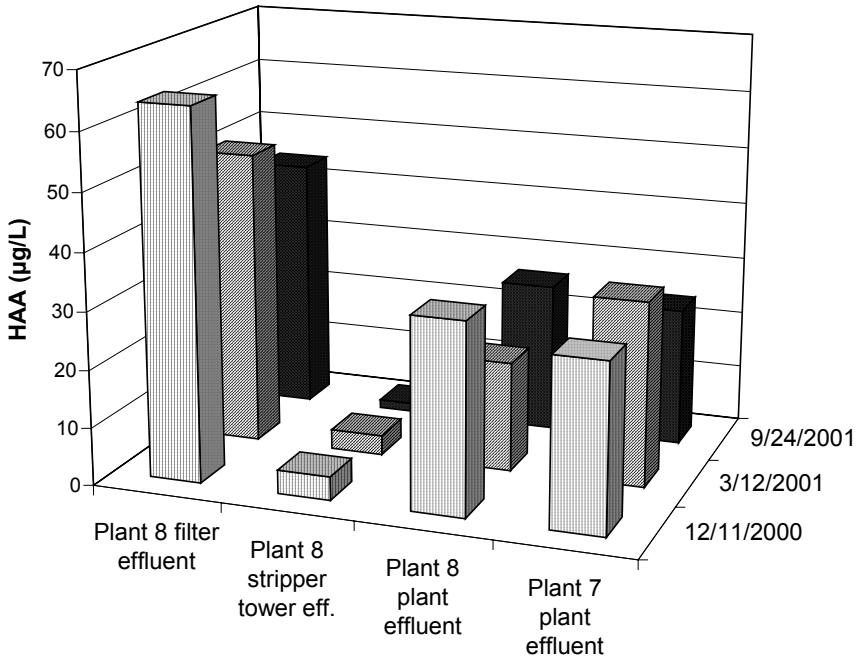
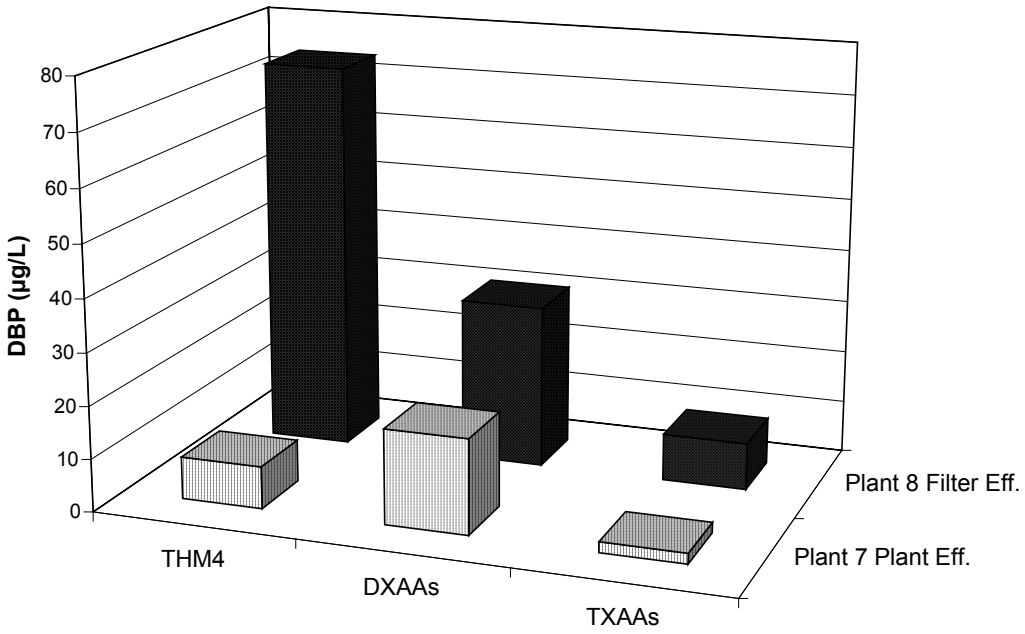


Figure 7

Effect of Treatment/Disinfection Process on Trihalomethane and Haloacetic Acid Formation at Plants 7 and 8 (September 24, 2001)

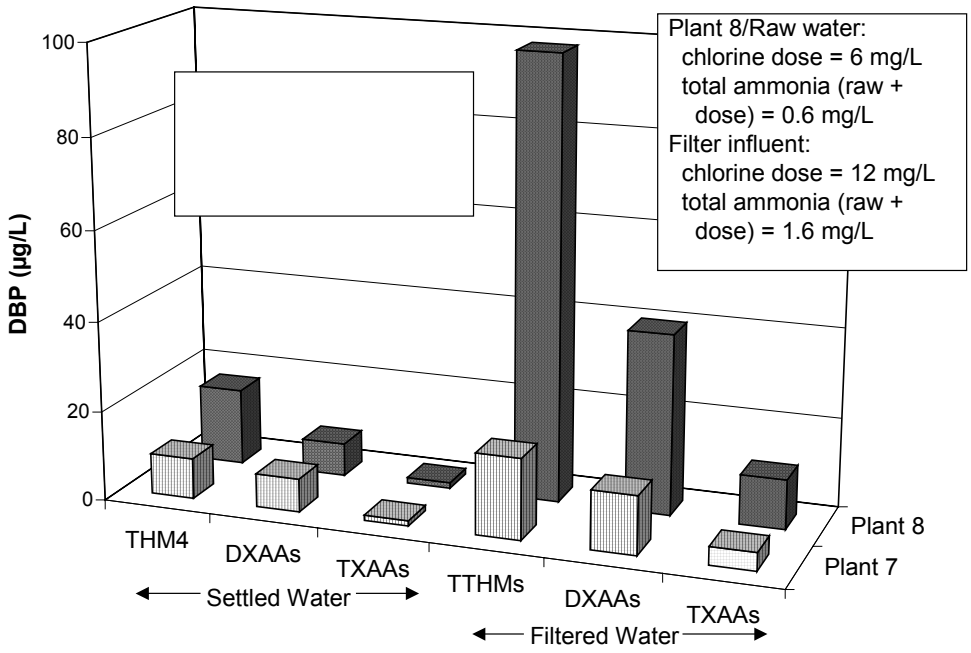


formed. Because DXAA formation was higher than THM4 formation at plant 7 in September 2001, the use of pre-chloramination was probably the major determinant of the relative proportion of these DBPs during that sampling date. Because THM4 formation was higher than DXAA formation in the softened water at plant 8, the effect of pH was probably the major determinant of the relative proportion of these DBPs.

For example, Figure 8 shows the effect of the disinfection scheme on DBP formation in lime-softened waters at plants 7 and 8 for March 12, 2001. At plant 7, chlorine (10 mg/L) and ammonia (1.1 mg/L) were added to the raw water that contained 0.69 mg/L of ammonia to begin with. At plant 8, on the lime-softening train, chlorine (6.0 mg/L) was added to the raw water. Although ammonia was not added at plant 8, the raw water contained 0.62 mg/L of ammonia. Therefore, both plants were operating with chloramines, which helped minimized DBP formation in this high-TOC groundwater. At plant 8, in the lime-softening portion of the plant, additional chlorine (12 mg/L) and ammonia (1.0 mg/L) were added to the softened water. Although chloramines were still present, it is possible that the "effective" chlorine-to-nitrogen ratio was much higher than in the raw water. At higher chlorine-to-nitrogen ratios, THM formation is more likely to occur (Diehl et al., 2000), as evidenced by the relatively high level of THMs (98 µg/L) in the filter influent sample at plant 8.

Figure 8

Effect of Disinfection Scheme on DBP Formation on Lime-Softened Waters at Plants 7 and 8: 3/12/01

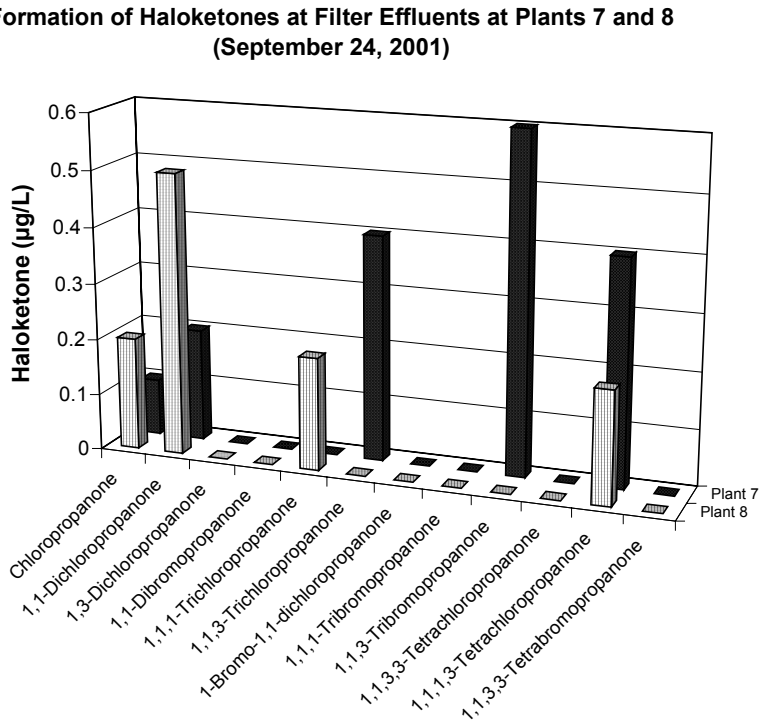


Haloacetonitriles. In other DBP research, haloacetonitriles (HANs) have been found to be produced at approximately one-tenth the level of the THMs (Oliver, 1983). HANs were only observed at plant 8 in the filter effluent sample in December 2000 and in selected samples at both plants in January 2002. HANs can undergo base-catalyzed hydrolysis (Croué and

Reckhow, 1989). Because of the high pH of the treated waters at these two plants, most of the HANs formed were degraded. None of the target HANs—that were not included in the Information Collection Rule (ICR)—were detected in these high-pH samples, except for chloroacetonitrile in the SDS sample at plant 8 in September 2001.

Haloketones. One of the haloketones (HKs) from the ICR—1,1-dichloropropanone (1,1-DCP)—was detected at both plant 7 and plant 8, whereas the other ICR HK (1,1,1-trichloropropanone) was detected in selected samples at plant 8 and in January 2002 at one sample location at plant 7. The latter HK also can undergo base-catalyzed hydrolysis at high pH (Croué and Reckhow, 1989). In addition, some of the other target HKs were detected in selected samples (Figure 9).

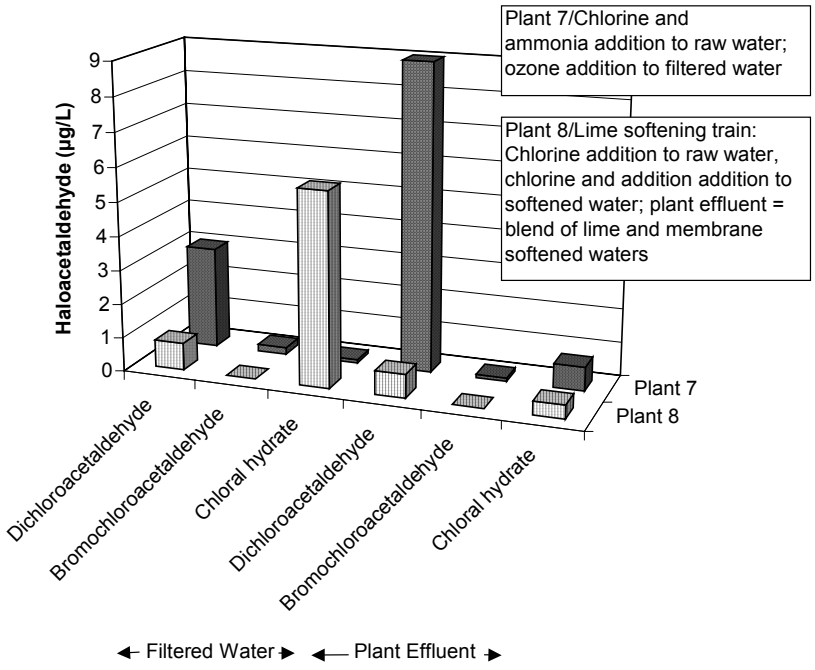
Figure 9



In addition to the target HKs, other HKs were detected in selected samples by the broadscreen GC/MS methods (Tables 10 and 16). A number of these HKs were analogous to the di- and tetrahalogenated HKs analyzed by MWDSC, except that these were mixed bromochloro species. For example, in December 2000, when the raw-water bromide was at 0.12 mg/L, MWDSC detected chloropropanone; 1,1-DCP; and 1,1,3,3-tetrabromopropanone (1,1,3,3-TeBP) after chloramination and ozonation at plant 7. Broadscreen GC/MS analysis of this same water also detected the bromochloro analogue of 1,1-DCP and four bromochloro analogues of 1,1,3,3-TeBP. Another HK that was detected at plant 7 by the broadscreen GC/MS methods was pentachloropropanone (PCP). MWDSC analysts had attempted to include PCP in its target compound list, but PCP degraded immediately and completely in water under all conditions evaluated (Gonzalez et al., 2000).

Figure 10

Effect of Disinfection/Treatment Scheme and pH (9-10) on Haloacetaldehyde Formation and Stability at Plants 7 and 8: 3/12/01



Haloaldehydes. Chloral hydrate (trichloroacetaldehyde) (an ICR DBP) was detected (2-13 µg/L) in the filter effluent sample at plant 8 (Figure 10). Chloral hydrate also undergoes base-catalyzed hydrolysis (Stevens et al., 1989) (it is converted to chloroform). Thus, its low concentration (0.2-2 µg/L) in the combined treated waters at plant 8 was a result of degradation, not only because of dilution with membrane-treated water. In addition, a low level ($\leq$3 µg/L) of dichloroacetaldehyde (a target DBP) was found at plant 8.

In contrast, at plant 7, very little chloral hydrate was detected (<1 µg/L), whereas a high amount of dichloroacetaldehyde (8-14 µg/L) was detected in the finished water (Figure 10). In other DBP research, acetaldehyde (an ozone by-product) was found to react with chlorine to form chloroacetaldehyde, which in the presence of free chlorine rapidly reacted to form chloral hydrate (McKnight and Reckhow, 1992). At plant 7, chlorine (in the presence of ammonia) may have reacted with acetaldehyde formed by the ozonation process to produce dichloro-acetaldehyde.

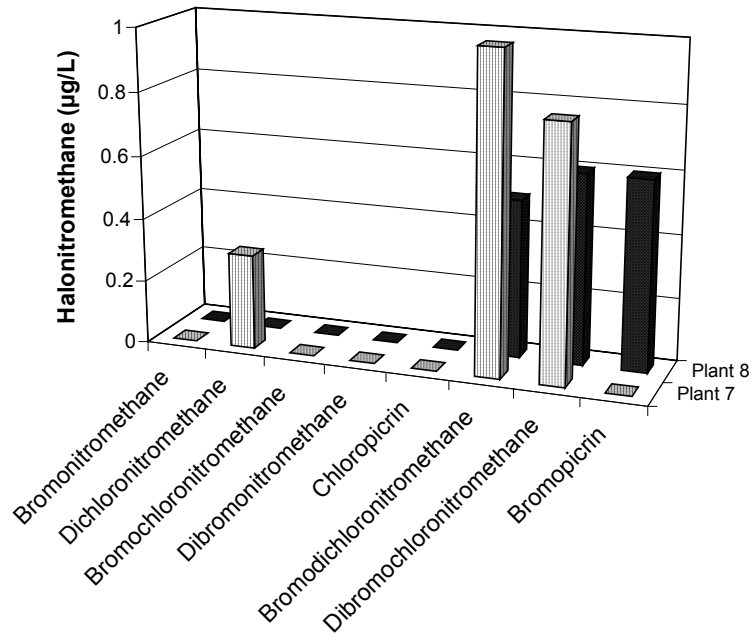
In addition, bromochloroacetaldehyde—a brominated analogue of dichloroacetaldehyde —was detected at sub-µg/L levels at two locations at plant 7 in March 2001. The results for chloral hydrate in December 2000 represented the sum of the concentrations of chloral hydrate and bromochloroacetaldehyde, since these two DBPs co-eluted in the original GC method (Krasner et al., 2001). However, based on the March 2001 results, bromochloro-acetaldehyde probably did not contribute that much to the December 2000 chloral hydrate results.

In addition to the target haloaldehydes, two other haloaldehydes were detected in selected samples by the broadscreen GC/MS methods (Tables 10 and 16). Dibromoacetaldehyde, the fully bromine-substituted analogue of dichloro- and bromochloroacetaldehyde, was detected at both plants. Another brominated aldehyde (2-bromo-2-methylpropanal) also was detected at both plants.

Halonitromethanes. Sub-µg/L levels of chloropicrin (trichloronitromethane) (an ICR DBP) were detected at selected sites at plant 8 and in January 2002 at plant 7. In addition, some of the target halonitromethanes were detected at both plant 7 and plant 8 (Figure 11; Tables 10, 16, 17, and 18).

Figure 11

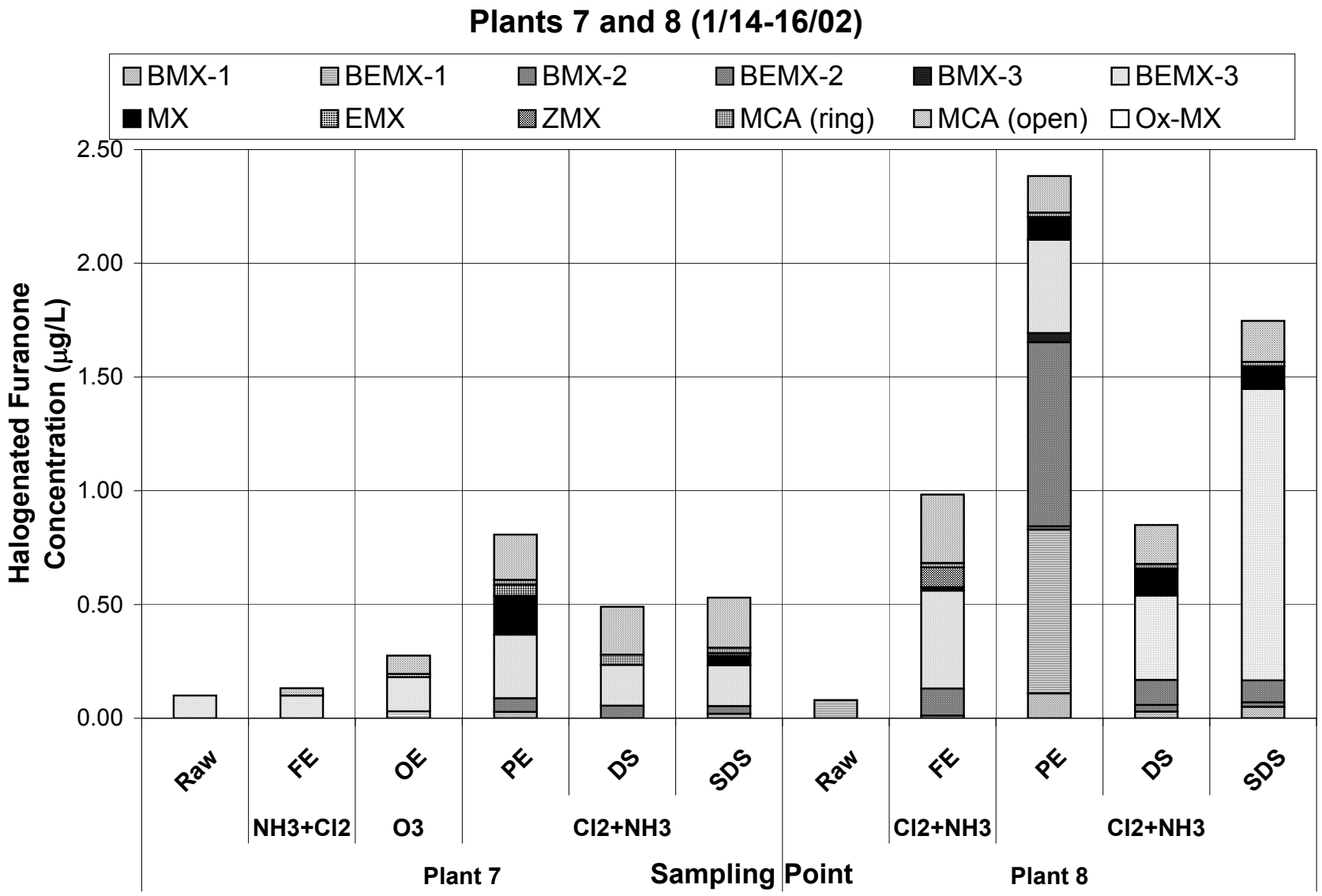
Formation of Halonitromethanes in Plant Effluents at Plants 7 and 8 (September 24, 2001)



Halogenated Furanones. Tables 20 and 21 show results for halogenated furanones in the January 2002 sampling for plant 7 and plant 8. Data are included for 3-chloro-4-(dichloromethyl)-5-hydroxy-2[5H]-furanone, otherwise known as MX; (E)-2-chloro-3-(dichloromethyl)-4-oxobutenoic acid, otherwise known as EMX; (Z)-2-chloro-3-(dichloromethyl)-4-oxobutenoic acid (ZMX); the oxidized form of MX (Ox-MX); brominated forms of MX and EMX (BMXs and BEMXs); and mucochloric acid (MCA), which can be found as a closed *ring* or in an *open* form. Results are displayed graphically in Figure 12.

At plant 7 (1/14/02), pre-chloramination and post-ozonation controlled (in part) the formation of MX and MX-analogues in a high-TOC (12.6 mg/L) groundwater, as compared

Figure 12


Plants 7 and 8 (1/14-16/02)
BMX-1
BEMX-1
BMX-2
BEMX-2
BMX-3
BEMX-3
MX
EMX
ZMX
MCA (ring)
MCA (open)
Ox-MX
Halogenated Furanone Concentration (µg/L)
2.50
2.00
1.50
1.00
0.50
0.00
Raw
FE
OE
PE
DS
SDS
Raw
FE
PE
DS
SDS
NH3+Cl2
O3
Cl2+NH3
Cl2+NH3
Cl2+NH3
Plant 7
Sampling Point
Plant 8

to plant 8 (1/16/02) (TOC = 11.3 mg/L) that used lime softening with pre-chlorination in one portion of the plant and membranes in the other portion of the plant to control DBP formation and remove TOC. Likewise, pre-chlorination in the lime softening portion of plant 8 produced more THMs and HAAs than chloramination/ozonation at plant 7 (Figure 7-8). These are the results of only one sample event. Additional measurements of membrane-treated water should be conducted in the future to determine whether these results are repeatable. However, the significant brominated MX-analogue production in plant 8 is consistent with the high-bromide, source-water quality (0.27 mg/L in the raw water and 0.1 mg/L in the membrane effluent).

Volatile Organic Compounds (VOCs). In December 2000, carbon tetrachloride was detected in one sample (distribution system of plant 7) just above its MRL (0.06 µg/L). In March 2001, this compound was found in all of the samples (0.2-0.7 µg/L) except for the raw waters and the effluent of the stripping towers (i.e., membrane-softened water). In September 2001, it was not detected in any of the samples with an MRL of 0.2 µg/L. In January 2002, carbon tetrachloride was detected in one sample (distribution system) of plant 7 at the revised MRL (0.2 µg/L) and in several samples at plant 8 (0.2-0.6 µg/L). Carbon tetrachloride is a VOC and a possible DBP. Carbon tetrachloride has been detected by some utilities in gaseous chlorine cylinders (EE&T, 2000). Incidents of carbon tetrachloride contamination have been traced to either imperfections in the manufacturing process or improper cleaning procedures. Carbon tetrachloride is used to clean out cylinders before filling with chlorine. If carbon tetrachloride is not allowed sufficient time to evaporate, it can contaminate the chlorine.

In September 2001, methyl ethyl ketone (MEK) was detected in selected samples at 0.9-1 µg/L. In January 2002, MEK was detected after ozonation at plant 7 (0.6-0.9 µg/L) and in two samples at plant 8 (<0.5-1 µg/L). MEK is a VOC and a possible DBP. Also in January 2002, methyl *tertiary* butyl ether (MTBE) was detected (0.3 µg/L) in one sample (stripper tower effluent) of plant 8 just above its MRL (0.2 µg/L). MTBE is a VOC, not a DBP.

Other Halogenated DBPs. A few additional, miscellaneous halogenated DBPs were also detected. UNC methods detected dichloroacetamide at 1.8 and 2.1 µg/L in finished waters from plant 7 and plant 8, respectively, in March 2001 (Table 13). In addition, the concentration of dichloroacetamide increased in SDS testing. In samples collected in January 2002, dichloroacetamide, dibromoacetamide, and trichloroacetamide were found in finished waters from both treatment plants at levels for individual species ranging from 0.1 to 3.0 µg/L (Table 19). The concentrations of these latter compounds either increased or remained steady in the distribution system. Broadscreen GC/MS analyses revealed the presence of hexachlorocyclopentadiene and bromopentachlorocyclopentadiene in finished water from plant 7 in December 2000 (Table 10) and plant 8 in September 2001 (Table 16). These compounds were not observed in the corresponding raw, untreated water.

Non-Halogenated DBPs. A few non-halogenated DBPs were also detected in finished waters from plants 7 and 8. Dimethylglyoxal was identified at 3.5 µg/L in finished waters from plant 7 in March 2001 (Table 13) and in finished waters at 2.8 µg/L from plant 7 in January 2002 (Table 19). Broadscreen GC/MS analysis also revealed the presence of formaldehyde, acetone, glyoxal, and methyl glyoxal in plant 7 finished waters in December 2002, and acetone, propanal, 2-butanone, 3-hexanone, 2-hexanone, glyoxal, and methyl glyoxal in finished waters from plant

8 in September 2001 (Table 16). Several non-halogenated carboxylic acids were also observed in the finished waters at significantly higher levels than found in the raw, untreated water (Table 16).

Other DBP Formation and Stability Issues. Figures 13-14 show the effect of seasonal variations on DBP formation at plant 7 (plant effluent) and at plant 8 (filter effluent). Essentially, there did not appear to be any significant seasonal variations in water quality, operations or DBP formation at either of these two treatment plants.

Figure 13

Effect of Seasonal Variations on DBP Formation at Plant 7: Plant Effluent

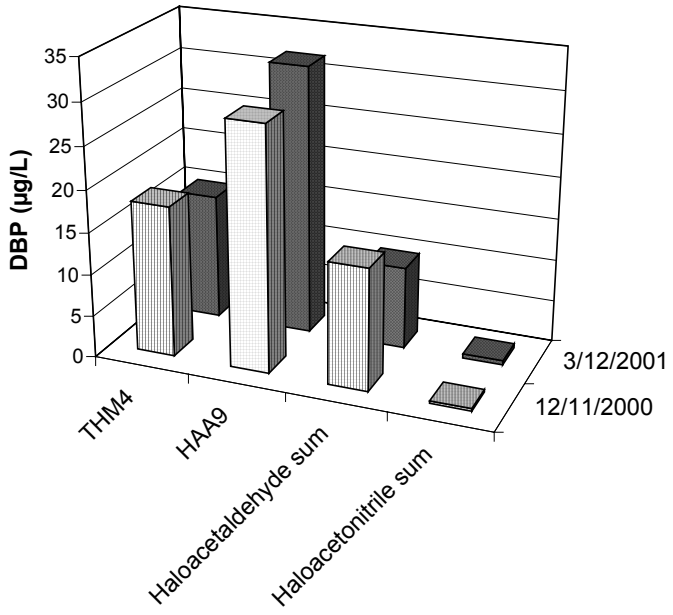
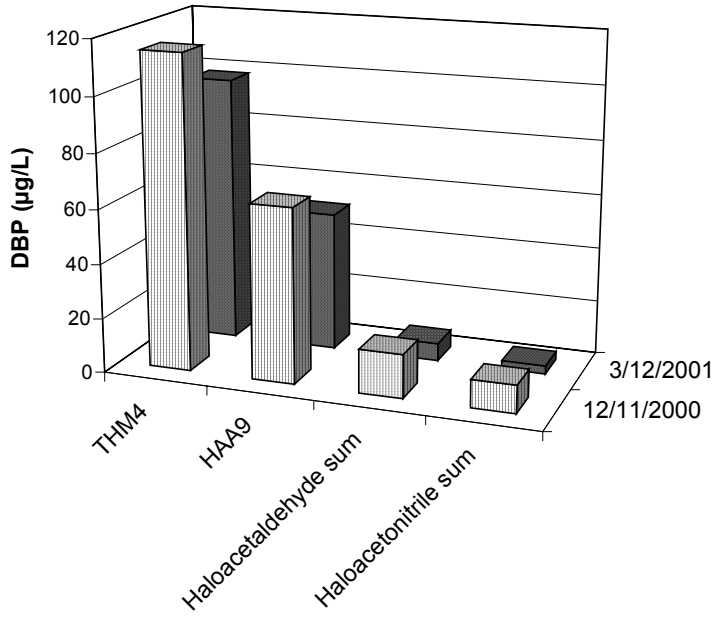


Figure 14

Effect of Seasonal Variations on DBP Formation at Plant 8: Filter Effluent



At plant 7, HAA formation (the sum of all nine species) was greater than THM formation (on a weight basis). The haloacetaldehydes were the third largest fraction (by weight) of halogenated DBPs. At plant 7, most of the haloacetaldehyde formation was due to dichloroacetaldehyde (a target DBP) and not due to chloral hydrate (an ICR DBP). HAN formation was quite small.

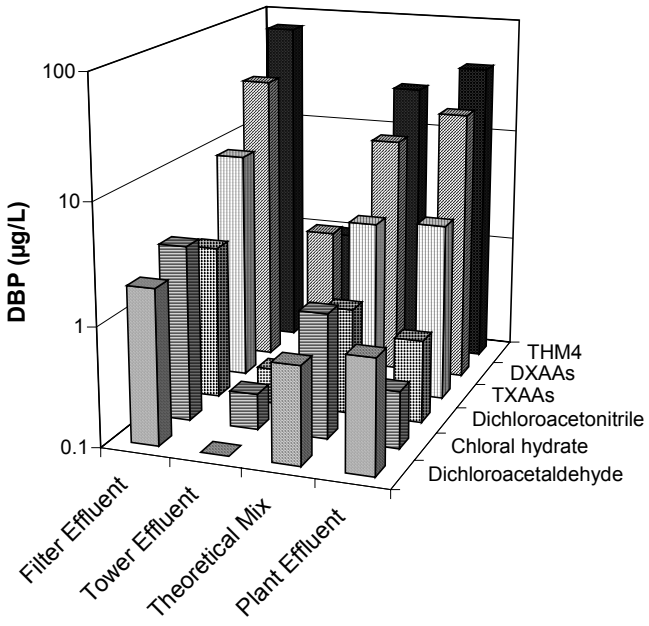
Alternatively, at plant 8, THM formation was greater than HAA formation. The haloacetaldehydes and HANs were the third and fourth largest fractions of halogenated DBPs. The formation of the latter two fractions was higher in December 2000 than in March 2001. During the December 2000 sampling, the pH of the settled water and filter effluent were 9.7 and 9.2, respectively, whereas during the March 2001 sampling, the pH of the settled water and filter effluent were 10.4 and 10.0, respectively. Because chloral hydrate and dichloroacetonitrile (the major components of the latter two fractions at plant 8, respectively) both undergo base-catalyzed hydrolysis, their formation may have been lower in March 2001 because of the somewhat higher pH.

Figure 15 shows the effect of blending lime-softened water (filter effluent) with membrane-softened water (effluent of stripper towers) and base-catalyzed hydrolysis on DBP concentrations in the plant effluent of plant 8 on September 24, 2001. The flows of the lime-softening and membrane-softening portions of the plant were 3.3 and 6.8 mgd, respectively. For the TXAAs, 8.9 µg/L was detected in the lime-softened water, whereas none was detected in the membrane-softened water. Based on blending, using the flows of each portion of the treatment plant, one would expect the TXAAs to be diluted down to 2.9 µg/L. In the actual plant effluent, there was 3.2 µg/L of TXAAs. In contrast, the theoretical levels of dichloroacetonitrile

(0.8 µg/L) and of chloral hydrate (1.1 µg/L) were greater than the measured values (i.e., 0.5 and 0.3 µg/L, respectively). As discussed previously, the lower measured values—especially for chloral hydrate—were due to base-catalyzed hydrolysis. On the other hand, the theoretical levels of DXAAs (11 µg/L) and of THM4 (25 µg/L) were significantly less than the measured values (i.e., 21 and 41 µg/L, respectively). These latter DBPs continued to form downstream of blending (and after additional chlorine addition). In addition, when chloral hydrate is hydrolyzed, chloroform (one of the THMs) is formed. Thus, some of the formation may also be due to the breakdown of other unstable DBPs (at least unstable at pH 9). Finally, dichloroacetaldehyde was relatively conservative (theoretical and measured values of 0.7 and 0.9 µg/L, respectively). Therefore, it did not undergo base-catalyzed hydrolysis as the chloral hydrate (trichloroacetaldehyde) did.

Figure 15

Effect of Blending and pH on Formation and Stability of DBPs at Plant 8 (September 24, 2001)



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EPA REGION 4: PLANTS 5 AND 6

Plant Operations and Sampling

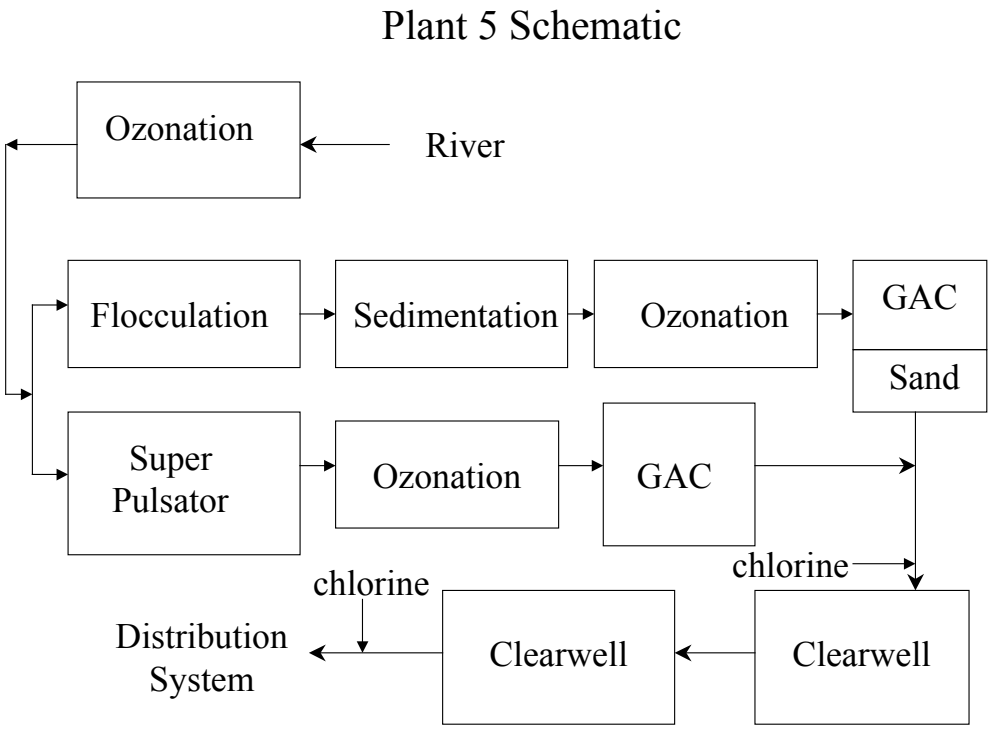
Plant 5 and plant 6 in EPA Region 4 treated water from the same river. On November 27, 2000, February 26, 2001, August 13, 2001, October 22, 2001, and April 15, 2002, these two plants were sampled

Plant 5 was an ozone plant (Figure 1). This plant consisted of two facilities operating simultaneously and parallel to one another:

- One was a conventional facility. After raw-water ozonation, the water underwent flocculation, coagulation, and sedimentation. The settled water then underwent intermediate ozonation. Ozonated settled water then entered biologically-activated filters, composed of granulated activated carbon (GAC) over sand.
- The other facility utilized solids contact – upflow clarification of coagulated water (Super Pulsator technology) following ozonation of the raw water. After clarification, the settled water underewent intermediate ozonation. Ozonated settled water then entered biologically activate filters, composed of deep-bed GAC filters.

Effluents from all of the filters were combined and final chemical adjustments were made. This included the addition of sodium hypochlorite for secondary disinfection and residual maintenance. Finished water then flowed first into one and then another closed reservoir for storage prior to being pumped into the distribution system.

Figure 1



Plant 5 was sampled at the following locations:

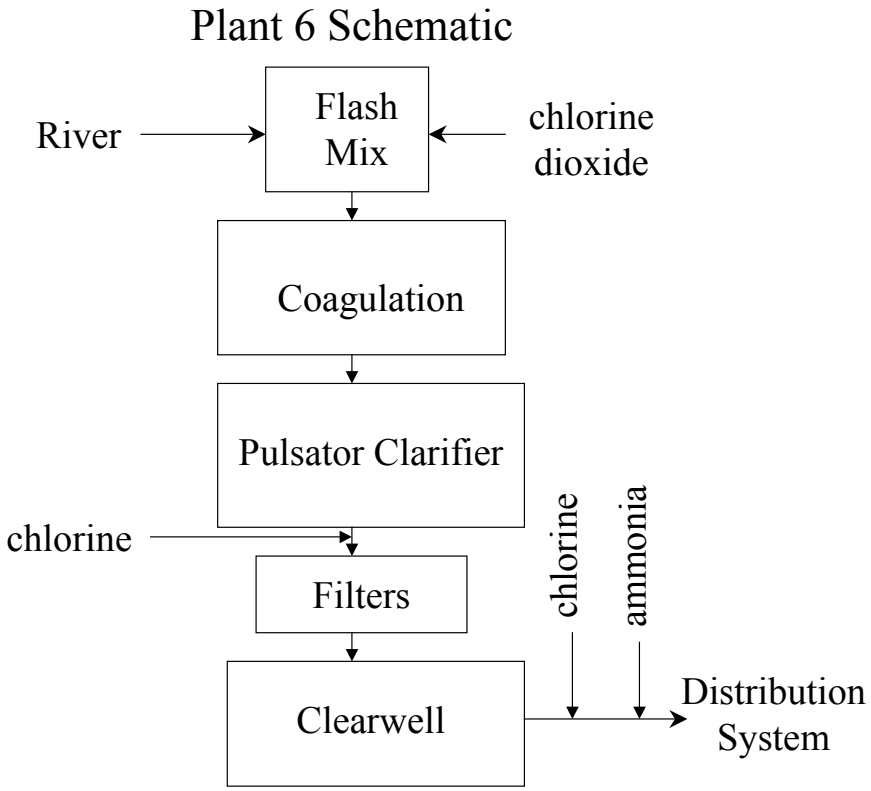
(1) raw water
(2) the effluent of the raw-water ozone contactor
(3) the GAC/sand influent on the conventional train
(4) the GAC/sand effluent on the conventional train
(5) the GAC influent on the Super Pulsator train
(6) the GAC effluent on the Super Pulsator train
(7) the composite filter effluent (on selected dates)
(8) the plant effluent

In addition, plant effluent was collected and simulated distribution system (SDS) testing was conducted for average and maximum detention times (Table 1). Furthermore, the distribution system was sampled at two locations, one representing an average detention time and the other representing a maximum detention time.

Plant 6 was a chlorine dioxide plant (Figure 2):

- After disinfection of the raw water with chlorine dioxide, the water underwent coagulation and clarification. The settled water was then chlorinated and filtered. Filtered water was then chloraminated and distributed.
- Starting with the August 2001 sampling, plant 6 moved their chlorine dioxide feed point up-stream of the plant. In November 2000 and February 2001, chlorine dioxide had been fed at the flash mixers. Plant 6 gained approximately 7-10 minutes of contact time (depending on flow) by adding the new feed point.

Figure 2



Plant 6 was sampled at the following locations:

(1) raw water
(2) settled water
(3) filter effluent
(4) clearwell effluent
(5) the plant effluent

In addition, plant effluent was collected and SDS testing was conducted for average and maximum detention times for that time of the year. Furthermore, the distribution system was sampled at two locations, one representing an average detention time and the other representing a maximum detention time.

Table 1. SDS holding times (days) at plants 5 and 6

Sample	11/27/00	2/26/01	8/13/01	10/22/01	4/15/02
Plant 5 average detention time	2.9	2.9	3.1	4	5.3
Plant 5 maximum detention time	6	6	7	8	7
Plant 6 average detention time	4	4	4	4	3
Plant 6 maximum detention time	7	7	7	7	7

On the day of sampling, information was collected on the operations at each plant (Tables 2-3).

Table 2. Operational information at plant 5

Parameter	11/27/00	2/26/01	8/13/01	10/22/01	4/15/02
Overall plant flow (mgd)	25[a]	12.3	19.35	17.26	17.4
Plant flow for conventional coag. train (mgd)	15[a]	6.0	9.97	9.41	7.59
Plant flow for Super Pulsator train (mgd)	10[a]	6.3	9.38	7.85	9.81
Raw-Water Ozone Contactor					
Ozone dose (mg/L)	4.33	3.4	3.90	2.80	4.50
CT (mg/L-min) achieved from ozonation	NA[b]	NA	NA	NA	9.0
Conventional Train					
Coagulant[c] (mg/L)	29.5	31	41.6	40.5	40.32
Ozone dose (mg/L)	3.98	1.0	2.30	2.20	2.52
Hydraulic retention time (t_{10}) in ozone contactor (min)	~20	~20	~20	~20	~20
CT (mg/L-min) achieved from ozonation	NA	NA	NA	7.0	7.0
GAC/sand filter loading rate (gpm/sq ft)	1.18	0.96	1.63	1.47	1.25
Super Pulsator Train					
Coagulant (mg/L)	38.4	29	46.7	45.7	45.4
Ozone dose (mg/L)	2.03	0.5	1.50	0.90	2.52
t_{10} in ozone contactor (min)	~20	~20	20	20	20
CT (mg/L-min) achieved from ozonation	NA	NA	NA	7.0	7.0
GAC filter loading rate (gpm/sq ft)	1.29	1.9	3.13	2.65	3.38
Composite Filter Effluent					
Chlorine dose at filter effluent (mg/L as Cl_2)	1.7	1.8	4.0	4.1	2.53
Chlorine dose at clearwell effluent (mg/L as Cl_2)	~2.0	1.6	1.5	1.9	1.02

[a]Design flows [b]NA = Not available [c]Alum [$Al_2(SO_4)_3$ $14H_2O$]

Table 3. Operational information at plant 6

Parameter	11/27/00	2/26/01	8/13/01	10/22/01	4/15/02
Plant flow (mgd)	8	8.2	9	8	7
Coagulant[a] (mg/L wet; mg/L dry)	16	18	38; ~19	32; 16	53; 26.5
Chlorine dioxide dose (mg/L as ClO_2)	1.95	1.5	1.98	2.1	1.5
Chlorine dose at filter influent (mg/L as Cl_2)	0.60	0.66	2.5	1.5	1.11
Chlorine dose at clearwell eff. (mg/L as Cl_2)	3.2	2.5	2.7	3.0	3.0
Ammonia dose at plant eff. (mg/L as NH_3-N)	1.0	0.76	0.87	1.0	1.0

[a]PAX 18 polyaluminum chloride [Al(OH)Cl] (17 % as Al_2O_3)

Water Quality

On the day of sampling, information was also collected on the water quality at each plant (Tables 4-5).

Data were collected for total organic carbon (TOC) and ultraviolet (UV) absorbance (Tables 6-7). The TOC ranged from 6.2 to 10 mg/L at plant 5 and from 6.4 to 10 mg/L at plant 6. The UV was 0.19 to 0.35 cm^{-1} at plant 5 and was 0.19 to 0.30 cm^{-1} at plant 6.

At plant 5, pre-ozonation reduced the level of TOC by 0-29 %, whereas the UV was reduced by 20-67 %. In the Super Pulsator treatment train, coagulation removed 43-54 % of the TOC and GAC filtration removed another 5-23 %. Coagulation reduced the UV by 63-83 %. The overall (cumulative) removal of TOC at the Super Pulsator treatment train—including from pre-ozonation—was 58-65 %, and the UV reduction was 85-93 %. The overall (cumulative) removal of TOC at the conventional train—including from pre-ozonation—was 62-69 %, and the UV reduction was 85-95 %.

At plant 6, coagulation removed 38-57 % of the TOC and filtration removed another 4-7 %. Coagulation reduced the UV by 68-77 %.

Table 8 shows the values of miscellaneous other water quality parameters in raw water at the two plants. Bromide ranged from 0.05 to 0.08 mg/L at plant 5 and from 0.04 to 0.08 mg/L at plant 6. For plant 5, the raw water was collected 23 miles upstream to eliminate the intake of salty water due to tidal changes. However, the presence of bromide in the raw water, which was higher in concentration in the fall, may indicate some saltwater intrusion.

The source water was low in alkalinity. Because of the low alkalinity, settled water (after the addition of coagulant) was acidic (Tables 4-5).

Table 4. Water quality information at plant 5

	pH					Temperature (ºC)					Disinfectant Residual[a] (mg/L)				
Location[b]	11/27/00	2/26/01	8/13/01	10/22/01	4/15/02	11/27/00	2/26/01	8/13/01	10/22/01	4/15/02	11/27/00	2/26/01	8/13/01	10/22/01	4/15/02
Raw water	6.8	6.5	6.4	6.6	6.2	13.8	16	29	21	21	---	---	---	---	---
Pre-O_3 eff.	6.8	6.6	6.4	6.5	6.2	13.0	16	29	22	21	**ND**[c]	**ND**	**ND**	**ND**	**ND**
Conventional Train															
GAC/s inf.	5.8	5.6	5.7	5.8	5.6	11.9	13	29	21	21	**ND**[d]	**0.05**	**0.08**	**0.1**	**0.09**
GAC/s eff.	5.9	5.6	5.7	5.9	5.7	12.0	13	29	22	20	---	---	---	---	---
Super Pulsator Train															
GAC inf.	5.9	5.7	5.7	5.7	5.6	11.9	12	29	21	21	**ND**[d]	**0.04**	**0.09**	**0.08**	**0.1**
GAC eff.	5.9	5.6	5.7	5.7	5.6	12.0	13	29	22	21	---	---	---	---	---
Composite Filter Effluent															
Filter eff.	5.9	NS[e]	NS	NS	NS	13.4	NS	NS	NS	NS	---	NS	NS	NS	NS
Plant eff.	7.0	7.0	7.0	7.1	7.0	15.8	16	29	22	20	2.0	1.6	1.7	1.5	1.6
DS/ave.	7.0	7.5	7.0	7.5	7.0	15	12	28	24.9	18	1.8	0.8	1.2	0.4	1.0
DS/max.	7.5	7.5	7.0	7.5	7.5	15	11	28	23.2	18	0.2	0.8	≤0.1	0.3	≤0.1
SDS/ave.	7.2	6.8	7.0	7.0	6.8	18	19	23.5	23	23	1.8	0.5	1.0	0.9	<0.1
SDS/max.	7.2	6.7	7.0	7.1	7.2	18	20	25.0	23	24	0.3	0.04	0.6	0.5	<0.1

[a]Ozone residuals (**values shown in bold**) in effluent of raw-water ozone contactor and in effluents of intermediate ozone contactors at GAC/sand and GAC influents; chlorine residuals at plant effluent, in distribution system, and in SDS testing.
[b]Pre-O_3 = raw-water ozone contactor, GAC/s = GAC/sand, DS = distribution system.
[c]ND = Not detected.
[d]Ozone sequestered with hydrogen peroxide prior to filtration.
[e]NS = Not sampled.

Table 5. Water quality information at plant 6

	pH					Temperature (ºC)					Disinfectant Residual[a] (mg/L)				
Location[b]	11/27/00	2/26/01	8/13/01	10/22/01	4/15/02	11/27/00	2/26/01	8/13/01	10/22/01	4/15/02	11/27/00	2/26/01	8/13/01	10/22/01	4/15/02
Raw water	7.0	6.9	6.5	7.0	6.7	13.0	13.6	28.4	19.9	18	---	**0.2**	---	---	---
Settled	6.6	6.4	6.2	6.7	6.2	13.4	13.8	27.3	19.8	20.2	**ND**/*0.2*	**0.04**	**0.02**	**.05**/*0.2*	**ND**
Filter eff.	6.5	6.7	7.4	7.5	8.0	13.0	12.6	28.1	20.3	19.9	**ND**/*0.4*	*0.3*	*0.5*/**.01**	*2.0*	*0.2*
Clearwell	7.0	6.8	6.9	7.1	6.9	12.8	12.4	28.5	20.1	19.0	**0.03**/*2.2*	*1.7*	*2.6*/**.02**	*2.2*	*2.9*
Plant eff.	7.1	6.8	7.2	7.2	7.1	13.9	12.5	27.4	20.5	20.9	2.2-2.6	2.2	2.9/**.05**	2.6	3.2
DS/ave.	7.3	7.2	7.1	7.9	6.8	12.0	12.0	27	21.0	18.4	2.0	1.7	2.2	1.4	3.2
DS/max.	7.7	7.4	7.5	8.1	7.4	13.0	12.0	26	21.0	18.3	0.9	1.2	1.5	1.3	1.8
SDS/ave.	7.3	NA	7.3	7.0	7.2	5.0	NA	28.5	20.3	21.8	2.1	NA	1.3	1.9	>2.2
SDS/max.	7.1	NA	7.2	7.0	6.9	5.0	NA	27.9	19.4	22.6	1.7	NA	1.1	1.4	2.0

[a]Chlorine dioxide residuals (**values shown in bold**) and chlorine residuals (values shown in italics) in raw water, settled water, filter effluent, clearwell effluent, and plant effluent; chloramine residuals (total chlorine residual as Cl_2) at plant effluent, in distribution system, and in SDS testing.
[b]DS = Distribution system

Table 6. TOC and UV removal at plant 5

Location	TOC (mg/L)	UV[a] (cm^{-1})	SUVA[b] (L/mg-m)	Removal/Unit (%)		Removal/Cumulative (%)	
				TOC	UV	TOC	UV
11/27/2000							
Raw	6.23	0.204	3.27	---	---	---	---
Pre-Ozone Eff.	6.07	0.157	2.59	2.6%	23%	2.6%	23%
GAC/Sand Inf.	3.22	0.024	0.75	47%	85%	48%	88%
GAC/Sand Eff.	2.24	0.019	0.85	30%	21%	64%	91%
GAC Inf.	2.88	0.026	0.90	53%	83%	54%	87%
GAC Eff.	2.22	0.019	0.86	23%	27%	64%	91%
02/26/2001							
Raw	7.44	0.244	3.28	---	---	---	---
Pre-Ozone Eff.	7.45	0.196	2.63	-0.1%	20%	-0.1%	20%
GAC/Sand Inf.	NR[b]	0.036	NA	NA	82%	NA	85%
GAC/Sand Eff.	2.81	0.030	1.07	NA	17%	62%	88%
GAC Inf.	3.41	0.035	1.03	54%	82%	54%	86%
GAC Eff.	3.14	0.033	1.05	7.9%	5.7%	58%	86%
08/13/2001							
Raw	7.26	0.251	3.46	---	---	---	---
Pre-Ozone Eff.	5.18	0.082	1.58	29%	67%	29%	67%
GAC/Sand Inf.	4.46	0.020	0.45	14%	76%	39%	92%
GAC/Sand Eff.	2.26	0.013	0.58	49%	35%	69%	95%
GAC Inf.	2.94	0.023	0.78	43%	72%	60%	91%
GAC Eff.	2.8	0.018	0.64	4.8%	22%	61%	93%
10/22/2001							
Raw	6.74	0.192	2.85	---	---	---	---
Pre-Ozone Eff.	5.26	0.082	1.56	22%	57%	22%	57%
GAC/Sand Inf.	3.22	0.029	0.90	39%	65%	52%	85%
GAC/Sand Eff.	2.45	0.028	1.14	24%	3.4%	64%	85%
GAC Inf.	2.87	0.030	1.05	45%	63%	57%	84%
GAC Eff.	2.66	0.029	1.09	7.3%	3.3%	61%	85%
04/15/2002							
Raw	10.28	0.351	3.41	---	---	---	---
Pre-Ozone Eff.	8.66	0.133	1.54	16%	62%	16%	62%
GAC/Sand Inf.	4.44	0.036	0.81	49%	73%	57%	90%
GAC/Sand Eff.	3.36	0.030	0.89	24%	17%	67%	91%
GAC Inf.	3.95	0.039	0.99	54%	71%	62%	89%
GAC Eff.	3.64	0.036	0.99	7.8%	7.7%	65%	90%

[a]UV = Ultraviolet absorbance reported in units of "inverse centimeters" (APHA, 1998)

[b]SUVA (L/mg-m) = Specific ultraviolet absorbance = 100*UV (cm^{-1})/DOC (mg/L) or UV (m^{-1})/DOC (mg/L), where DOC = dissolved organic carbon, which typically = 90-95% TOC (used TOC values in calculating SUVA) (e.g., UV = 0.204/cm = 0.204/(0.01 m) = 20.4/m, DOC = 6.23 mg/L, SUVA = (20.4 m^{-1})/(6.23 mg/L) = 3.27 L/mg-m)

[b]NR = Not reported; sample very turbid (white cloudy material that stayed in suspension)

Table 7. TOC and UV removal at plant 6

Location	TOC (mg/L)	UV[a] (cm^{-1})	SUVA[b] (L/mg-m)	Removal/Unit (%)		Removal/Cumulative (%)	
				TOC	UV	TOC	UV
11/27/2000							
Raw	6.36	0.210	3.30	---	---	---	---
Settled Water	3.76	0.062	1.65	41%	70%	41%	70%
Filter Eff.	3.51	0.058	1.65	6.6%	6.5%	45%	72%
02/26/2001							
Raw	8.09	0.261	3.23	---	---	---	---
Settled Water	4.24	0.070	1.65	48%	73%	48%	73%
Filter Eff.	3.99	0.069	1.73	5.9%	1.4%	51%	74%
08/13/2001							
Raw	7.86	0.264	3.36	---	---	---	---
Settled Water	4.7	0.085	1.81	40%	68%	40%	68%
Filter Eff.	4.53	0.070	1.55	3.6%	18%	42%	73%
10/22/2001							
Raw	6.66	0.189	2.84	---	---	---	---
Settled Water	4.16	0.071	1.71	38%	62%	38%	62%
Filter Effluent	3.93	0.066	1.68	5.5%	7.0%	41%	65%
04/15/2002							
Raw	9.5	0.305	3.21	---	---	---	---
Settled Water	4.07	0.070	1.72	57%	77%	57%	77%
Filter Effluent	3.88	0.062	1.60	4.7%	11%	59%	80%

Table 8. Miscellaneous water quality parameters in raw water at plant 5 and plant 6

Plant 5

Date	Bromide (mg/L)	Alkalinity (mg/L)	Ammonia (mg/L as N)
11/27/2000	0.08	26	ND
02/26/2001	0.047	22	ND
08/13/2001	0.06	19	ND
10/22/2001	0.08	28	0.04
04/15/2002	0.06	20	0.08

Plant 6

Date	Bromide (mg/L)	Alkalinity (mg/L)	Ammonia (mg/L as N)
11/27/2000	0.08	25	ND
02/26/2001	0.039	21	0.08
08/13/2001	0.05	20	ND
10/22/2001	0.08	27	ND
04/15/2002	0.06	20	0.05

DBPs

Oxyhalides. Tables 9-10 show the formation of oxyhalides at the two plants. At plant 5, ozonation resulted in the formation of from <3 to 6 μg/L of bromate when bromate was detected (Table 9). The conversion of bromide to bromate—when bromate was detected—was 2-5 % (on a molar basis), which is a typical conversion rate for an ozone plant operating for Giardia inactivation (Douville and Amy, 2000). Because the pH of ozonation was acidic (Table 4), bromate was often not detected, since low-pH ozonation minimizes bromate formation (Krasner

Table 9. Oxyhalide formation at Plant 5

Location	Bromate[a] (µg/L)	Chlorate (µg/L)	Bromate/Bromide (µmol/µmol)
11/27/2000			
Pre-Ozone Eff.	ND	5.8	---
Plant Eff.	3.8	79	3.0%
02/26/2001			
Pre-Ozone Effl.	ND	*4.6*	---
GAC/Sand Inf.	ND	8.4	---
GAC Inf.	ND	5.7	---
Plant Eff.	ND	45	---
08/13/2001			
Pre-Ozone Effl.	5	5	5.2%
GAC/Sand Inf.	ND	12	---
GAC Inf.	ND	14	---
Plant Eff.	ND	245	---
10/22/2001			
Pre-Ozone Effl.	5.6	ND	4.4%
GAC/Sand Inf.	*2.1*	ND	1.6%
GAC Inf.	ND	ND	---
Plant Eff.	*1.9*	162	1.5%
04/15/2002			
Pre-Ozone Effl.	3.5	ND	3.6%
GAC/Sand Inf.	*2.2*	ND	2.3%
GAC Inf.	ND	ND	---
Plant Eff.	*2.98*	184	3.1%

[a]Reporting detection level (RDL) for bromate = 3 µg/L; value in italics < RDL

Table 10. Oxyhalide formation at Plant 6

Location	Chlorite (µg/L)	Chlorate (µg/L)	ClO_2^-/ClO_2 %
11/27/2000			
Settled Water	1180	106	61%
Plant Eff.	1300	146	67%
02/26/2001			
Settled Water	783	69	51%
Plant Eff.	651	77	43%
08/13/2001			
Settled Water	772	137	39%
Clearwell Eff.	697	283	35%
10/22/2001			
Settled Water	1300	90	62%
Plant Eff.	1040	184	50%
04/15/2002			
Settled Water	765	100	51%
Plant Eff.	694	139	46%

et al., 1993). In addition, sodium hypochlorite can be contaminated with low or sub-µg/L levels of bromate (Delcomyn et al., 2000). Because the reporting detection level for bromate was 3 µg/L, it was not possible to determine if there was a significant increase in the concentration of bromate in the treated water after secondary disinfection. Low levels (<15 µg/L) of chlorate were detected at plant 5 until the plant effluent (Table 9). Chlorate was primarily introduced into the finished water after the secondary disinfection (chlorate is a by-product formed during the decomposition of the hypochlorite stock solution [Bolyard et al. [1992]).

It has been reported that during water treatment, approximately 50-70 % of the chlorine dioxide (ClO_2) reacted will immediately appear as chlorite (ClO_2^-) and the remainder as chloride (Aieta and Berg, 1986). An amount of chlorite consistent with this report was detected at plant 6 in the settled water (Table 10). The residual chlorite can continue to degrade in the water system. At plant 6, the concentration of chlorite was typically somewhat lower in the plant effluent, whereas the level of chlorate was somewhat higher.

Biodegradable Organic Matter. Ozone can convert natural organic matter in water to carboxylic acids (Kuo et al., 1996) and other assimilable organic carbon (AOC) (van der Kooij et al., 1982). Table 11 shows the carboxylic acid and AOC data for plant 5. Because AOC data are expressed in units of micrograms of carbon per liter (µg C/L), the carboxylic acid data were converted to the same units. A portion of the molecular weight (MW) of each carboxylic acid is due to carbon atoms (i.e., 27-49 %), and the remainder due to oxygen and hydrogen atoms. The sums of the five carboxylic acids (on a µg C/L basis) were compared to the AOC data. On a median basis for each sample date, 29 to 70 % of the AOC was accounted for by the carboxylic acids. For the raw-water sample in February 2001, >>100 % of the AOC was accounted for by the carboxylic acids. Because the amount of AOC in the raw water was low, this comparison was not as accurate as for the other samples in the plant.

Pre-ozonation significantly increased the concentration of the carboxylic acids (Table 11, Figure 3). In August 2001 (and in October 2001 and April 2002), formation of carboxylic acids (e.g., oxalate) was much higher during pre-ozonation (Table 11, Figure 4). The concentrations of the carboxylic acids were significantly decreased in both trains prior to the filters in August 2001 (Figure 3) (and in October 2001 and April 2002 [Table 11]). In the previous two samplings, the concentration of most of the carboxylic acids (e.g., oxalate) increased after intermediate ozonation (e.g., see GAC/sand influent data) (Figure 4). In the August 2001, October 2001, and April 2002 samplings, some of the carboxylic acids may have been removed during the coagulation process and/or biodegraded in the basins (Volk and LeChevallier, 2002). Biological filtration on the GAC/sand filters in the conventional treatment train and the GAC filters in the Super Pulsator treatment train resulted in further removal of the carboxylic acids that were present in the filter influent (Table 11, Figures 3-4). Moreover, the residual amount of carboxylic acids (e.g., oxalate) in the filtered water was somewhat similar in each season regardless of the level produced by the ozonation process (Table 11, Figure 3).

Table 11. Formation and removal of carboxylic acids and AOC at plant 5

	Concentration[a] (µg/L)					Concentration (µg C/L)							Sum/
Location	Acetate	Propionate	Formate	Pyruvate	Oxalate	Acetate	Propionate	Formate	Pyruvate	Oxalate	Sum	AOC	AOC
11/27/2000													
Raw	*5.0*	*6.5*	*8.3*	ND[b]	17	*2.0*	*3.2*	*2.2*	ND	4.7	12	18	68%
Pre-Ozone Eff.	37	ND	120	38	185	15	ND	32	16	50	113		
GAC/Sand Inf.	127	*9.4*	244	20	328	52	*4.6*	65	8.3	89	219	420	52%
GAC/Sand Eff.	19	ND	50	19	52	7.6	ND	13	8.0	14	43		
GAC Inf.	98	ND	202	ND	220	40	ND	54	ND	60	154	428	36%
GAC Eff.	18	ND	38	17	51	7.4	ND	10	7.2	14	38	349	11%
												median	44%
02/26/2001													
Raw	20	ND	42	22	43	8.1	ND	11	9.1	12	40	13	310%
Pre-Ozone Eff.	28	ND	34	27	398	11	ND	9.1	11	109	140		
GAC/Sand Inf.	136	ND	313	79	468	55	ND	83	33	128	299	430	70%
GAC/Sand Eff.	31	ND	66	26	67	13	ND	18	11	18	59		
GAC Inf.	NR[c]	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	331	
GAC Eff.	15	ND	22	ND	72	6.1	ND	5.9	ND	20	32	237	13%
												median	70%
08/13/2001													
Raw	17	ND	*11*	ND	24	6.9	ND	*2.9*	ND	6.5	16	38	44%
Pre-Ozone Eff.	600	ND	880	94	1800	244	ND	235	39	491	1009		
GAC/Sand Inf.	156	ND	264	53	472	63	ND	70	22	129	285	329	87%
GAC/Sand Eff.	37	ND	57	*8.5*	49	15	ND	15	*3.5*	13	47		
GAC Inf.	54	ND	78	19	159	22	ND	21	7.9	43	94	218	43%
GAC Eff.	32	ND	44	*13*	58	13	ND	12	*5.4*	16	46	87	53%
												median	48%
10/22/2001													
Raw	*9.6*	ND	*8.1*	ND	16	*3.9*	ND	*2.2*	ND	4.4	10	31	34%
Pre-Ozone Eff.	174	*3.1*	367	82	857	71	*1.5*	98	34	234	438		
GAC/Sand Inf.	111	ND	193	37	312	45	ND	51	15	85	197	759	26%
GAC/Sand Eff.	21	ND	40	*8.4*	45	8.5	ND	11	*3.5*	12	35		
GAC Inf.	25	ND	52	*9.7*	66	10	ND	14	*4.0*	18	46	161	29%
GAC Eff.	37	ND	36	*7.1*	33	15	ND	9.6	*2.9*	9.0	37	128	29%
												median	29%
04/15/2002													
Raw	*7.4*	ND	17	*9.0*	30	*3.0*	ND	4.5	*3.7*	8.2	19	46	42%
Pre-Ozone Eff.	343	*5.2*	618	88	2021	140	*2.6*	165	36	551	894		
GAC/Sand Inf.	159	*4.8*	235	69	713	65	*2.4*	63	29	194	353	317	111%
GAC/Sand Eff.	37	ND	72	22	101	15	ND	19	9.1	28	71		
GAC Inf.	71	ND	137	36	286	29	ND	37	15	78	158	553	29%
GAC Eff.	31	ND	82	23	88	13	ND	22	9.5	24	68	315	22%
												median	35%
Formula	CH_3COO^-	$CH_3CH_2COO^-$	$HCOO^-$	CH_3COCOO^-	$C_2O_4^{2-}$								
MW (gm/mole)	59	73	45	87	88								
C portion (gm/mole)	24	36	12	36	24								
C% of MW	41%	49%	27%	41%	27%								

[a]Method detection limit (MDL) = 3 µg/L; reporting detection level (RDL) = 15 µg/L; value in italics is < RDL

[b]ND = Not detected, value is < MDL

[c]NR = Not reported; apparent problems with the results of this sample

Figure 3

Formation and Removal of Carboxylic Acids at Plant 5
(August 13, 2001)

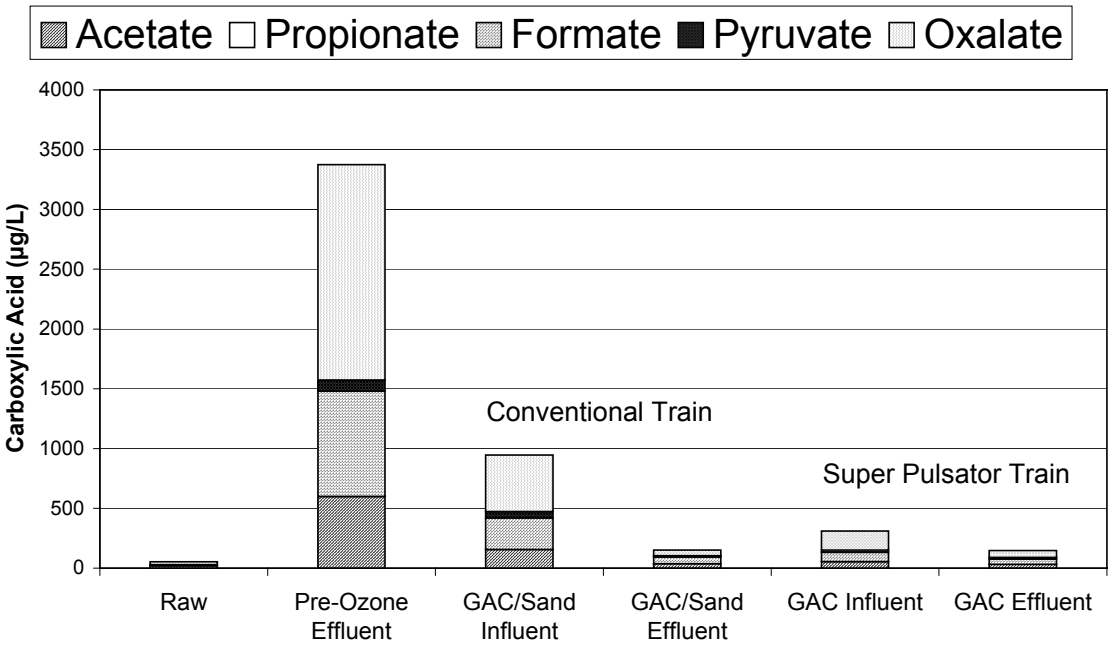
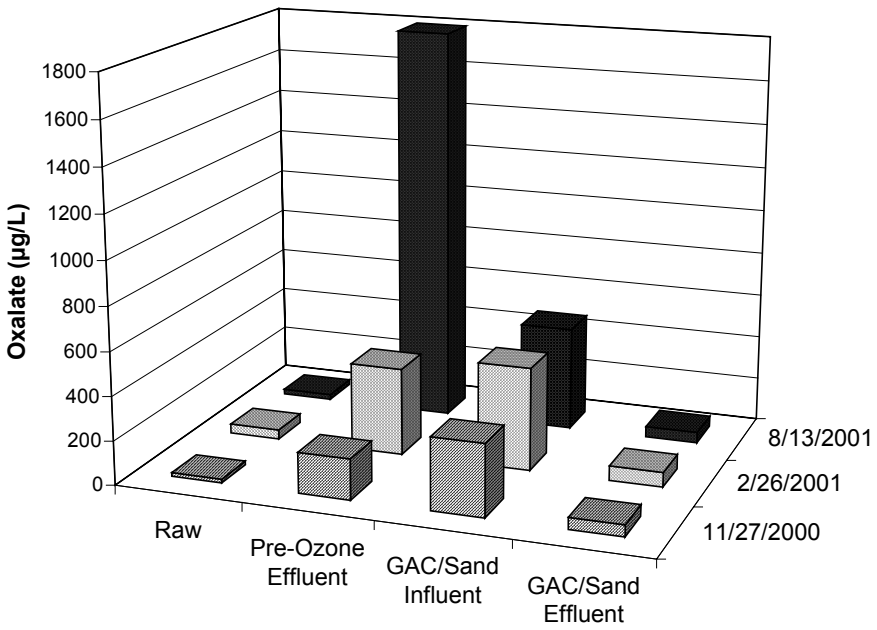


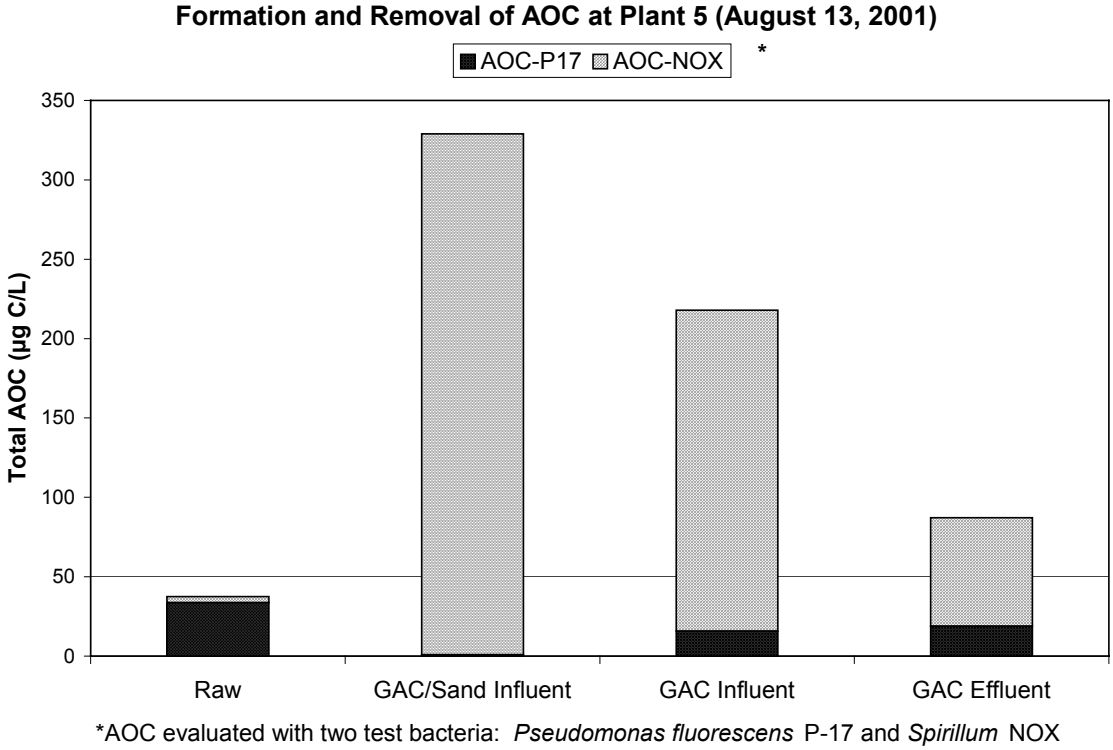
Figure 4

Seasonal Variation in Formation and Degradation
of Oxalate at Plant 5



Ozonation resulted in a significant increase in the concentration of AOC (Table 11, Figure 5). (Note, one of the bacterial strains used in the AOC method [i.e., *Spirillum NOX*] is used to estimate oxalate-carbon equivalents of the AOC [van der Kooij and Hijnen, 1984].) In August 2001, there was a significant reduction in the AOC on the GAC filter in the Super Pulsator train. (AOC was not sampled at the GAC/sand filter effluent in the conventional train, but based on carboxylic acid data [Figure 3], AOC should have been reduced in concentration.) In the other seasons, there was less AOC removal. The higher removal in August 2001 may have been due, in part, to the higher water temperature in the summer, which would have supported more biological activity.

Figure 5



Halogenated Organic and Other Nonhalogenated Organic DBPs. Tables 12 and 13 (11/27/00), Tables 15 and 16 (2/26/01), Tables 18 and 19 (8/13/01), Tables 22 and 23 (10/22/01), and Tables 24 and 25 (4/15/02) show results for the halogenated organic DBPs that were analyzed at Metropolitan Water District of Southern California (MWDSC). Table 14 (11/27/00), Table 20 (8/13/01), and Table 26 (4/15/02) show results for additional target DBPs that were analyzed for at the University of North Carolina (UNC). Table 17 (2/26/01 [plant 6] and 10/22/01 [plant 5]) shows results from broadscreen DBP analyses conducted at the U.S. Environmental Protection Agency (USEPA). Table 21 (8/13/01) and Table 27 (4/15/02) show results for halogenated furanones that were analyzed at UNC.

Table 12. DBP results at Plant 5 (11/27/00)

11/27/2000	MRL[a]	Plant 5[b]							
Compound	µg/L	Raw	GAC/Sand Inf	GAC Inf	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes									
Chloromethane	0.15	ND[c]			ND	ND		ND	
Bromomethane	0.20	ND			ND	ND		ND	
Bromochloromethane	0.14	ND			ND	ND		ND	
Dibromomethane	0.11	ND			ND	ND		ND	
Chloroform[d]	0.10	0.8	NR[e]	NR	12	15	NR	48	NR
Bromodichloromethane[d]	0.10	0.3	NR	NR	14	16	NR	30	NR
Dibromochloromethane[d]	0.12	0.2	NR	NR	13	15	NR	16	NR
Bromoform[d]	0.12	ND	NR	NR	2	2	NR	2	NR
THM4[f]		1.3	NR	NR	41	48	NR	96	NR
Dichloroiodomethane	0.25	ND	NR	NR	ND	ND	NR	ND	NR
Bromochloroiodomethane	3	ND	ND	ND	<3[g]	<3	NR	<1[h]	NR
Dibromoiodomethane	0.64	ND	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.10	ND	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.12	ND	ND	ND	ND	ND	ND	ND	ND
Iodoform	3	ND	ND	ND	ND	ND	NR	ND	NR
Carbon tetrachloride	0.06	ND			ND	ND		ND	
Haloacetic acids									
Monochloroacetic acid[d]	2				3.5	3.5		3.4	
Monobromoacetic acid[d]	1				ND	ND		ND	
Dichloroacetic acid[d]	1				8.7	9.8		22	
Bromochloroacetic acid[d]	1				7.0	7.7		12	
Dibromoacetic acid[d]	1				2.2	2.5		4.9	
Trichloroacetic acid[d]	1				3.8	5.3		9.0	
Bromodichloroacetic acid	1				5.7	7.0		8.1	
Dibromochloroacetic acid	1				2.9	3.4		4.2	
Tribromoacetic acid	2				ND	ND		ND	
HAA5[i]					18	21		39	
HAA9[j]					34	39		64	
DXAA[k]					18	20		39	
TXAA[l]					12	16		21	
Haloacetonitriles									
Chloroacetonitrile	0.10	ND	ND	ND	0.1	0.2	ND	ND	ND
Bromoacetonitrile	0.10	ND	0.2	ND	0.1	ND	ND	ND	ND
Dichloroacetonitrile[d]	0.10	ND	ND	ND	1	1	2	2	2
Bromochloroacetonitrile[d]	0.10	ND	ND	ND	1	1	2	2	2
Dibromoacetonitrile[d]	0.10	ND	ND	ND	0.7	0.7	0.9	0.9	0.8
Trichloroacetonitrile[d]	0.10	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetaldehydes									
Dichloroacetaldehyde	0.16	ND	ND	ND	1	1	1	1	1
Bromochloroacetaldehyde[m] Chloral hydrate[d]	0.20	ND	ND	ND	6	7	21	27	29
Tribromoacetaldehyde	0.10	ND	ND	ND	0.1	0.1	ND	ND	ND

Table 12 (continued)

11/27/2000	MRL[a]	Plant 5[b]							
Compound	µg/L	Raw	GAC/Sand Inf	GAC Inf	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloketones									
Chloropropanone	0.10	ND	ND	ND	0.3	0.2	0.3	0.2	0.3
1,1-Dichloropropanone[d]	0.10	ND	ND	ND	0.5	0.4	0.2	0.2	ND
1,3-Dichloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	3	ND			ND	ND		ND	
1,1,1-Trichloropropanone[d]	0.10	ND	ND	ND	4	4	8	9	8
1,1,3-Trichloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	3	ND			<3	3		<1	
1,1,1-Tribromopropanone	3	ND			ND	ND		ND	
1,1,3-Tribromopropanone	3	ND			ND	ND		ND	
1,1,3,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.10	ND	ND	ND	0.1	0.1	ND	ND	ND
Halonitromethanes									
Bromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	3	ND			ND	ND		<3	
Dibromonitromethane	0.10	ND	ND	ND	ND	ND	0.1	ND	ND
Chloropicrin[d]	0.10	ND	ND	ND	0.4	0.4	3	2	3
Miscellaneous Compounds									
Methyl ethyl ketone	1.90	ND			ND	ND		ND	
Methyl *tertiary* butyl ether	0.16	ND			ND	ND		ND	
Benzyl chloride	0.50	ND	ND	ND	ND	ND	NR	ND	NR

[a]MRL = Minimum reporting level, which equals method detection limit (MDL) or lowest calibration standard or concentration of blank

[b]Treatment plant sampled at (1) raw water, conventional train sampled at (2) GAC/sand influent, Super Pulsator train sampled at (3) GAC influent, (4) plant effluent, (5) DS at average detention time and (6) at maximum detention time, and (7) SDS testing of plant effluent held for average detention time and (8) held for maximum detention time.

[c]ND = Not detected at or above MRL

[d]DBP in the Information Collection Rule (ICR) (note: some utilities collected data for all 9 haloacetic acids for the ICR, but monitoring for only 6 haloacetic acids was required)

[e]NR = Not reported, due to interference problem on gas chromatograph or to problem with quality assurance

[f]THM4 = Sum of 4 THMs (chloroform, bromodichloromethane, dibromochloromethane, bromoform)

[g]<3: Concentration less than MRL of 3 µg/L

[h]<1: Concentration less than lowest calibration standard (i.e., 1 µg/L)

[i]HAA5 = Sum of 5 haloacetic acids (monochloro-, monobromo-, dichloro-, dibromo-, trichloroacetic acid)

[j]HAA9 = Sum of 9 haloacetic acids

[k]DXAA = Sum of dihaloacetic acids (dichloro-, bromochloro-, dibromoacetic acid)

[l]TXAA = Sum of trihaloacetic acids (trichloro-, bromodichloro-, dibromochoro-, tribromoacetic acid)

[m]Bromochloroacetaldehyde and chloral hydrate co-eulte; result = sum of 2 DBPs

Table 13. DBP results at Plant 6 (11/27/00)

11/27/2000	MRL[a]	Plant 6[n]								
Compound	µg/L	Raw	Settled	Filter Eff	Clearwell Eff	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes										
Chloromethane	0.15	ND[c]		ND		ND	ND		ND	
Bromomethane	0.20	ND		ND		ND	ND		ND	
Bromochloromethane	0.14	ND		ND		ND	ND		ND	
Dibromomethane	0.11	ND		ND		ND	ND		ND	
Chloroform[d]	0.10	0.3	0.8	4	NR[e]	8	8	NR	10	NR
Bromodichloromethane[d]	0.10	0.3	1	4	NR	8	8	NR	9	NR
Dibromochloromethane[d]	0.12	ND	0.5	2	NR	5	5	NR	5	NR
Bromoform[d]	0.12	ND	ND	0.5	NR	1	1	NR	1	NR
THM4[f]		0.6	2	11	NR	22	22	NR	25	NR
Dichloroiodomethane	0.25	ND	NR	ND	NR	0.3	0.3	NR	0.4	NR
Bromochloroiodomethane	3	ND	NR	ND	NR	<3[g]	<3	NR	<1[h]	NR
Dibromoiodomethane	0.64	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.10	ND	ND	ND	ND	ND	ND	ND	0.1	0.2
Bromodiiodomethane	0.12	ND	ND	ND	ND	ND	ND	ND	ND	ND
Iodoform	3	ND	NR	ND	NR	ND	ND	ND	ND	ND
Carbon tetrachloride	0.06	ND		ND		ND	ND		ND	
Haloacetic acids										
Monochloroacetic acid[d]	2		2.0	2.4	2.6	ND	2.3		2.2	
Monobromoacetic acid[d]	1		ND	ND	1.0	ND	ND		ND	
Dichloroacetic acid[d]	1		11	14	16	16	17		16	
Bromochloroacetic acid[d]	1		5.2	7.8	9.1	9.3	9.5		9.4	
Dibromoacetic acid[d]	1		ND	1.5	2.0	2.0	2.1		2.0	
Trichloroacetic acid[d]	1		ND	2.7	3.7	3.5	3.2		3.6	
Bromodichloroacetic acid	1		ND	1.7	2.1	2.0	1.9		2.0	
Dibromochloroacetic acid	1		ND	1.0	1.1	1.0	1.1		1.1	
Tribromoacetic acid	2		ND	ND	ND	ND	ND		ND	
HAA5[i]			13	20	25	22	25		24	
HAA9[j]			18	31	38	34	37		37	
DXAA[k]			16	23	27	28	29		28	
TXAA[l]			ND	5.4	6.9	6.5	6.2		6.7	
Haloacetonitriles										
Chloroacetonitrile	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromoacetonitrile	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[d]	0.10	ND	0.2	0.5	0.7	0.7	0.8	0.9	0.8	1
Bromochloroacetonitrile[d]	0.10	ND	0.1	0.3	0.4	0.4	0.4	0.6	0.5	0.5
Dibromoacetonitrile[d]	0.10	ND	ND	ND	0.1	0.1	0.1	0.1	0.1	0.1
Trichloroacetonitrile[d]	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetaldehydes										
Dichloroacetaldehyde	0.16	ND	0.6	1	1	2	2	5	2	2
Bromochloroacetaldehyde[m]										
Chloral hydrate[d]	0.20	ND	ND	1	2	2	2	3	2	2
Tribromoacetaldehyde	0.10	ND	ND	0.1	ND	ND	ND	ND	0.1	0.1

Table 13 (continued)

11/27/2000	MRL[a]	Plant 6[n]								
Compound	µg/L	Raw	Settled	Filter Eff	Clearwell Eff	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloketones										
Chloropropanone	0.10	ND	0.4	0.5	0.6	0.6	0.6	1	0.8	0.9
1,1-Dichloropropanone[d]	0.10	ND	0.5	0.9	1	1	1	2	1	2
1,3-Dichloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	3	ND		ND		ND	ND		ND	
1,1,1-Trichloropropanone[d]	0.10	ND	0.1	0.5	0.5	0.5	0.4	0.1	0.4	0.5
1,1,3-Trichloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	3	ND		<1		<1	<1		<1	
1,1,1-Tribromopropanone	3	ND		ND		ND	ND		ND	
1,1,3-Tribromopropanone	3	ND		ND		ND	ND		ND	
1,1,3,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes										
Bromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	3	ND		ND		ND	ND		<1	
Dibromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloropicrin [d]	0.10	ND	ND	ND	0.2	0.2	0.3	0.7	0.4	0.8
Miscellaneous Compounds										
Methyl ethyl ketone	1.90	ND		ND		ND	ND		ND	
Methyl *tertiary* butyl ether	0.16	ND		ND		ND	ND		ND	
Benzyl chloride	0.50	ND	NR	ND	NR	ND	ND	NR	ND	NR

[n]Treatment plant sampled at (1) raw water, (2) settled water, (3) filter effluent, (4) clearwell effluent, (5) plant effluent, (6) DS at average detention time and (7) at maximum detention time, and SDS testing of plant effluent (8) held for average detention time and (9) held for maximum detention time.

Table 14. Additional target DBP results (µg/L) at plants 5 and 6 (11/27/00)

11/27/2000	Plant 5[a]						Plant 6[b]					
Compound	Raw	OE1	Comb FE	PE	DS/ave	SDS/max	Raw	Settled	FE	PE	DS/ave	SDS/max
Monochloroacetaldehyde	0	0	0	0.2	0.1	0.6	0	0.6	0.7	0.3	0.4	0.3
Dichloroacetaldehyde	0	0	0	2.0	1.9	2.6	0	0.6	1.0	1.3	1.8	1.3
Bromochloroacetaldehyde	0	0	0	2.2	2.0	2.3	0	0.7	1.2	1.8	2.3	1.8
3,3-Dichloropropenoic acid	0.2	0.1	0.1	0.9	1.3	0.6	0.1	0.4	0.5	0.7	0.9	1.4
Bromochloromethylacetate	0	0	0	0	0	0	0	0	0	1.1	0	0
2,2-Dichloroacetamide	0	0	0	0	0	0	0	0	0	1.5	1.2	2.5
TOX (µg/L as Cl^-)	36.9		16.1	205	227	245	15.2	88.8	120	146	124	148
Cyanoformaldehyde	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1
5-Keto-1-hexanal	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6-Hydroxy-2-hexanone	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Dimethyglyoxal	<0.4	0.7	3.2	2.1	2.1	2.1	<0.4	1.1	0.6	1.7	1.3	1.8
trans -2-Hexenal	<0.1	0.3	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

[a]OE1= Raw-water ozone contactor effluent, Comb FE = combined filter effluent, PE = plant effluent

[b]FE = Filter effluent, PE = plant effluent

Table 15. DBP results at plant 5 (2/26/01)

2/26/2001	MRL[a]	Plant 5[b]							
Compound	µg/L	Raw	GAC/Sand Inf	GAC Inf	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes									
Chloromethane	0.15	ND[c]			ND	ND		ND	
Bromomethane	0.20	ND			ND	ND		ND	
Bromochloromethane	0.14	ND			ND	ND		ND	
Dibromomethane	0.11	ND			ND	ND		ND	
Chloroform[d]	0.1	0.1	ND	0.1	3	17	15	34	41
Bromodichloromethane[d]	0.1	ND	ND	ND	8	12	12	16	14
Dibromochloromethane[d]	0.10	ND	ND	ND	6	7	7	6	5
Bromoform[d]	0.12	ND	ND	ND	0.6	1	ND	0.6	ND
THM4[f]		0.1	ND	0.1	18	37	34	57	60
Dichloroiodomethane	0.25	ND	NR[e]	NR	0.3	0.3	NR	0.3	NR
Bromochloroiodomethane	0.20	ND	NR	NR	ND	ND	NR	ND	NR
Dibromoiodomethane	0.48	ND	NR	NR	ND	ND	NR	ND	NR
Chlorodiiodomethane	0.51	ND	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.56	ND	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.54	ND	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.06	ND			ND	ND		ND	
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids									
Monochloroacetic acid[d]	2				ND	4.9		5.4	
Monobromoacetic acid[d]	1				ND	1.1		ND	
Dichloroacetic acid[d]	1				9.8	16		20	
Bromochloroacetic acid[d]	1				5.0	9.2		7.4	
Dibromoacetic acid[d]	1				1.2	2.8		1.5	
Trichloroacetic acid[d]	1				4.8	13		8.5	
Bromodichloroacetic acid	1				4.8	10		5.1	
Dibromochloroacetic acid	1				2.2	3.4		1.9	
Tribromoacetic acid	2				ND	ND		ND	
HAA5[i]					16	38		35	
HAA9[j]					28	60		50	
DXAA[k]					16	28		29	
TXAA[l]					12	26		16	
Haloacetonitriles									
Chloroacetonitrile	0.1	ND	ND	ND	0.1	0.2	0.2	0.3	0.3
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[d]	0.10	ND	ND	ND	1	1	1	2	2
Bromochloroacetonitrile[d]	0.1	ND	ND	ND	0.8	0.8	0.8	1	0.8
Dibromoacetonitrile[d]	0.17	ND	ND	ND	ND	ND	ND	ND	ND
Trichloroacetonitrile[a]	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetaldehydes									
Dichloroacetaldehyde	0.16	ND	ND	0.2	0.7	0.5	0.5	0.7	0.5
Bromochloroacetaldehyde	0.1	ND	ND	ND	0.4	0.3	0.2	0.2	0.1
Chloral hydrate[d]	0.1	ND	ND	ND	3	5	5	9	10
Tribromoacetaldehyde	0.1	ND	ND	ND	ND	ND	ND	ND	ND

Table 15 (continued)

2/26/2001	MRL[a]	Plant 5[b]							
Compound	µg/L	Raw	GAC/Sand Inf	GAC Inf	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloketones									
Chloropropanone	0.5	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloropropanone[d]	0.11	ND	ND	ND	0.5	0.2	0.2	0.3	0.2
1,3-Dichloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	3	ND			ND	ND		ND	
1,3-Dibromopropanone	3	ND			ND	ND		ND	
1,1,1-Trichloropropanone[d]	0.10	ND	ND	ND	3	4	4	8	6
1,1,3-Trichloropropanone	0.11	ND	ND	ND	0.1	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	3	ND			<3[g]	<1[h]		<1	
1,1,1-Tribromopropanone	3	ND			ND	ND		ND	
1,1,3-Tribromopropanone	3	ND			ND	ND		ND	
1,1,3,3-Tetrachloropropanone	0.12	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	3	ND			<1	<1		<1	
1,1,3,3-Tetrabromopropanone	0.12	ND	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes									
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	3	ND			<1	<3		<1	
Bromochloronitromethane	3	ND			<3	3		<3	
Dibromonitromethane	0.12	ND	ND	ND	0.2	0.2	0.2	0.1	0.1
Chloropicrin[d]	0.1	ND	ND	ND	0.2	1	0.9	0.9	1
Miscellaneous Compounds									
Methyl ethyl ketone	1.90	ND			ND	ND		ND	
Methyl *tertiary* butyl ether	0.16	ND			ND	ND		ND	
Benzyl chloride	2	ND	ND	ND	ND	ND	ND	ND	ND

Table 16. DBP results at plant 6 (2/26/01)

2/26/2001	MRL[a]	Plant 6[n]								
Compound	µg/L	Raw	Settled	Filter Eff	Clearwell Eff	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes										
Chloromethane	0.15	ND[c]		ND		ND	ND		ND	
Bromomethane	0.20	ND		ND		ND	ND		ND	
Bromochloromethane	0.14	ND		ND		ND	ND		ND	
Dibromomethane	0.11	ND		ND		ND	ND		ND	
Chloroform[d]	0.1	0.1	0.2	1	1	2	5	1	2	2
Bromodichloromethane[d]	0.1	ND	0.1	0.8	2	2	5	4	3	3
Dibromochloromethane[d]	0.10	ND	ND	0.2	0.6	0.4	1	1	0.6	0.6
Bromoform[d]	0.12	ND	ND	ND	ND	ND	ND	ND	ND	ND
THM4[f]		0.1	0.3	2	4	4	11	6	6	6
Dichloroiodomethane	0.25	ND	NR[e]	0.2	NR	0.3	0.4	NR	0.3	NR
Bromochloroiodomethane	0.20	ND	NR	ND	NR	ND	ND	NR	ND	NR
Dibromoiodomethane	0.48	ND	NR	ND	NR	ND	ND	NR	ND	NR
Chlorodiiodomethane	0.51	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.56	ND	ND	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.54	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.06	ND		ND		ND	ND		ND	
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids										
Monochloroacetic acid[d]	2		ND	ND	2.0	ND	2.8		ND	
Monobromoacetic acid[d]	1		ND	ND	1.2	ND	1.2		ND	
Dichloroacetic acid[d]	1		10	14	17	16	22		18	
Bromochloroacetic acid[d]	1		1.8	3.2	4.5	4.3	7.1		4.1	
Dibromoacetic acid[d]	1		ND	ND	ND	ND	1.0		ND	
Trichloroacetic acid[d]	1		ND	2.4	4.7	3.8	5.7		3.1	
Bromodichloroacetic acid	1		ND	ND	1.5	1.3	2.0		ND	
Dibromochloroacetic acid	1		ND	ND	ND	ND	ND		ND	
Tribromoacetic acid	2		ND	ND	ND	ND	ND		ND	
HAA5[i]			10	16	25	20	33		21	
HAA9[j]			12	20	31	25	42		25	
DXAA[k]			12	17	22	20	30		22	
TXAA[l]			ND	2.4	6.2	5.1	7.7		3.1	
Haloacetonitriles										
Chloroacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[d]	0.10	ND	0.1	0.2	0.5	0.3	0.9	0.6	0.6	0.7
Bromochloroacetonitrile[d]	0.1	ND	ND	0.1	0.2	0.1	0.3	0.3	0.2	0.2
Dibromoacetonitrile[d]	0.17	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trichloroacetonitrile[d]	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetaldehydes										
Dichloroacetaldehyde	0.16	ND	0.3	0.5	1	0.8	1	1	1	2
Bromochloroacetaldehyde	0.1	<0.1	0.2	0.3	0.3	0.4	0.5	0.8	0.5	0.5
Chloral hydrate[d]	0.1	<0.1	0.1	0.4	0.5	0.4	1	0.5	0.6	0.6
Tribromoacetaldehyde	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table 16 (continued)

2/26/2001	MRL[a]	Plant 6[n]								
Compound	µg/L	Raw	Settled	Filter Eff	Clearwell Eff	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloketones										
Chloropropanone	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloropropanone[d]	0.11	ND	0.4	0.6	1	0.9	2	1	1	1
1,3-Dichloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	3	ND		ND		ND	ND		ND	
1,3-Dibromopropanone	3	ND		ND		ND	ND		ND	
1,1,1-Trichloropropanone[d]	0.10	ND	ND	0.3	0.6	0.4	0.8	0.3	0.4	0.4
1,1,3-Trichloropropanone	0.11	ND	ND	ND	ND	ND	0.2	ND	ND	ND
1-Bromo-1,1-dichloropropanone	3	ND		<1[h]		<1	<1		<1	
1,1,1-Tribromopropanone	3	ND		ND		ND	ND		ND	
1,1,3-Tribromopropanone	3	ND		ND		ND	ND		ND	
1,1,3,3-Tetrachloropropanone	0.12	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	3	ND		<1		<1	<1		<1	
1,1,3,3-Tetrabromopropanone	0.12	ND	ND	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes										
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	3	ND		ND		ND	ND		ND	
Bromochloronitromethane	3	ND		ND		ND	ND		ND	
Dibromonitromethane	0.12	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[d]	0.1	ND	ND	0.1	0.3	0.1	0.4	0.4	0.4	0.5
Miscellaneous Compounds										
Methyl ethyl ketone	1.90	ND		ND		ND	ND		ND	
Methyl *tertiary* butyl ether	0.16	ND		ND		ND	ND		ND	
Benzyl chloride	2	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table 17. Occurrence of other DBPs[a] at plants 5 and 6

Compound	Plant 6 (2/26/01)		Plant 5 (10/22/01)	
	ClO_2	$ClO_2 + Cl_2/NH_2Cl$	O_3	$O_3 + Cl_2$
Halomethanes				
Bromodichloromethane[b]	x	x	x	x
Dibromochloromethane	x	x	x	x
Bromoform	x	x	x	x
Dichloroiodomethane	x	x	-	x
Bromochloroiodomethane	x	x	-	-
Haloacids				
Chloroacetic acid	x	x	-	-
Dichloroacetic acid	x	x	x	x
Bromochloroacetic acid	x	x	-	-
Dibromoacetic acid	x	x	-	-
Bromodichloroacetic acid	-	x	-	-
Trichloroacetic acid	x	x	-	-
3,3-Dichloropropenoic acid	x	x	-	-
Trichloropropenoic acid	x	x	-	-
3,4,4-Trichloro-3-butenoic acid	-	-	-	x
Haloacetonitriles				
Dichloroacetonitrile	x	x	x	x
Bromochloroacetonitrile	x	x	-	x
Dibromoacetonitrile	x	x	-	x
Tribromoacetonitrile	x	x	-	-
Haloaldehydes				
Dichloroacetaldehyde	x	x	-	-
Trichloroacetaldehyde	x	x	x	x
2-Bromo-2-methylpropanal	x	x	x	x
*Iodobutanal	x	x	-	-
Haloketones				
Chloropropanone	x	x	-	-
1,1-Dichloropropanone	x	x	x	x
1-Bromo-1-chloropropanone	x	x	-	-
1,1,1-Trichloropropanone	x	x	x	x
1-Bromo-1,1-dichloropropanone	-	x	-	x
1,1,3,3-Tetrachloropropanone	x	x	-	-
1,1,1,3-Tetrachloropropanone	-	x	-	-
1-Bromo-1,3,3-trichloropropanone	x	x	-	-
1,1-Dibromo-3,3-dichloropropanone	x	x	-	-
Pentachloropropanone	-	x	-	x
Halonitromethanes				
Trichloronitromethane	-	x	-	X
Miscellaneous Halogenated DBPs				
Hexachlorocyclopentadiene	-	x	-	-
Dichloroacetic acid methyl ester	x	x	-	-
Non-halogenated DBPs				
Glyoxal	-	-	x	x
Methyl glyoxal	-	-	x	x
Hexanoic acid	x	-	-	-
Decanoic acid	x	x	-	-
Hexadecanoic acid	-	x	-	-

[a]DBPs detected by broadscreen gas chromatography/mass spectrometry (GC/MS) technique
[b]Compounds listed in italics were confirmed through the analysis of authentic standards; haloacids and non-halogenated carboxylic acids identified as their methyl esters.

Table 18. DBP results at plant 5 (8/13/01)

8/13/2001	MRL[a]	Plant 5[b]							
Compound	µg/L	Raw	GAC/Sand	GAC Inf	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes									
Chloromethane	0.2	ND[c]			ND	ND		ND	
Bromomethane	0.2	ND			ND	ND		ND	
Bromochloromethane	0.5	ND			ND	ND		ND	
Dibromomethane	0.5	ND			ND	ND		ND	
Chloroform[d]	0.1	ND	ND	ND	9	15	20	12	25
Bromodichloromethane[d]	0.1	ND	ND	ND	11	15	17	11	18
Dibromochloromethane[d]	0.1	ND	ND	ND	5	6	6	5	6
Bromoform[d]	0.11	ND	ND	ND	0.5	0.6	0.7	0.4	0.5
THM4[f]		ND	ND	ND	26	37	44	28	50
Dichloroiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND
Bromochloroiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND
Dibromoiodomethane	0.52	ND	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.2	ND			ND	ND		ND	
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids									
Monochloroacetic acid[d]	2				ND	2.5		7.1	
Monobromoacetic acid[d]	1				ND	ND		1.2	
Dichloroacetic acid[d]	1				18	21		40	
Bromochloroacetic acid[d]	1				11	12		14	
Dibromoacetic acid[d]	1				4.2	4.2		4.4	
Trichloroacetic acid[d]	1				12	16		18	
Bromodichloroacetic acid	1				7.9	8.6		1.1	
Dibromochloroacetic acid	1				2.6	2.8		2.0	
Tribromoacetic acid	2				ND	ND		ND	
HAA5[i]					34	44		71	
HAA9[j]					56	67		88	
DXAA[k]					33	37		58	
TXAA[l]					23	27		21	
Haloacetonitriles									
Chloroacetonitrile	0.1	ND	ND	ND	0.2	0.2	0.2	0.3	0.3
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[d]	0.10	ND	ND	ND	2	2	2	3	5
Bromochloroacetonitrile[d]	0.1	ND	ND	ND	1	1	1	1	0.8
Dibromoacetonitrile[d]	0.14	ND	ND	ND	0.8	0.9	0.7	0.3	0.2
Trichloroacetonitrile[d]	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Bromodichloroacetonitrile	0.5	ND			ND	ND			ND
Dibromochloroacetonitrile	0.5	ND			ND	ND			ND
Tribromoacetonitrile	0.5	ND			ND	ND			ND
Haloacetaldehydes									
Dichloroacetaldehyde	0.1	*2*[o]	*0.4*[o]	*ND*	*0.8*[o]	*1*[o]	*0.8*[o]	*4*[o]	*1*[o]
Bromochloroacetaldehyde	0.5	*1*[o]	*ND*	*ND*	*ND*	*ND*	*ND*	2	ND
Chloral hydrate[d]	0.1	*2*[o]	*0.1*[o]	ND	*11*[o]	*15*[o]	*18*[o]	*17*[o]	*26*[o]
Tribromoacetaldehyde	0.1	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	ND	ND

[o]Quality control problems with haloacetaldehydes

Table 18 (continued)

8/13/2001	MRL[a]	Plant 5[b]							
Compound	µg/L	Raw	GAC/Sand	GAC Inf	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloketones									
Chloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloropropanone[d]	0.10	ND	ND	ND	0.6	0.5	0.2	0.3	0.2
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloropropanone[d]	0.1	ND	ND	ND	5	5	2	6	5
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1-Tribromopropanone	0.29	ND	ND	ND	ND	ND	ND	ND	NR[e]
1,1,3-Tribromopropanone	0.14	ND	ND	ND	ND	ND	ND	ND	NR
1,1,3,3-Tetrachloropropanone	0.5	ND			ND	ND		ND	
1,1,1,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes									
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	0.1	ND	ND	ND	0.7	0.9	0.8	0.1	0.5
Bromochloronitromethane	0.1	ND	ND	ND	0.2	0.2	0.2	ND	0.1
Dibromonitromethane	0.10	ND	ND	ND	ND	0.1	ND	ND	ND
Chloropicrin[d]	0.1	ND	ND	ND	0.4	0.6	0.7	0.6	1
Bromodichloronitromethane	0.5	ND			0.8	1			ND
Dibromochloronitromethane	0.5	ND			0.8	0.7			0.8
Bromopicrin	2.0	ND			ND	ND			ND
Miscellaneous Compounds									
Methyl ethyl ketone	0.5	7			2	1		3	
Methyl *tertiary* butyl ether	0.2	0.4			0.3	0.4		1	
1,1,2,2-Tetrabromo-2-chloroethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Benzyl chloride	0.25	ND	NR	NR	ND	ND	NR	ND	NR

Table 19. DBP results at plant 6 (8/13/01)

8/13/2001	MRL[a]	Plant 6[n]								
Compound	µg/L	Raw	Settled	Filt Eff	Clearwell	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes										
Chloromethane	0.2	ND[c]		ND		ND	ND		ND	
Bromomethane	0.2	ND		ND		ND	ND		ND	
Bromochloromethane	0.5	ND		ND		ND	ND		ND	
Dibromomethane	0.5	ND		ND		ND	ND		ND	
Chloroform[d]	0.1	ND	0.2	10	18	17	14	9	NR[e]	18
Bromodichloromethane[d]	0.1	ND	0.1	5	8	8	8	8	6	11
Dibromochloromethane[d]	0.1	ND	ND	0.9	2	1	2	2	1	2
Bromoform[d]	0.11	ND	ND	ND	ND	ND	ND	0.1	ND	0.1
THM4[f]	0	ND	0.3	16	28	26	24	19	NR	31
Dichloroiodomethane	0.5	ND	ND	0.8	0.5	0.9	0.5	ND	0.5	ND
Bromochloroiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibromoiodomethane	0.52	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.2	ND		ND		ND	ND		ND	
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids										
Monochloroacetic acid[d]	2		ND	ND	6.3	6.2	5.3		4.5	
Monobromoacetic acid[d]	1		ND	3.7	ND	ND	3.5		ND	
Dichloroacetic acid[d]	1		4.8	29	38	40	40		48	
Bromochloroacetic acid[d]	1		1.2	8.2	11	11	12		14	
Dibromoacetic acid[d]	1		ND	ND	1.2	ND	1.7		1.9	
Trichloroacetic acid[d]	1		ND	20	21	22	19		25	
Bromodichloroacetic acid	1		ND	7.5	7.9	8.0	8.1		10	
Dibromochloroacetic acid	1		ND	ND	1.5	1.2	1.3		1.5	
Tribromoacetic acid	2		ND	ND	ND	ND	ND		ND	
HAA5[i]			5	53	67	68	70		79	
HAA9[j]			6	68	87	88	91		105	
DXAA[k]			6	37	50	51	54		64	
TXAA[l]			ND	28	35	31	28		37	
Haloacetonitriles										
Chloroacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[d]	0.10	ND	0.2	2	2	2	2	2	3	3
Bromochloroacetonitrile[d]	0.1	ND	ND	0.3	0.5	0.5	0.6	0.7	0.4	0.7
Dibromoacetonitrile[d]	0.14	ND	ND	ND	ND	ND	0.2	0.2	0.1	0.1
Trichloroacetonitrile[d]	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodichloroacetonitrile	0.5	ND		ND		ND				ND
Dibromochloroacetonitrile	0.5	ND		ND		ND				ND
Tribromoacetonitrile	0.5	ND		ND		ND				ND
Haloacetaldehydes										
Dichloroacetaldehyde	0.1	*2*[o]	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*6*[o]	*3*[o]
Bromochloroacetaldehyde	0.5	*0.7*[o]	*ND*	*0.8*[o]	*ND*	*ND*	*ND*	*ND*	2	0.6
Chloral hydrate[d]	0.1	*1*[o]	*ND*	*3*[o]	*4*[o]	*4*[o]	*4*[o]	*3*[o]	*10*[o]	*6*[o]
Tribromoacetaldehyde	0.1	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	ND	ND

[o]Quality control problems with haloacetaldehydes

Table 19 (continued)

8/13/2001	MRL[a]	Plant 6[n]								
Compound	µg/L	Raw	Settled	Filt Eff	Clearwell	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloketones										
Chloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloropropanone[d]	0.10	ND	0.7	1	0.7	0.9	2	1	2	2
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloropropanone[d]	0.1	ND	ND	2	2	2	1	0.3	0.5	0.3
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1-Tribromopropanone	0.29	ND	ND	ND	ND	ND	ND	ND	ND	NR
1,1,3-Tribromopropanone	0.14	ND	ND	ND	ND	ND	ND	ND	ND	NR
1,1,3,3-Tetrachloropropanone	0.5	ND		ND		ND	ND		ND	
1,1,1,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes										
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	0.1	ND	ND	ND	ND	0.1	ND	ND	0.1	0.1
Bromochloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[d]	0.1	ND	ND	0.1	0.2	0.2	0.3	0.3	0.3	0.9
Bromodichloronitromethane	0.5	ND		ND		ND				ND
Dibromochloronitromethane	0.5	ND		ND		ND				ND
Bromopicrin	2.0	ND		ND		ND				ND
Miscellaneous Compounds										
Methyl ethyl ketone	0.5	3		4		2	1		0.5	
Methyl *tertiary* butyl ether	0.2	0.3		0.3		0.5	ND		0.5	
1,1,2,2-Tetrabromo-2-chloroethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzyl chloride	0.25	ND	NR	ND	NR	ND	ND	NR	ND	NR

Table 20. Additional target DBP results (µg/L) at plants 5 and 6 (8/13/01)

8/13/2001	Plant 5[a]						Plant 6					
Compound	Raw	OE1	GAC FE	PE	DS/ave	SDS/max	Raw	Settled	FE	PE	DS/ave	SDS/max
Monochloroacetaldehyde	0	0	0	0.1	0.2	0.3	0	0.3	0.2	0.1	0.1	0.1
Dichloroacetaldehyde	0	0	0	2.1	1.8	5.1	0	0.5	2.5	3.5	2.8	4.2
Bromochloroacetaldehyde	0	0	0	0.8	1.1	1.5	0	0	0.4	0.6	1.0	1.2
3,3-Dichloropropenoic acid	0	0	0	0	0	4.4	0	0	2.5	4.7	4.8	5.5
Bromochloromethylacetate	0	0	0	0	0	0	0	0	0	0	0	0
2,2-Dichloroacetamide	0	0	0	0	0	0	0	0	0	5.6	4.1	3.9
TOX (µg/L as Cl^-)	10.5		11.5	284	257	327	12.7	52.9	203	245	238	241
Cyanoformaldehyde	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1		<0.1	<0.1	<0.1	<0.1
5-Keto-1-hexanal	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6-Hydroxy-2-hexanone	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Dimethyglyoxal	<0.4	2.4	0.8	1.8	1.2	1.9	<0.4	1.6	0.5	1.2	1.4	1.6
trans -2-Hexenal	<0.1		<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

[a]GAC FE = GAC filter effluent

Table 21. Halogenated furanone results (µg/L) at plants 5 and 6 (8/13/01)

8/13/2001	Plant 5			Plant 6				
Compound	GAC FE	PE	DS/ave	Raw	Settled	FE	PE	DS/ave
MX	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	0.31	0.30
ZMX	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
EMX	<0.04	<0.04	<0.04	<0.04	<0.04	0.23	<0.04	0.12
Mucochloric acid (ring)	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Mucochloric acid (open)	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04

Table 22. DBP results at plant 5 (10/22/01)

10/22/2001	MRL[a]	Plant 5[b]							
Compound	µg/L	Raw	GAC/Sand	GAC Inf	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes									
Chloromethane	0.2	ND[c]			ND	ND		ND	
Bromomethane	0.2	ND			ND	ND		ND	
Bromochloromethane	0.5	ND			ND	ND		ND	
Dibromomethane	0.5	ND			ND	ND		ND	
Chloroform[d]	0.5	ND	ND	ND	10	34	NR[e]	58	60
Bromodichloromethane[d]	0.1	ND	ND	ND	19	31	NR	30	30
Dibromochloromethane[d]	0.1	ND	ND	ND	12	19	20	14	12
Bromoform[d]	0.1	ND	ND	ND	2	2	1	2	2
THM4[f]		ND	ND	ND	43	86	NR	104	104
Dichloroiodomethane	0.5	ND	ND	ND	0.5	<0.5[p]	NR	ND	ND
Bromochloroiodomethane	0.5	ND	NR	NR	ND	ND	NR	ND	NR
Dibromoiodomethane	0.52	ND	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.1-0.5[q]	ND	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND
Iodoform	1.0	ND	NR	NR	ND	ND	NR	ND	NR
Carbon tetrachloride	0.2	ND			ND	ND		ND	
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids									
Monochloroacetic acid[d]	2				ND	ND		4.1	
Monobromoacetic acid[d]	1				ND	ND		1.2	
Dichloroacetic acid[d]	1				4.5	5.9		28	
Bromochloroacetic acid[d]	1				4.2	4.9		19	
Dibromoacetic acid[d]	1				2.5	2.1		5.2	
Trichloroacetic acid[d]	1				2.7	6.4		9.4	
Bromodichloroacetic acid	1				3.8	6.2		8.3	
Dibromochloroacetic acid	1				2.0	2.5		3.0	
Tribromoacetic acid	2				ND	ND		ND	
HAA5[i]					10	14		48	
HAA9[j]					20	28		78	
DXAA[k]					11	13		52	
TXAA[l]					8.5	15		21	
Haloacetonitriles									
Chloroacetonitrile	0.1	ND	ND	ND	0.2	0.4	ND	0.4	0.5
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[d]	0.1	ND	ND	ND	1	4	4	2	3
Bromochloroacetonitrile[d]	0.1	ND	ND	ND	1	2	2	2	1
Dibromoacetonitrile[d]	0.1	0.2	ND	ND	0.9	1	0.7	1	0.6
Trichloroacetonitrile[d]	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Bromodichloroacetonitrile	0.5	ND			ND	ND			ND
Dibromochloroacetonitrile	0.5	ND			ND	ND			ND
Tribromoacetonitrile	0.9	ND			ND	ND			ND
Haloacetaldehydes									
Dichloroacetaldehyde	1.1	0.4	ND	0.2	1	2	2	4	3
Bromochloroacetaldehyde	0.5	ND	ND	0.1	0.5	0.2	1	ND	ND
Chloral hydrate[d]	0.1	1	ND	0.4	3	8	8	13	22
Tribromoacetaldehyde	0.1	ND	ND	0.6	ND	ND	ND	ND	ND

Table 22 (continued)

10/22/2001	MRL[a]	Plant 5[b]							
Compound	µg/L	Raw	GAC/Sand	GAC Inf	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloketones									
Chloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloropropanone[d]	0.10	ND	ND	ND	0.7	0.8	0.7	0.5	0.2
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloropropanone[d]	0.1	ND	ND	ND	4	5	4	4	3
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	0.1	ND	ND	ND	0.4	ND	ND	ND	ND
1,1,1-Tribromopropanone	0.1-0.3[q]	ND	ND	0.1	ND	ND	ND	ND	ND
1,1,3-Tribromopropanone	0.1-0.7[q]	ND	ND	0.1	ND	ND	ND	ND	ND
1,1,3,3-Tetrachloropropanone	2.5	ND	ND	ND	ND	ND	ND	ND	NR
1,1,1,3-Tetrachloropropanone	0.10	ND	ND	0.2	0.1	ND	ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.5-2[q]	ND	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes									
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	0.1	0.5
Dichloronitromethane	0.1	ND	ND	ND	0.3	1	1	2	2
Bromochloronitromethane	0.1	ND	ND	ND	0.4	0.5	0.5	0.3	0.2
Dibromonitromethane	0.10	ND	ND	ND	0.6	0.5	0.4	0.2	0.1
Chloropicrin[d]	0.1	ND	ND	ND	0.3	2	2	1	NR
Bromodichloronitromethane	0.5	ND			ND	ND			1
Dibromochloronitromethane	0.5-2[r]	ND			ND	ND			1
Bromopicrin	0.5	ND			2	2			ND
Miscellaneous Compounds									
Methyl ethyl ketone	0.5	0.6			ND	ND		ND	
Methyl *tertiary* butyl ether	0.2	ND			ND	ND		ND	
1,1,2,2-Tetrabromo-2-chloroethane	0.5-2[q]	ND	ND	ND	ND	ND	ND	ND	ND
Benzyl chloride	0.25	ND	NR	NR	ND	ND	NR	ND	NR

[p]<0.5 = Detected by GC/MS below its MRL of 0.5 µg/L;
quality assurance problem with gas chromatograph method

[q]Higher MRL for SDS samples

[r]Lower MRL for SDS samples

Table 23. DBP results at plant 6 (10/22/01)

10/22/2001	MRL[a]	Plant 6[n]								
Compound	µg/L	Raw	Settled	Filt Eff	Clearwell	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes										
Chloromethane	0.2	ND[c]		ND		ND	ND		ND	
Bromomethane	0.2	ND		ND		ND	ND		ND	
Bromochloromethane	0.5	ND		ND		ND	ND		ND	
Dibromomethane	0.5	ND		ND		ND	ND		ND	
Chloroform[d]	0.5	0.5	0.6	13	NR[e]	18	24	NR	17	22
Bromodichloromethane[d]	0.1	0.1	0.2	12	NR	21	24	NR	19	26
Dibromochloromethane[d]	0.1	ND	ND	4	6	7	8	NR	8	6
Bromoform[d]	0.1	ND	ND	0.4	0.5	0.5	0.5	0.5	0.6	0.8
THM4[f]		0.6	0.8	29	NR	47	57	NR	45	55
Dichloroiodomethane	0.5	ND	0.5	3	2	3	4	NR	3	2
Bromochloroiodomethane	0.5	ND	NR	ND	NR	<0.5[p]	<0.5	NR	<0.5	NR
Dibromoiodomethane	0.52	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.1-0.5[q]	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Iodoform	1.0	ND	NR	ND	NR	ND	ND	NR	ND	NR
Carbon tetrachloride	0.2	ND		ND		ND	ND		ND	
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids										
Monochloroacetic acid[d]	2		ND	ND	2.4	2.2	2.6		3.0	
Monobromoacetic acid[d]	1		ND	ND	ND	ND	ND		ND	
Dichloroacetic acid[d]	1		2.8	9.7	13	12	14		23	
Bromochloroacetic acid[d]	1		1.3	4.7	6.6	6.3	7.2		11	
Dibromoacetic acid[d]	1		ND	1.6	2.2	2.0	2.2		3.1	
Trichloroacetic acid[d]	1		ND	4.6	7.4	6.5	6.9		10	
Bromodichloroacetic acid	1		ND	3.7	4.8	4.5	4.5		6.2	
Dibromochloroacetic acid	1		ND	2.2	2.3	2.1	2.0		2.0	
Tribromoacetic acid	2		ND	ND	ND	ND	ND		ND	
HAA5[i]			2.8	16	25	23	26		39	
HAA9[j]			4.1	27	39	36	39		58	
DXAA[k]			4.1	16	22	20	23		37	
TXAA[l]			ND	11	15	13	13		18	
Haloacetonitriles										
Chloroacetonitrile	0.1	ND	ND	ND	ND	ND	0.4	ND	0.4	ND
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[d]	0.1	ND	0.1	1	2	2	3	NR	3	4
Bromochloroacetonitrile[d]	0.1	ND	ND	0.6	0.9	1	1	NR	1	2
Dibromoacetonitrile[d]	0.1	ND	ND	0.2	0.3	0.4	0.4	NR	0.4	0.7
Trichloroacetonitrile[d]	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodichloroacetonitrile	0.5	ND		ND		ND				ND
Dibromochloroacetonitrile	0.5	ND		ND		ND				0.5
Tribromoacetonitrile	0.9	ND		ND		ND				ND
Haloacetaldehydes										
Dichloroacetaldehyde	1.1	0.4	ND	2	2	2	2	8	12	12
Bromochloroacetaldehyde	0.5	ND	ND	0.4	0.5	0.5	0.7	0.8	2	3
Chloral hydrate[d]	0.1	ND	ND	ND	3	2	3	2	6	6
Tribromoacetaldehyde	0.1	ND	ND	ND	ND	ND	ND	0.9	ND	1

Table 23 (continued)

10/22/2001	MRL[a]	Plant 6[n]								
Compound	µg/L	Raw	Settled	Filt Eff	Clearwell	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloketones										
Chloropropanone	0.1	ND	ND	ND	ND	ND	0.1	0.2	ND	ND
1,1-Dichloropropanone[d]	0.10	ND	ND	1	0.9	1	2	2	2	NR
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	0.1
1,1-Dibromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloropropanone[d]	0.1	0.1	ND	2	2	2	2	NR	2	2
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	0.1	ND	ND	0.4	0.5	0.4	ND	ND	ND	ND
1,1,1-Tribromopropanone	0.1-0.3[q]	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3-Tribromopropanone	0.1-0.7[q]	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrachloropropanone	2.5	ND	ND	ND	ND	ND	ND	ND	ND	NR
1,1,1,3-Tetrachloropropanone	0.10	ND	ND	0.1	0.2	0.1	ND	0.4	ND	0.5
1,1,3,3-Tetrabromopropanone	0.5-2[q]	ND	ND	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes										
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	0.1	ND	ND	ND	ND	ND	0.2	ND	0.2	0.3
Bromochloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[d]	0.1	ND	ND	0.2	0.2	0.2	0.4	0.5	0.6	0.9
Bromodichloronitromethane	0.5	ND		ND		ND				0.8
Dibromochloronitromethane	0.5-2[r]	ND		ND		ND				0.5
Bromopicrin	0.5	ND		ND		ND				ND
Miscellaneous Compounds										
Methyl ethyl ketone	0.5	0.7		ND		ND	0.6		ND	
Methyl *tertiary* butyl ether	0.2	ND		ND		ND	ND		ND	
1,1,2,2-Tetrabromo-2-chloroethane	0.5-2[q]	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzyl chloride	0.25	ND	NR	ND	NR	ND	ND	NR	ND	NR

Table 24. DBP results at plant 5 (4/15/02)

4/15/2002	MRL[a]	Plant 5[b]							
Compound	µg/L	Raw	GAC/Sand	GAC Inf	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes									
Chloromethane	0.2	ND[c]			ND	ND		ND	
Bromomethane	0.2	ND			ND	ND		ND	
Bromochloromethane	0.5	ND			ND	ND		ND	
Dibromomethane	0.5	ND			ND	ND		ND	
Chloroform[d]	0.2	ND	ND	ND	11	26	NR[e]	49	NR
Bromodichloromethane[d]	0.2	ND	ND	ND	14	17	NR	26	NR
Dibromochloromethane[d]	0.2	ND	ND	ND	7	8	NR	7	NR
Bromoform[d]	0.1	ND	ND	ND	0.9	0.9	0.7	1	1
THM4[f]		ND	ND	ND	33	52	NR	83	NR
Dichloroiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND
Bromochloroiodomethane	0.5	ND	NR	NR	ND	ND	NR	ND	NR
Dibromoiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND
Iodoform	2	ND	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.2	ND			ND	ND		ND	
Tribromochloromethane	0.5	ND	NR	NR	ND	ND	NR	ND	NR
Haloacetic acids									
Monochloroacetic acid[d]	2				2.2	3.6		6.2	
Monobromoacetic acid[d]	1				ND	ND		1.1	
Dichloroacetic acid[d]	1				12	17		26	
Bromochloroacetic acid[d]	1				5.3	6.3		6.4	
Dibromoacetic acid[d]	1				1.9	1.9		2.4	
Trichloroacetic acid[d]	1				6.9	11		9.2	
Bromodichloroacetic acid	1				7.3	7.7		7.1	
Dibromochloroacetic acid	1				2.1	2.1		2.0	
Tribromoacetic acid	2				ND	ND		ND	
HAA5[i]					23	34		45	
HAA9[j]					38	50		60	
DXAA[k]					19	25		35	
TXAA[l]					16	21		18	
Haloacetonitriles									
Chloroacetonitrile	0.1	ND	ND	ND	0.4	0.3	0.5	0.8	0.6
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[d]	0.1	ND	ND	ND	NR	1	NR	5	NR
Bromochloroacetonitrile[d]	0.1	ND	ND	ND	1	1	0.8	2	1
Dibromoacetonitrile[d]	0.1	ND	ND	ND	0.4	0.4	0.4	0.6	0.6
Trichloroacetonitrile[d]	0.5	ND	NR	NR	ND	ND	NR	ND	NR
Bromodichloroacetonitrile	0.5	ND			ND	ND			ND
Dibromochloroacetonitrile	0.5	ND			ND	ND			ND
Tribromoacetonitrile	0.96	ND			ND	ND			ND
Haloacetaldehydes									
Dichloroacetaldehyde	0.5	ND	ND	0.5	2	2	3	4	4
Bromochloroacetaldehyde	0.5	ND	ND	ND	0.5	ND	ND	0.7	0.6
Chloral hydrate[d]	0.1	ND	0.1	0.3	6	6	13	22	18
Tribromoacetaldehyde	0.1	ND	ND	0.3	ND	ND	ND	ND	ND

Table 24 (continued)

4/15/2002	MRL[a]	Plant 5[b]							
Compound	µg/L	Raw	GAC/Sand	GAC Inf	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloketones									
Chloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloropropanone[d]	1.0	ND	ND	ND	<1[s]	1	NR	ND	NR
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	0.5	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloropropanone[d]	0.5	ND	ND	ND	4	8	NR	13	NR
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	0.3	ND	NR	NR	0.4	0.4	NR	ND	NR
1,1,1-Tribromopropanone	>5	ND	NR	NR	ND	ND	NR	ND	NR
1,1,3-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrachloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.5	ND	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes									
Chloronitromethane	0.2	ND			0.6	2			
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	0.1	ND	ND	ND	0.4	0.5	0.7	0.7	0.3
Bromochloronitromethane	0.1	ND	ND	ND	ND	ND	ND	0.3	ND
Dibromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[d]	0.1	ND	ND	ND	1	1	3	3	3
Bromodichloronitromethane	0.5	ND			ND	ND			ND
Dibromochloronitromethane	2	ND			ND	ND			ND
Bromopicrin	0.5	ND			ND	ND			ND
Miscellaneous Compounds									
Methyl ethyl ketone	0.5	0.7			0.8	0.7		0.7	
Methyl *tertiary* butyl ether	0.2	ND			ND	ND		ND	
1,1,2,2-Tetrabromo-2-chloroethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND
Benzyl chloride	0.25	ND	NR	NR	ND	ND	NR	ND	NR

[s]<1 = Detected by GC/MS below its MRL of 1.0 µg/L;
quality assurance problem with gas chromatograph method

Table 25. DBP results at plant 6 (4/15/02)

4/15/2002	MRL[a]	Plant 6[n]								
Compound	µg/L	Raw	Settled	Filt Eff	Clearwell	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes										
Chloromethane	0.2	ND[c]		ND		0.2	ND		ND	
Bromomethane	0.2	ND		ND		ND	ND		ND	
Bromochloromethane	0.5	ND		ND		ND	ND		ND	
Dibromomethane	0.5	ND		ND		ND	ND		ND	
Chloroform[d]	0.2	ND	ND	8	NR[e]	13	19	NR	13	18
Bromodichloromethane[d]	0.2	ND	0.4	6	NR	10	10	NR	11	10
Dibromochloromethane[d]	0.2	ND	ND	2	NR	3	2	NR	3	3
Bromoform[d]	0.1	ND	ND	0.4	0.4	0.4	0.2	ND	0.4	0.5
THM4[f]		ND	0.4	16	NR	26	31	NR	27	32
Dichloroiodomethane	0.5	ND	ND	1	NR	1	1	ND	0.7	0.5
Bromochloroiodomethane	0.5	ND	NR	<1[s]	NR	<1	<1	NR	<1	ND
Dibromoiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Iodoform	2	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.2	ND		ND		ND	ND		ND	
Tribromochloromethane	0.5	ND	NR	ND	NR	ND	ND	NR	ND	ND
Haloacetic acids										
Monochloroacetic acid[d]	2	ND	ND	2.3	2.4	2.5	2.8		3.3	
Monobromoacetic acid[d]	1	ND	ND	ND	ND	ND	ND		ND	
Dichloroacetic acid[d]	1	ND	5.2	16	21	22	27		27	
Bromochloroacetic acid[d]	1	ND	ND	5.0	5.8	8.3	5.5		6.7	
Dibromoacetic acid[d]	1	ND	ND	ND	1.2	1.2	ND		1.6	
Trichloroacetic acid[d]	1	ND	ND	5.0	7.0	6.7	8.6		7.2	
Bromodichloroacetic acid	1	ND	ND	3.1	4.0	4.0	3.4		4.0	
Dibromochloroacetic acid	1	ND	ND	1.2	3.2	3.5	2.2		1.1	
Tribromoacetic acid	2	ND	ND	ND	ND	ND	ND		ND	
HAA5[i]		ND	5.2	23	32	32	38		39	
HAA9[j]		ND	5.2	33	45	48	50		51	
DXAA[k]		ND	5.2	21	28	32	33		35	
TXAA[l]		ND	ND	9.3	14	14	14		12	
Haloacetonitriles										
Chloroacetonitrile	0.1	ND	ND	ND	ND	0.1	0.2	ND	0.2	0.2
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[d]	0.1	ND	NR	0.7	NR	1	1	NR	4	2
Bromochloroacetonitrile[d]	0.1	ND	ND	0.4	ND	0.6	0.6	ND	0.9	1
Dibromoacetonitrile[d]	0.1	ND	ND	ND	0.2	0.1	<0.5[p]	ND	0.2	0.2
Trichloroacetonitrile[d]	0.5	ND	NR	ND	NR	ND	ND	NR	ND	ND
Bromodichloroacetonitrile	0.5	ND		ND		ND				ND
Dibromochloroacetonitrile	0.5	ND		ND		ND				ND
Tribromoacetonitrile	0.96	ND		ND		ND				ND
Haloacetaldehydes										
Dichloroacetaldehyde	0.5	ND	0.5	5	3	2	4	6	5	6
Bromochloroacetaldehyde	0.5	ND	ND	1	0.6	ND	ND	ND	0.7	0.8
Chloral hydrate[d]	0.1	1	0.2	2	3	2	4	4	4	4
Tribromoacetaldehyde	0.1	ND	ND	0.9	ND	ND	ND	ND	ND	ND

Table 25 (continued)

4/15/2002	MRL[a]	Plant 6[n]								
Compound	µg/L	Raw	Settled	Filt Eff	Clearwell	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloketones										
Chloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloropropanone[d]	1.0	ND	NR	2	NR	2	3	NR	2	3
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloropropanone[d]	0.5	ND	ND	2	NR	2	2	NR	2	0.9
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	0.3	ND	NR	0.6	NR	<1	ND	NR	ND	ND
1,1,1-Tribromopropanone	>5	ND	NR	ND	NR	ND	ND	NR	ND	NR
1,1,3-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrachloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes										
Chloronitromethane	0.2	ND		0.3		0.8				1
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	0.1	ND	ND	0.1	ND	0.1	0.1	ND	0.1	0.1
Bromochloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibromonitromethane	0.1	ND	ND	0.1	ND	ND	ND	ND	ND	ND
Chloropicrin[d]	0.1	ND	ND	0.5	1	0.8	1	2	2	NR
Bromodichloronitromethane	0.5	ND		ND		ND				ND
Dibromochloronitromethane	2	ND		ND		ND				ND
Bromopicrin	0.5	ND		ND		ND				ND
Miscellaneous Compounds										
Methyl ethyl ketone	0.5	0.7		ND		ND	0.6		ND	
Methyl *tertiary* butyl ether	0.2	ND		ND		ND	ND		ND	
1,1,2,2-Tetrabromo-2-chloroethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzyl chloride	0.25	ND	NR	ND	NR	ND	ND	NR	ND	ND

Table 26. Additional target DBP results (µg/L) at plants 5 and 6 (4/15/02)

4/15/2002	Plant 5						Plant 6					
Compound	Raw	OE1	Comb FE	PE	DS/max	SDS/max	Raw	Settled	FE	PE	DS/max	SDS/max
Monochloroacetaldehyde	0	0	0	0.4	0.5	0.6	0	0.7	1.6	1.4	2.1	1.7
Dichloroacetaldehyde	0	0	0	2.0	2.0	2.8	0	1.0	2.3	2.8	4.9	3.9
Bromochloroacetaldehyde	0	0	0	0.4	0.4	0.6	0	0	0.5	0.5	0.4	0.7
3,3-Dichloropropenoic acid	0	0	0	0.7	0.2	0.4	0	0	0	0	0	0
Bromochloromethylacetate	0	0	0	0	0	0	0	0	0	0	0	0
Monochloroacetamide	0	0	0	0	0	0	0	0	0	0.2	0.8	0.3
Monobromoacetamide	0	0	0	0	0	0	0	0	0	0	0	0.1
2,2-Dichloroacetamide	0	0	0	0.5	0.2	0.5	0	0	0.8	2.7	7.6	9.4
Dibromoacetamide	0	0	0	0	0.1	0	0	0	0.1	0.2	0	0.2
Trichloroacetamide	0	0	0	0.3	0.1	0	0	0	0.2	1.1	2.2	4.1
TOX (µg/L as Cl^-)	26.0		54.4	177	259	247	29.7	90.2	154	210	243	
TOBr (µg/L as Br^-)	5.5		10.1	41.5	36.0	51.0	11.9	33.2	25.9		19.2	
TOCl (µg/L as Cl^-)	26.9		25.8	161	194	220	17.3	76.3	152		229	
Cyanoformaldehyde	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
5-Keto-1-hexanal	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.4
6-Hydroxy-2-hexanone	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Dimethyglyoxal	<0.1	0.8	<0.1	0.4	0.2	0.3	<0.1	<0.1	0.5	<0.1	<0.1	<0.1
trans -2-Hexenal	<0.1	0.8	0.4	<0.1	<0.1	<0.1	<0.1	0.2	0.1	<0.1	<0.1	0.5

Table 27. Halogenated furanone results (µg/L) at plants 5 and 6 (4/15/02)

4/15/2002	Plant 5				Plant 6				
Compound	Comb FE	PE	DS/max	SDS/max	Raw	Settled	FE	PE	DS/max
BMX-1	<0.02	<0.02	<0.02 (0.012)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
BEMX-1	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.04	<0.02	<0.02
BMX-2	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
BEMX-2	<0.02	0.03	<0.02	<0.02	<0.02	<0.02	0.05	<0.02	0.11
BMX-3	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
BEMX-3	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
MX	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.05	<0.02	0.09
Red-MX	<0.02	<0.02 (0.01)	<0.02	<0.02	<0.02	0.02	0.04	0.58	0.28
EMX	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
ZMX	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.23	<0.02
Ox-MX	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Mucochloric acid (ring)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Mucochloric acid (open)	0.02	0.31	0.40	<0.02	<0.02	0.02	0.08	0.08	0.11

Summary of tables for halogenated organic and other nonhalogenated organic DBPs

DBP Analyses (Laboratory)	11/27/00	2/26/01	8/13/01	10/22/01	4/15/02
Halogenated organic DBPs (MWDSC)	Tables 12-13	Tables 15-16	Tables 18-19	Tables 22-23	Tables 24-25
Additional target DBPs (UNC)	Table 14		Table 20		Table 26
Halogenated furanones (UNC)			Table 21		Table 27
Broadscreen analysis (USEPA)		Table 17[a]		Table 17[b]	

[a]Plant 6
[b]Plant 5

Halomethanes. For the five sample dates, pre-ozonation/post-chlorination at plant 5 resulted in the formation of 18-43 µg/L of the four regulated trihalomethanes (THM4) in the plant effluent samples. Chlorine dioxide/chlorine/chloramine disinfection at plant 6 resulted in the formation of 4-47 µg/L of THM4.

Figure 6 shows the effect of bromide on THM speciation in the distribution systems of both utilities. Because of the lower level of bromide in this source water in February 2001 (0.04-0.05 mg/L), the major THM species were chloroform and bromodichloromethane, whereas in November 2000 (bromide = 0.08 mg/L), there was a higher mixture of brominated species formed.

Figure 6

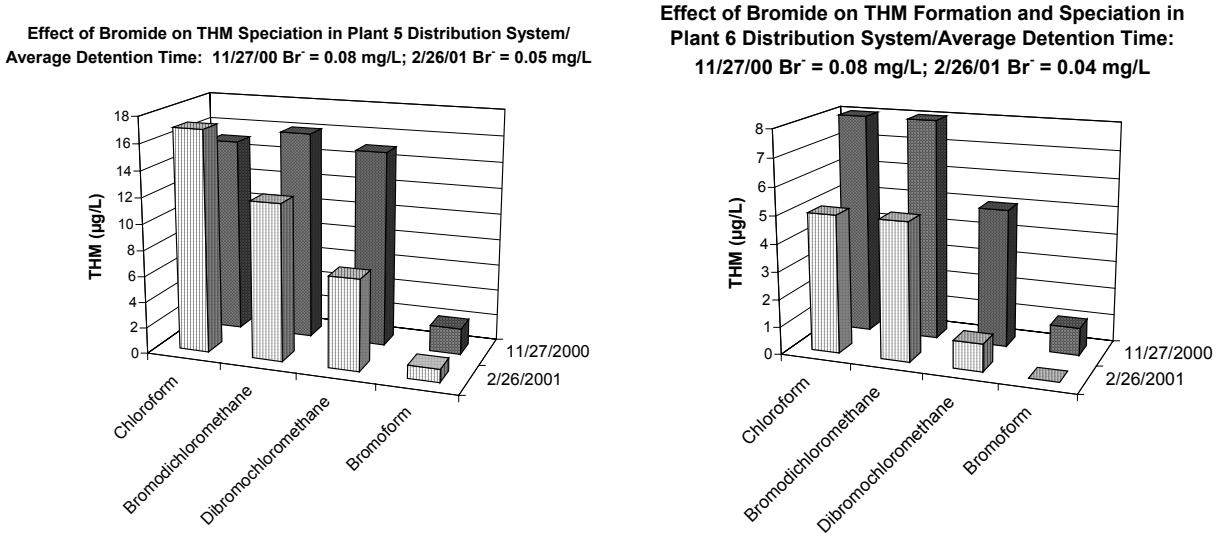
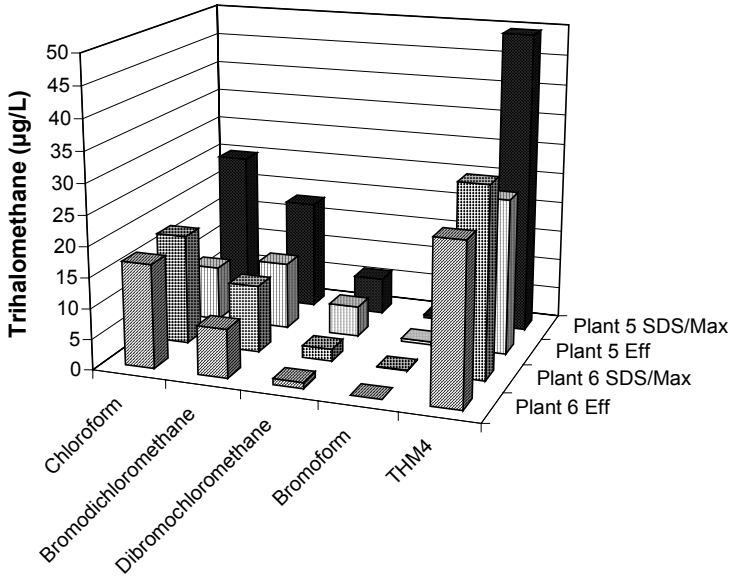


Figure 7 shows the impact of pre-ozonation/post-chlorination at plant 5 versus chlorine dioxide/chlorine/chloramine disinfection at plant 6 on THM formation and speciation for the August 13, 2001 sampling. On this date, both plant effluents had 26 µg/L THM4. At plant 6, the major THM formed was chloroform, whereas at plant 5 the major THM formed was bromodichloromethane. Although both plants treated water with a similar amount of bromide (0.05-0.06 mg/L), the amount of TOC at the point of chlorination was lower at plant 5 than at

Figure 7

Impact of Ozonation/Chlorination at Plant 5 versus Chlorine Dioxide/Chlorine/Chloramine Disinfection at Plant 6 on Trihalomethane Formation and Speciation (August 13, 2001)

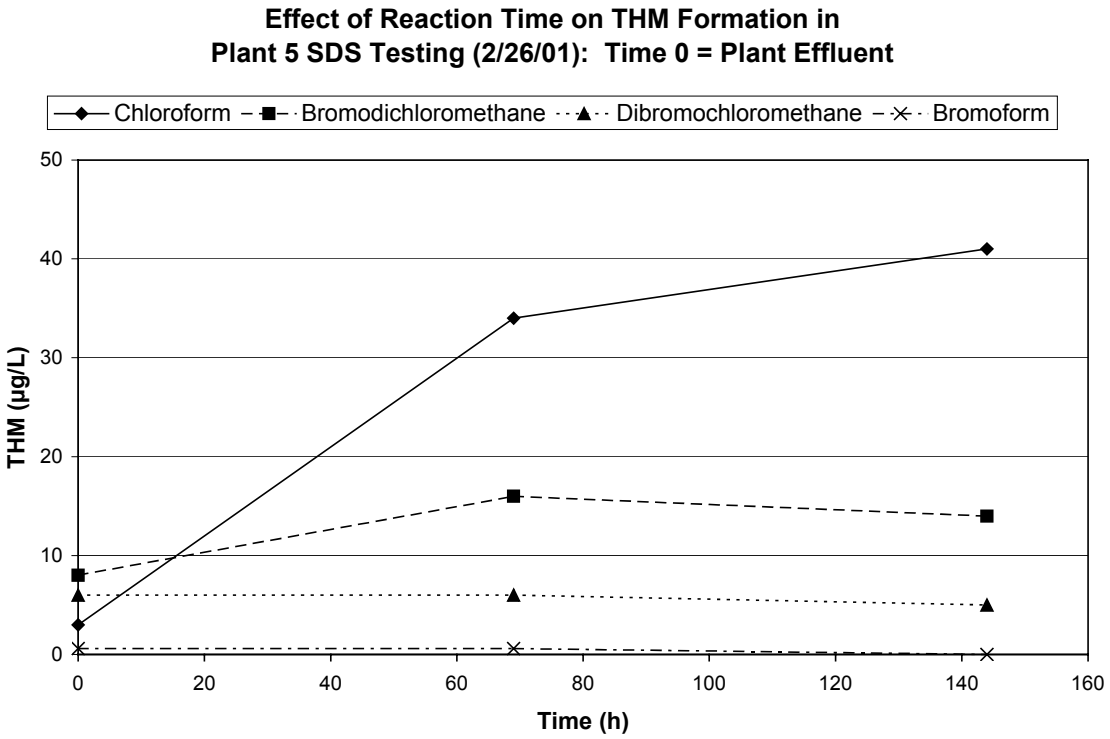


plant 6: 2.3-2.8 mg/L in the plant 5 filter effluent versus 4.5-4.7 mg/L in the plant 6 filter influent and effluent. At plant 5, the ozonation and biofiltration processes provided additional TOC reduction. As a result, the bromide-to-TOC ratio was higher at plant 5 than at plant 6. Other research has shown that a higher bromide-to-TOC ratio can result in a shift in speciation to the more brominated THMs (Symons et al., 1993). In addition, in some waters, pre-ozonation has been found to shift the THM formation to more brominated species (Jacanglo et al., 1989) because ozone converts some of the bromide to hypobromous acid.

Because plant 6 used chloramines in the distribution system, the THMs were found to not increase significantly in concentration in the SDS testing in August 2001 (Figure 7), where the SDS/maximum sample was held for seven days. Because plant 5 used free chlorine in the distribution system, the THMs were found to increase in concentration in the SDS testing in August 2001 (Figure 7), where the SDS/maximum sample was held for seven days. In this plant 5 SDS sample, the major THM was chloroform rather than bromodichloro-methane. The THM speciation at plant 5 is consistent with the difference in kinetics of halogenation between hypobromous acid and chlorine; that is, halogenation by hypobromous acid is quicker (Krasner et al., 1996). Thus, bromodichloromethane formed quicker than chloroform (plant effluent sample), whereas more of chloroform formed while the SDS sample was held for seven days.

Figure 8 shows more fully the effect of reaction time on THM formation in the SDS testing conducted on February 26, 2001. The concentration of chloroform increased over time,

Figure 8

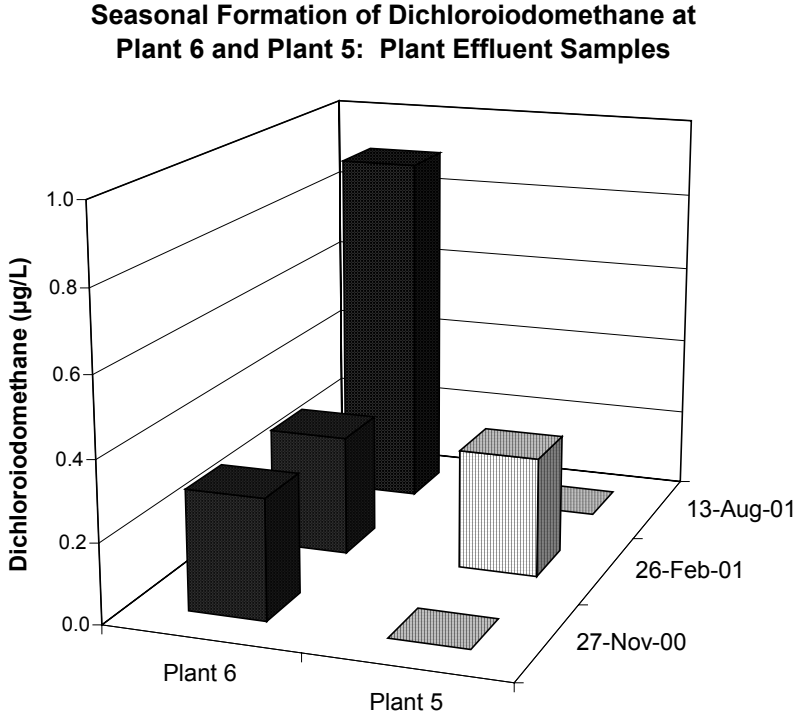


the formation of bromodichloromethane plateaued out during the SDS testing, and the amounts of the more brominated species were at their maximum values in the plant effluent. Again, this phenomenon was due to the fact that the kinetics of brominated DBP formation are faster than the kinetics of chlorinated DBP formation (Krasner et al., 1996).

In addition, low levels of certain iodinated THMs (e.g., dichloroiodomethane) were detected in selected samples, especially at plant 6 (Figure 9). In October 2001, 3 µg/L of dichloroiodomethane was detected in the plant 6 effluent, whereas 0.5 µg/L was detected in the plant 5 effluent. Bromochloroiodomethane was also detected in the plant 6 effluent in February 2001 using broadscreen GC/MS techniques (Table 17). Waters that contain bromide may also contain iodide. Iodide is oxidized to hypoiodous acid in the presence of ozone, chlorine, or chloramines (Bichsel and von Gunten, 2000). Hypoiodous acid can react with the TOC to form iodinated THMs. Bichsel and von Gunten (2000) found that ozone could also oxidize iodide to iodate and, depending on ozonation conditions, form little to no iodinated THMs; whereas chlorine lead to the formation of iodate and iodinated THMs. Although iodate was not measured in this study, the use of ozone at plant 5 did result in the formation of less iodinated THMs in the finished water than at plant 6.

Haloacids. Pre-ozonation/post-chlorination at plant 5 resulted in the formation of 10-34 µg/L of the five regulated haloacetic acids (HAA5) in the plant effluent samples, whereas chlorine dioxide/chlorine/chloramine disinfection at plant 6 resulted in the formation of 20-68

Figure 9



µg/L of HAA5. In addition, all nine HAAs (HAA9) were measured, which includes all of the brominated HAA species. The levels of HAA9 in the plant 5 effluent were 20-56 µg/L, whereas the levels of HAA9 in the plant 6 effluent were 25-88 µg/L.

Figure 10 shows the effect of bromide on HAA speciation in SDS testing at plant 5 (a similar effect was observed at plant 6). Because of the lower level of bromide in this water in February 2001, the two major HAAs were di- and trichloroacetic acid (DCAA and TCAA), whereas in November 2000 there was a higher mixture of brominated species formed.

Figure 11 shows the effect of the two disinfection schemes on the seasonal formation of THMs and HAAs in the plant effluents of plant 5 and plant 6. At plant 5, the sum of the dihalogenated HAAs (DXAAs) was somewhat higher than the sum of the trihalogenated HAAs (TXAAs) (Figure 11). This is consistent with the research of Reckhow and Singer (1984), in which ozonation was found to control the formation of TCAA better than that of DCAA.

At plant 6, in the settled water after chlorine dioxide disinfection, almost all of the HAAs that were formed were DXAAs; no TXAAs were detected (Figure 12). (In addition, the level of THMs was almost non-detectable at this sample location.) At this point in the treatment process, only chlorine dioxide disinfection had been utilized. In other DBP research, chlorine dioxide has been shown to produce little or no THMs and TXAAs, whereas DXAAs were formed (Zhang et al., 2000). After the addition of free chlorine at plant 6, the levels of HAAs increased, including the formation of TXAAs (Figure 12). However, DXAAs still predominated in the plant 6 samples (more so than at plant 5) (Figure 11).

Figure 10

Effect of Bromide on HAA Speciation in Plant 5 SDS Testing/
Average Detention Time: 11/27/00 Br^- = 0.08 mg/L; 2/26/01 Br^- = 0.05 mg/L

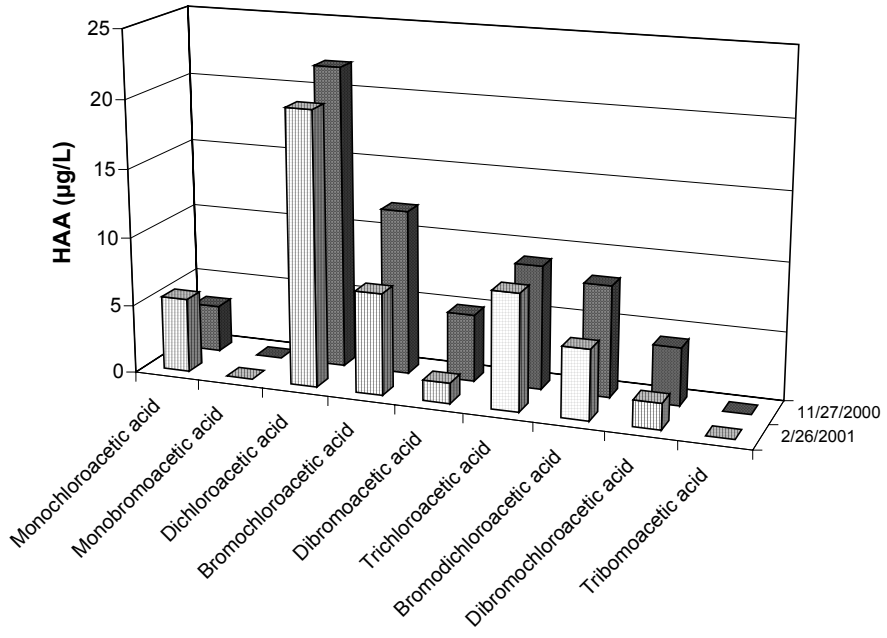


Figure 11

Seasonal Formation of Trihalomethanes and Haloacetic Acids
at Plant 5 and Plant 6: Plant Effluent Samples

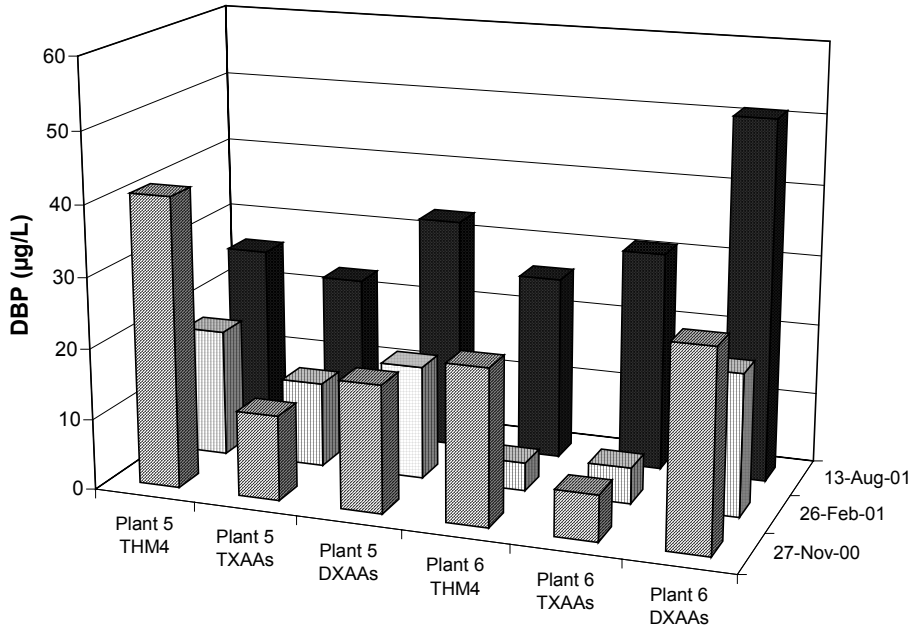
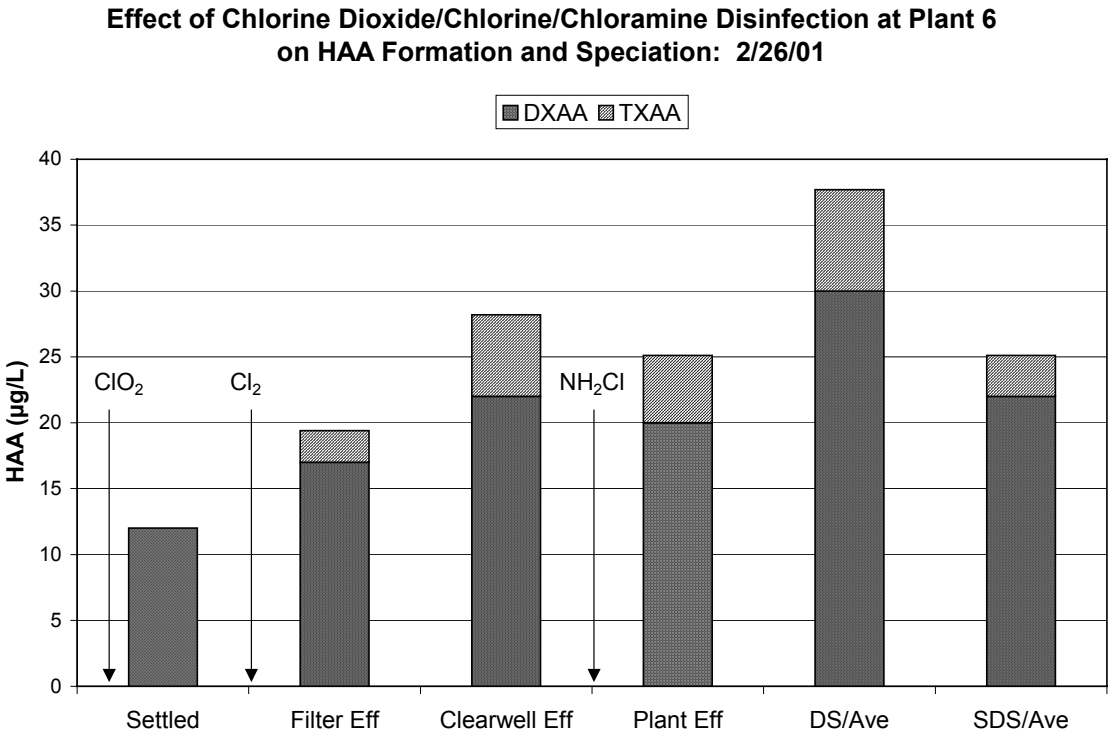


Figure 12



In the presence of chlorine, HAAs were formed in the plant 5 SDS testing (Figure 13). The SDS/average samples for plant 5 in November 2000 - August 2001 were held for three days. The increase in formation of the DXAAs was much higher than for the TXAAs, which may be due (in part) to the ability of ozone to better destroy TXAA precursors. In the presence of chloramines, HAA concentrations were typically stable within analytical variability in the plant 6 SDS testing (Figure 13). The SDS/average samples for plant 6 in November 2000 - August 2001 were held for four days.

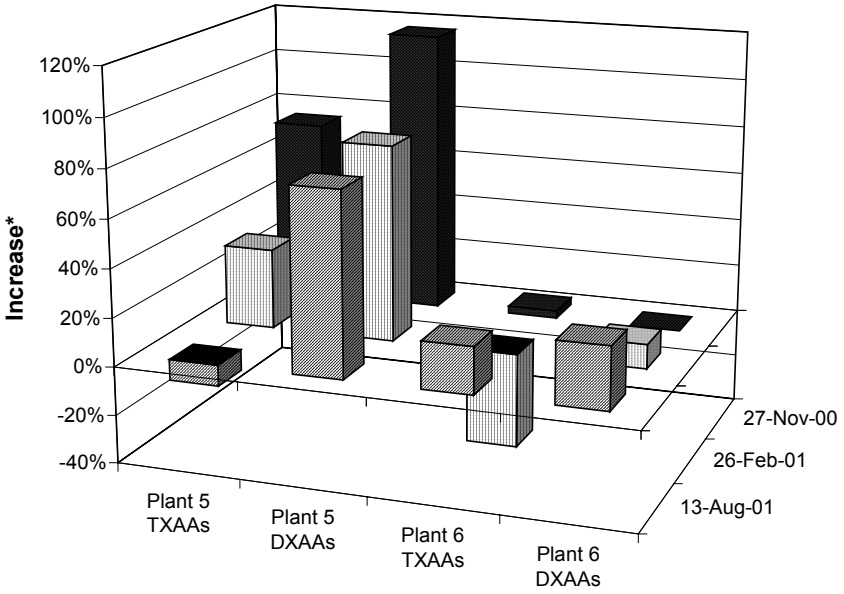
In addition to the target HAAs, other haloacids were detected in selected samples by the broadscreen GC/MS methods (Table 17). Plant 6—which had 0.04 mg/L bromide in February 2001—produced two other chlorinated acids (i.e., di- and trichloropropenoic acid). These were detected following the chlorine dioxide disinfection. A different chlorinated acid was detected at plant 5 after post-chlorination (3,4,4-trichloro-3-butenoic acid).

UNC detected 3,3-dichloropropenoic acid in finished waters from several samplings (plant 5 and plant 6, November 2000; plant 6, August 2001; and plant 5, April 2002). Levels ranged from 0.7 to 4.7 µg/L in the finished waters, and generally increased in concentration in the distribution system.

Haloacetonitriles. In other research, haloacetonitriles (HANs) have been found to be produced at approximately one-tenth the level of the THMs (Oliver, 1983). This was also generally observed in the plant 5 and plant 6 samples (Figure 14). Trichloroacetonitrile (TCAN)—an Information Collection Rule (ICR) DBP—was not detected. Likewise, the

Figure 13

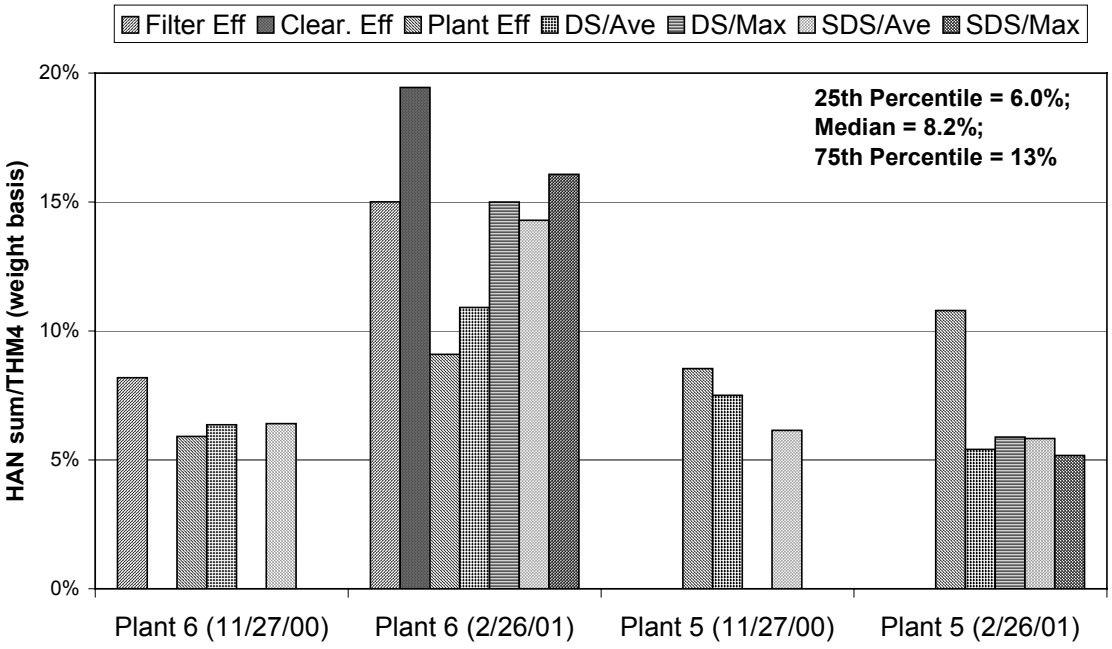
Impact of Residual Disinfectant on Formation of Haloacetic Acids in Simulated Distribution System Samples with Average Detention Time: Chlorine at Plant 5, Chloramines at Plant 6



*Negative value = decrease in concentration rather than an increase

Figure 14

Relationship of the Sum of HANs (up to 6 Species) to THM4 at Plant 5 and Plant 6

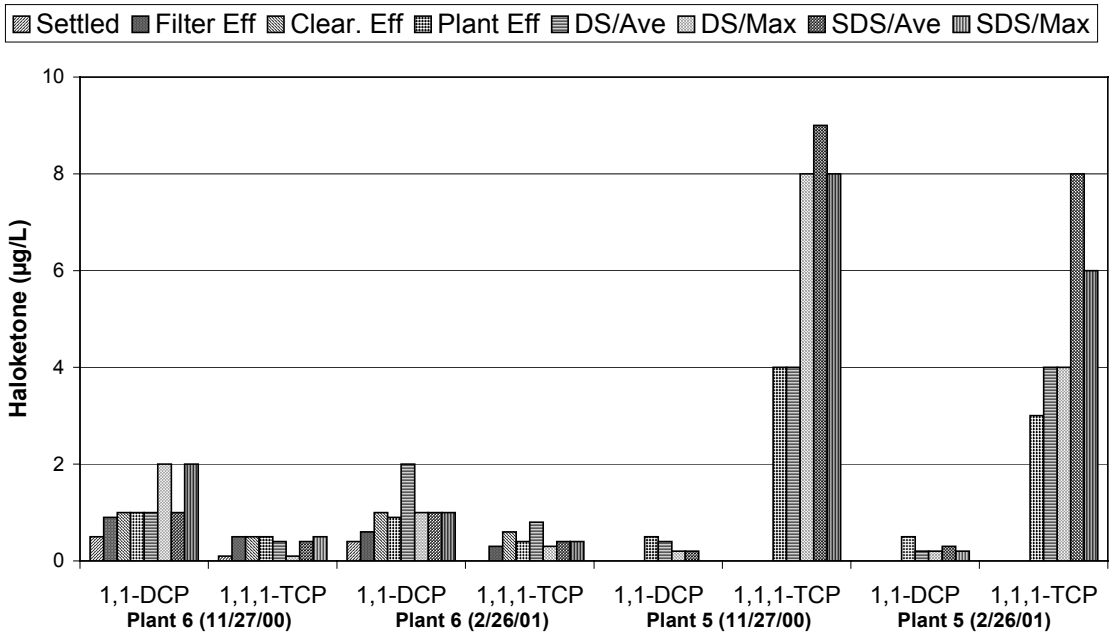


brominated analogues of TCAN were not detected in the plant 5 samples. However, at plant 6, dibromochloroacetonitrile was detected in an SDS sample in October 2001 and tribromoacetonitrile was detected in February 2001 by the broadscreen GC/MS methods (Table 17). In addition, sub-µg/L levels of another target HAN (i.e., chloroacetonitrile) were detected in selected samples at both utilities.

Haloketones. The level of 1,1,1-trichloropropanone (1,1,1-TCP)—which is a precursor to chloroform formation—was higher at plant 5 (Figure 15). More of this haloketone (HK) formed with free chlorine than with chloramines. The level of 1,1-dichloropropanone (1,1-DCP) was typically higher at plant 6 (Figure 15). The latter compound was often detected in the settled water after chlorine dioxide disinfection. Thus, at plant 6, chlorine dioxide and chloramines were found to be better at controlling the formation of 1,1,1-TCP (and THMs and TXAAs) than the formation of 1,1-DCP (and DXAAs).

Figure 15

Effect of Ozone/Chlorine Disinfection at Plant 5 and Chlorine Dioxide/Chlorine/Chloramine Disinfection at Plant 6 on the Formation of Haloketones



In addition to the formation of low levels of HK compounds from the ICR (i.e., 1,1-DCP and 1,1,1-TCP), low levels of some of the target HKs were detected in selected samples. In addition to the target HKs, other HKs were detected in selected samples by the broadscreen GC/MS methods (Table 17). A number of these HKs were analogous to the di- and tetrahalogenated target HKs, except that these were mixed bromochloro species.

Haloaldehydes. In addition to the formation of chloral hydrate (trichloroacetaldehyde)—an ICR DBP—dichloroacetaldehyde was formed. The level of chloral hydrate was higher at plant 5. More of this DBP formed with free chlorine than with chloramines. On the other hand,

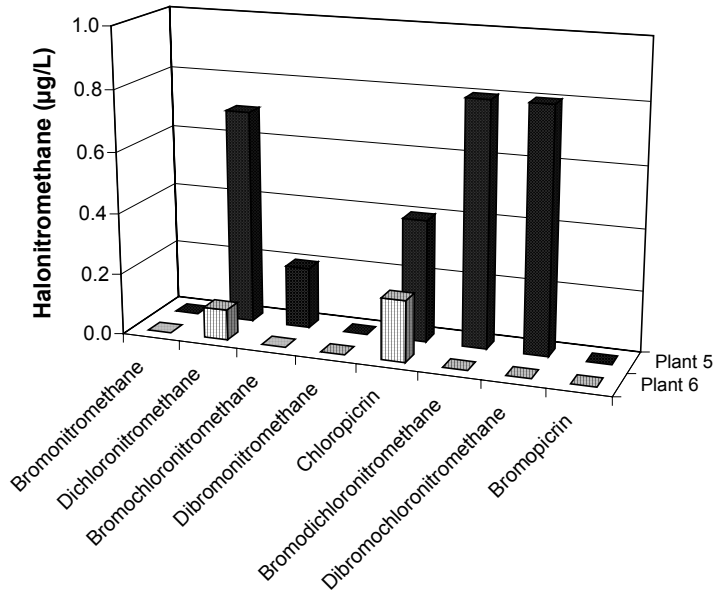
dichloroacetaldehyde was often higher in concentration at plant 6. In addition, brominated analogues of both of these haloacetaldehydes were detected in selected samples.

In addition to the target haloaldehydes, two other haloaldehydes were detected in selected samples by the broadscreen GC/MS methods (Table 17). Another brominated aldehyde (2-bromo-2-methylpropanal) and an iodinated aldehyde were detected (tentatively identified as iodobutanal). This is the first report of an iodoaldehyde as a DBP in drinking water. High resolution mass spectrometry confirmed the presence of the iodine in the structure of this molecule, and also its overall empirical formula (C_4H_7OI, molecular weight of 198). At this point, the identification is tentative, however—it is highly likely that the molecule is an iodo-aldehyde with four carbons, but the exact isomer assignment cannot be determined by its mass spectrum. An attempt to obtain synthetic standards of iodobutanal forms is currently underway in order to obtain a confirmed assignment.

Halonitromethanes. Low levels of chloropicrin (trichloronitromethane) (an ICR DBP) were detected. Other halonitromethanes (HNMs) were detected in selected samples. The levels of chloropicrin and the bromine-containing trihalonitromethanes were higher at plant 5 (Figure 16). Other research has shown that pre-ozonation can increase the formation of chloropicrin upon post-chlorination (Hoigné and Bader, 1988). Similar to the THM speciation in the plant effluent samples in August 2001 (Figure 7), in terms of the trihalonitromethanes, mixed bromochloro species predominated at plant 5, whereas the trichloro species was the only trihalonitromethane detected at plant 6 on that sample date (Figure 16).

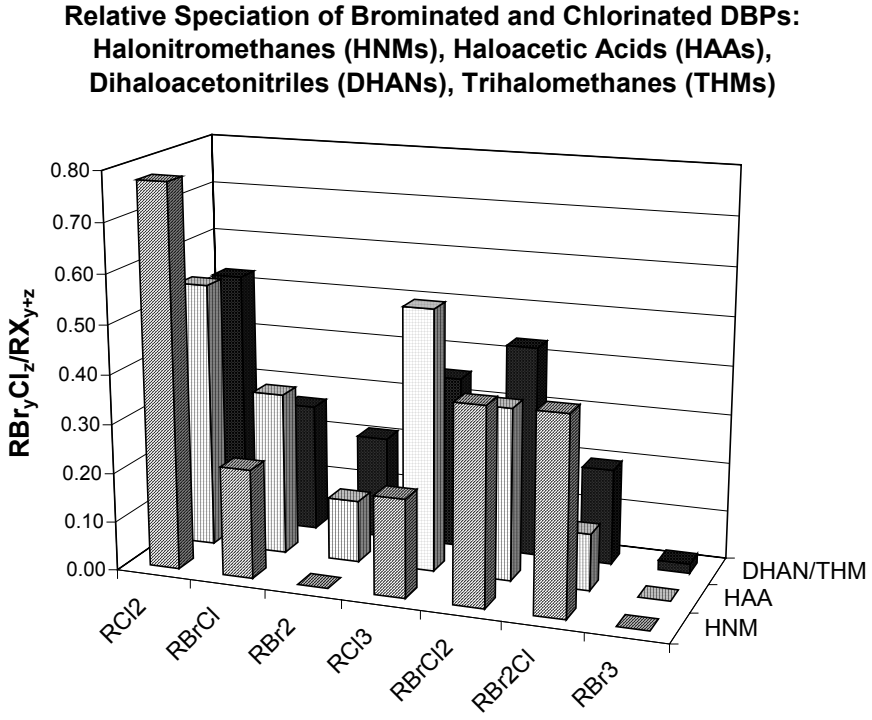
Figure 16

Impact of Ozonation/Chlorination at Plant 5 versus Chlorine Dioxide/Chlorine/Chloramine Disinfection at Plant 6: Plant Effluents (August 13, 2001)



The relative speciation of brominated and chlorinated HNMs (for the di- and trihalogenated species) was compared to the HAAs, THMs, and the dihaloacetonitriles (DHANs) for the August 2001 data. Each DBP can be abbreviated based on the number of halogens and the speciation of the halogens as follows: RBr_yCl_z, where the number of bromine and chlorine atoms are y and z, respectively, and R corresponds to the remainder of the DBP molecule (i.e., carbon, hydrogen, oxygen, and nitrogen atoms). The concentration of each DBP was "normalized" by dividing its concentration by the sum of the concentrations of all of the DBPs for that "subclass" of DBPs (RX_{y+z}) (Figure 17). For example, the concentration of DCAA was divided by the sum of all the DXAAs.

Figure 17. Plant 5 effluent (August 13, 2001)



For the dihalogenated DBPs (RX_2), the dichlorinated species represented 53 to 78 % of the sum of the dihalogenated DBPs in that class of DBPs. The bromochloro species represented 22 to 33 % of the class sum, and the dibromo species represented 0 to 21 % of the class sum. For the trihalogenated DBPs (RX_3), the trichlorinated, bromodichlorinated, dibromochlorinated, and tribrominated species represented 20 to 53 %, 35 to 43 %, 12 to 40 %, and 0 to 2 % of the class sum, respectively. For the THMs, HAAs, DHANs, and HNMs, there was a similar relative speciation of brominated and chlorinated DBPs for the dihalogenated species and a similar relative speciation of brominated and chlorinated DBPs for the trihalogenated species.

Halogenated furanones. Tables 21 and 27 show the results for halogenated furanones in the August 2001 and April 2002 samplings for plant 5 and plant 6. Data are included for 3-chloro-4-(dichloromethyl)-5-hydroxy-2[5H]-furanone, otherwise known as MX; (E)-2-chloro-3-(dichloromethyl)-4-oxobutenoic acid, otherwise known as EMX; (Z)-2-chloro-3-

(dichloromethyl)-4-oxobutenoic acid (ZMX); the oxidized form of MX (Ox-MX); the reduced form of MX (Red-MX); brominated forms of MX and EMX (BMXs and BEMXs); and mucochloric acid (MCA), which can be found as a closed *ring* or in an *open* form. Results are displayed graphically in Figures 18 and 19.

The combination of ozonation and biofiltration (with GAC filters) removed MX and MX-analogue precursors in plant 5, whereas chlorine dioxide pretreatment at plant 6 did not. At plant 6, intermediate chlorination and chloramine post-disinfection produced MX and MX-analogues (Tables 21 and 27). In August 2001, MX was not detected at the plant 6 filter effluent, whereas it was detected in the plant 6 effluent (310 ng/L) (Figure 18). Alternatively, EMX was detected at the plant 6 filter effluent (230 ng/L), but it was not detected in the plant effluent. EMX is the *open* ring analogue of MX, and these two halogenated furanones are in equilibrium with each other. It appears as if EMX may have been converted to MX between the plant 6 filter effluent and the plant effluent.

In the second sampling of plants 5 and 6 (4/15/02) for halogenated furanones, brominated MX-analogues were also measured, but did not appear, except in low concentrations (up to 50 ng/L) (Figure 19), within plant 6 due to the low concentration of bromide (0.06 mg/L) in the source water. The reduced form of MX (red-MX) increased in concentration from the filter effluent (40 ng/L) to the plant effluent (580 ng/L) at plant 6 due to residual chloramines (3.2 mg/L) reaction with TOC (3.88 mg/L). Mucochloric acid (MCA open) was detected in the plant effluent (310 ng/L) of plant 5 due to the filter effluent chlorine (2.5 mg/L dose) and clearwell effluent chlorine (1.02 mg/L dose) reacting with the TOC (~3.5 mg/L) of the combined filter effluent.

Figure 18

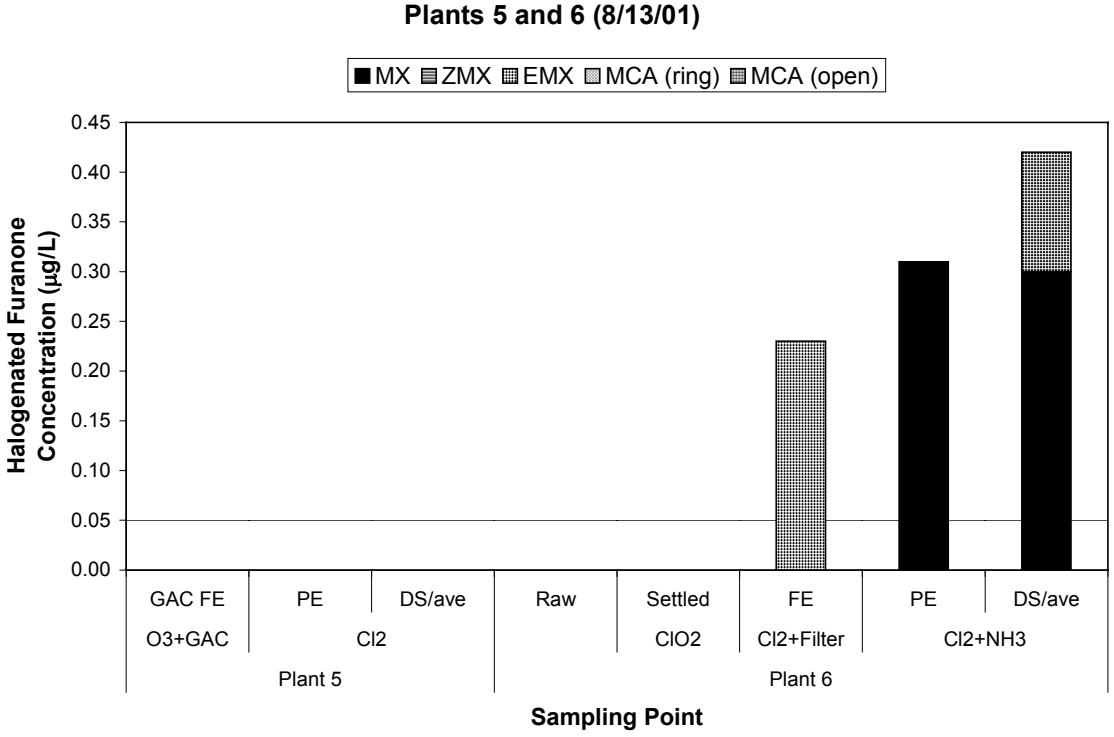
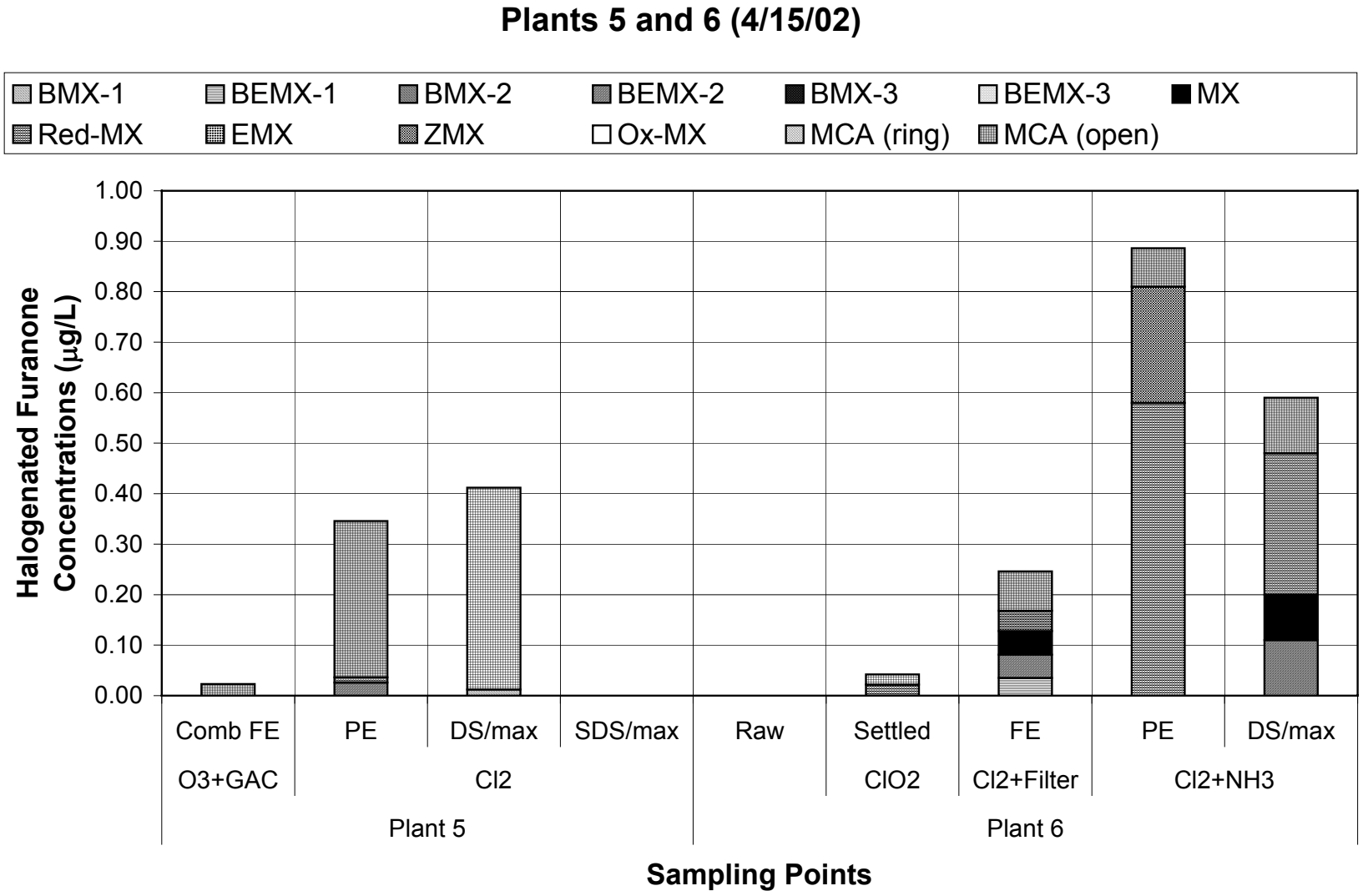


Figure 19


Plants 5 and 6 (4/15/02)
BMX-1
BEMX-1
BMX-2
BEMX-2
BMX-3
BEMX-3
MX
Red-MX
EMX
ZMX
Ox-MX
MCA (ring)
MCA (open)
Halogenated Furanone Concentrations (µg/L)
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
Comb FE
PE
DS/max
SDS/max
Raw
Settled
FE
PE
DS/max
O3+GAC
Cl2
ClO2
Cl2+Filter
Cl2+NH3
Plant 5
Plant 6
Sampling Points

Volatile Organic Compounds. Methyl ethyl ketone (MEK) was detected in the raw water of both plants on August 13, 2001 at concentrations of 3-7 µg/L. The level of MEK decreased through the treatment plant and in the distribution system. MEK was detected in the raw water on October 22, 2001 and April 15, 2002 at 0.6-0.7 µg/L and in other selected samples at similar concentrations. Methyl *tertiary* butyl ether (MtBE) was detected in the raw water of both plants on August 13, 2001 at a concentration of 0.3-0.4 µg/L. The level of MtBE was unchanged through the treatment plant. MEK is an industrial solvent and MtBE is a gasoline additive.

Other Halogenated DBPs. A few additional, miscellaneous halogenated DBPs were also detected. UNC methods detected dichloroacetamide at 1.5, 5.6, and 2.7 µg/L in finished water from plant 6 (11/27/00, 8/13/01, and 4/15/02) (Tables 14, 20, and 26). Dichloroacetamide was also observed in finished water from plant 5 at 0.5 µg/L in April 2002 (Table 26). Levels either increased or remained fairly steady in the distribution system and in SDS testing. Also, four additional haloamides-- monochloroacetamide, monobromoacetamide, dibromoacetamide, and trichloroacetamide—were found in finished water samples collected in April 2002 from both plants (Table 26). Bromochloromethylacetate was observed in November 2000 in finished waters from plant 6 (1.1 µg/L), but was not detected in the distribution system or SDS testing (Table 14), presumably due to degradation.

Broadscreen GC/MS analyses revealed the presence of hexachlorocyclopentadiene and dichloroacetic acid methyl ester in finished water collected from plant 6 in February 2001 (Table 17). These compounds were not observed in the corresponding raw, untreated water.

Non-Halogenated DBPs. A few non-halogenated DBPs were detected in finished waters from plant 5 and plant 6. Dimethylglyoxal was identified at 2.1 and 1.7 µg/L in finished waters from plant 5 and plant 6, respectively (November 2000, Table 14). It was also found in later samplings from both plants (Tables 20 and 26), and it did not appear to degrade in the distribution system. *Trans*-2-hexenal was also identified in waters from two samplings (Tables 14 and 26) and appears to be formed both by ozonation and treatment with chlorine dioxide. However, it does not appear to be stable; levels were diminished at the plant effluent.

Broadscreen GC/MS analysis revealed the presence of glyoxal and methyl glyoxal in both the ozone effluent and the finished water from plant 5 (Table 17). Also, decanoic acid and hexadecanoic acid were found in finished waters from plant 6 at levels significantly higher than in the raw, untreated water (Table 17).

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EPA REGION 3: PLANTS 3 AND 4

Plant Operations and Sampling

On November 13, 2000, February 5, 2001, August 1, 2001, October 16, 2001, and January 28, 2002, plants 3 and 4 (EPA Region 3) were sampled. Plants 3 and 4 operated in parallel on a common source water (Figures 1-2).

The treatment processes at plant 3 (Figure 3) included flocculation, coagulation, sedimentation, and filtration. The settled water was first filtered through a multimedia filter and then through a granular activated carbon (GAC) filter. The raw water was disinfected with free chlorine. In November 2000, August 2001, and October 2001, ammonia was added to convert the chlorine to chloramines after a 30-sec or 1-min chlorine contact time, whereas ammonia was not added until the plant effluent in February 2001. (Information on the disinfection scheme for January 2002 is not available.) After the GAC and at the plant effluent, additional chlorine was added. In addition, in August and October 2001, chlorine was applied at the end of the sedimentation basin.

The treatment processes at plant 4 (Figures 1-2) included flocculation, coagulation, sedimentation, and filtration. The settled water was filtered through a GAC filter. Chlorine was applied to the raw and filtered waters and at the plant effluent. Chloramines were not used at plant 4.

Plant 3 was sampled at the following locations (Figure 3):

(1) raw water
(2) the rapid mix effluent (prior to ammonia addition)
(3) the GAC influent
(4) the GAC effluent
(5) the plant effluent

Plant 4 was sampled at the following locations:

(1) GAC influent
(2) GAC effluent
(3) the plant effluent

In addition, plant effluent samples were collected for both plants, and simulated distribution system (SDS) testing was conducted for average and maximum detention times for that time of year (Table 1). Furthermore, the distribution systems for both plants were sampled at two locations, one representing an average detention time and the other representing a maximum detention time. (Raw water was not sampled at plant 4, as it is the same as is used at plant 3.)

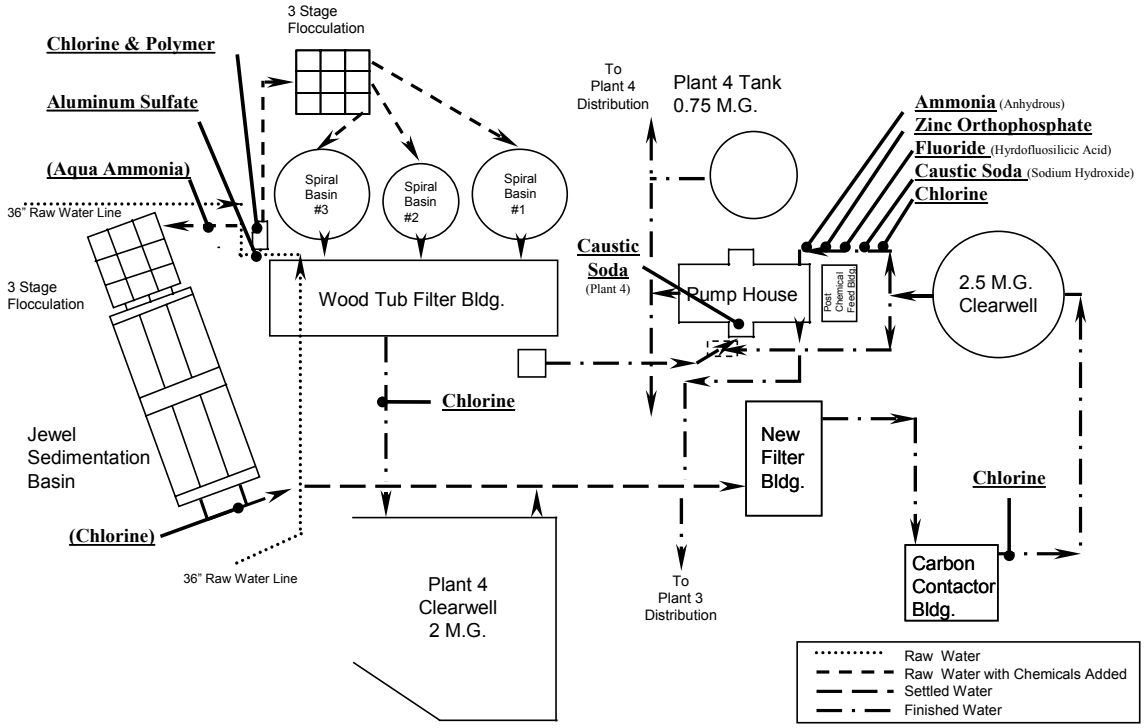


Figure 1. Chemical application points at plants 3 and 4.

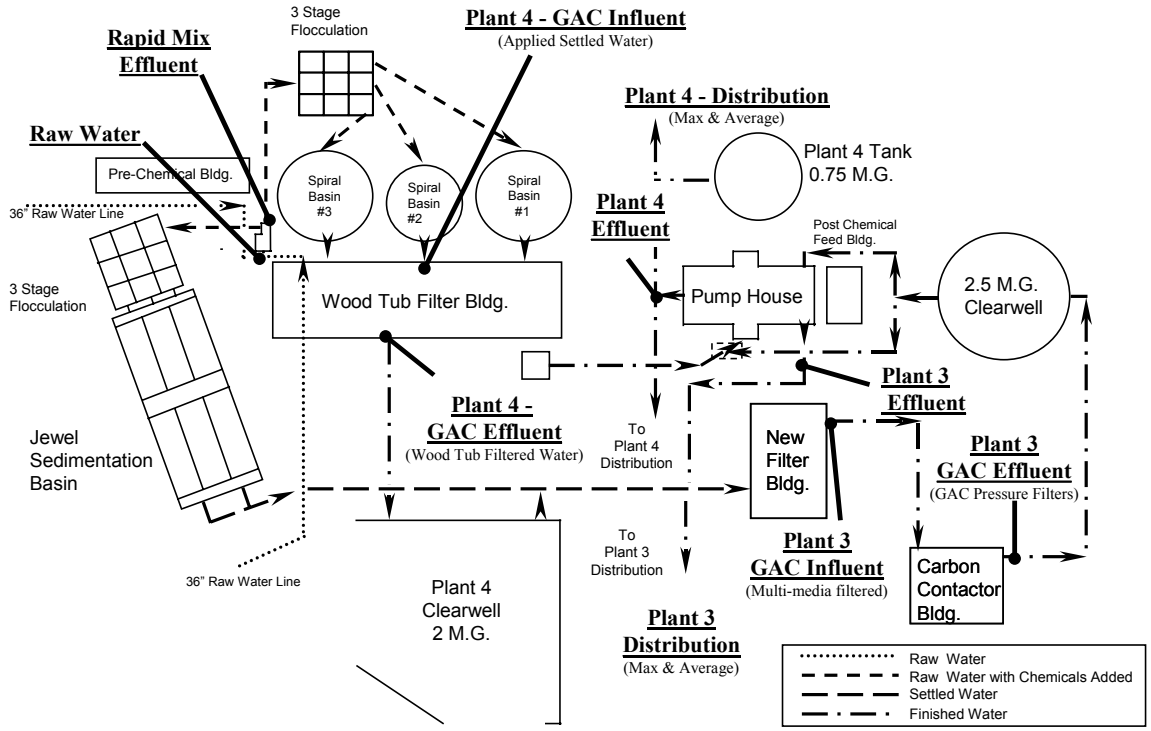


Figure 2. Sampling points at plants 3 and 4.

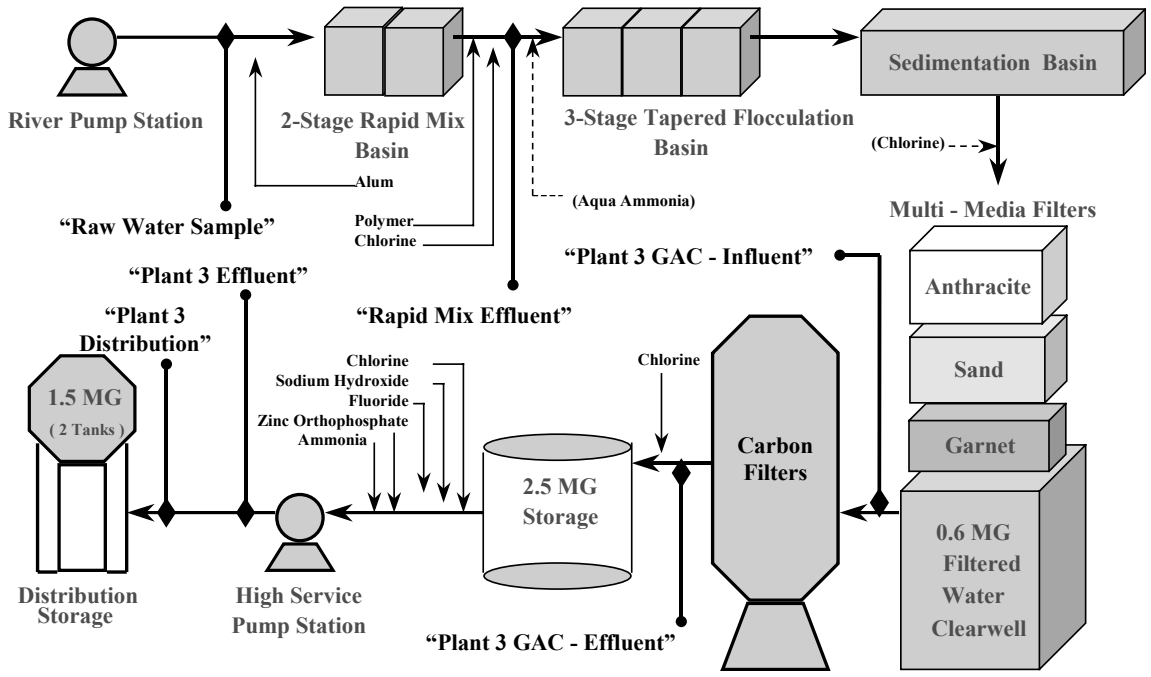


Figure 3. Simplified line diagram of chemical application and sampling points at plant 3.

Table 1. SDS holding times (hr) at plants 3 and 4

Sample	11/13/00	2/5/01	8/1/01	10/16/01	1/28/02
Plant 3 average detention time	20	18	18	77	NA[a]
Plant 3 maximum detention time	28	48	48	140	NA
Plant 4 average detention time	20	20	8	77	NA
Plant 4 maximum detention time	28	30	24	140	NA

[a]NA = Not available

On the day of sampling, information was collected on the operations at each plant (Tables 2-3). In February 2001, several of the plant 4 filters had been removed from service. In order to maintain filtered water quality on the plant 4 side, plant 3 carbon contactor filtered (CCF) water was added to the plant 4 suction (clearwell). Thus, 6.0 million gallons per day (mgd) of plant 3 CCF water was added to the plant 4 side. This resulted in 35 % of the plant 4 water being plant 3 CCF water. This affected the results of the plant 4 distribution-system and SDS samples. Likewise, in August and October 2001, blending occurred at the entrance to the plant 4 distribution system, which was a combination of plant 4 and "deep bed GAC" filtered waters (the plant 4 effluent was a combination of water from the plant 3 clearwell and the plant 4 clearwell).

Table 2. Operational information at plant 3

Parameter	11/13/00	2/5/01	8/1/01	10/16/01	1/28/02
Plant flow (mgd)	8	10	9	9	NA
Coagulant[a] dose (mg/L)	60	39	56	91	NA
GAC filter loading rate (gpm/sq ft)	6.14	7.7	6.91	6.91	NA
GAC EBCT[b] (min)	14.9	11.9	13.3	13.3	NA
Chlorine dose at rapid mix (mg/L)	3.3	5.7	6.6	6.6	NA
Ammonia dose at rapid mix eff. (mg/L as N)	0.55	0	0.9	0.9	NA
Chlorine dose at end of sed. basin (mg/L)	0	0	4.0	3.0	NA
Chlorine dose at GAC effluent (mg/L)	1.2	1.2	1.3	1.3	NA
Chlorine dose at plant effluent (mg/L)	2.05	2.5	2.03	2.8	NA
Ammonia dose at plant effluent (mg/L as N)	0.85	0.90	0.82	0.94	NA

[a]Aluminum sulfate [$Al_2(SO_4)_3$ $14H_2O$]
[b]Empty bed contact time

Table 3. Operational information at plant 4

Parameter	11/13/00	2/5/01	8/1/01	10/16/01	1/28/02
Plant flow (before addition of plant 3 GAC effluent) (mgd)	11.8	11	11	9.9	NA
Flow of plant 3 GAC effluent added to plant 4 (mgd)	0	6.0	4.2	4.9	NA
Coagulant[a] dose (mg/L)	60	39	56	91	NA
GAC filter loading rate (gpm/sq ft)	1.3	1.2	1.13	1.01	NA
GAC EBCT (min)	11.5	12.9	13.3	14.8	NA
Chlorine dose at rapid mix (mg/L)	4.5	5.7	7.6	6.0	NA
Chlorine dose at entrance of plant 4 (filtered water) clearwell (mg/L)	NA	NA	1.35	1.21	NA
Chlorine dose at plant effluent (mg/L)	0.6	0.4	1.2	0.9	NA

[a]Aluminum sulfate

Water Quality

On the day of sampling, information was collected on the water quality at each plant (Tables 4-5). At plant 3, seasonal control of disinfection by-products (DBPs)—especially trihalomethanes (THMs)—was being achieved using pre-chloramination. During warmer months (e.g., August, October, November), ammonia was added to convert the chlorine to chloramines after a 1-min chlorine contact time, whereas ammonia was not added until the plant effluent during colder months (e.g., February).

Table 4. Water quality information at plant 3

	pH					Temperature (ºC)					Disinfectant Residual[a] (mg/L)				
Location	11/13/00	2/5/01	8/1/01	10/16/01	1/28/02	11/13/00	2/5/01	8/1/01	10/16/01	1/28/02	11/13/00	2/5/01	8/1/01	10/16/01	1/28/02
Raw	7.3	6.9	7.3	7.6	NA	13.9	7	25.6	18.9	NA	---	---	---	---	NA
RM[b] eff.	6.1	5.9	6.3	6.0	NA	13.9	7	25.6	18.9	NA	*2.2*	*3.5*	*3.2*	*3.2*	NA
GAC inf.	6.2	5.5	6.0	6.0	NA	13.9	9	25.6	18.1	NA	0.9	*0.5*	1.6	1.6	NA
GAC eff.	6.0	5.5	6.1	5.9	NA	13.9	8	24.6	18.9	NA	0.1	*0*	ND[c]	ND	NA
Plant eff.	7.4	7.2	7.4	7.4	NA	13.9	10	25.6	19.6	NA	3.2	3.5	3.1	3.8	NA
DS[d]/ave.	7.5	7.2	7.4	7.4	NA	13.9	9	26.4	20.2	NA	2.5	2.6	2.8	2.8	NA
DS/max	7.3	7.2	7.4	7.4	NA	13.9	9	26.4	20.2	NA	2.0	2.4	2.4	2.4	NA
SDS/ave.	7.4	7.2	7.4	7.4	NA	13.9	9	24.5	20.2	NA	2.5	2.3	2.8	2.4	NA
SDS/max	7.5	7.2	7.4	7.4	NA	13.9	9	24.5	20.2	NA	2.4	2.0	2.4	2.0	NA

[a]11/13/00, 8/1/01, 10/16/01: Chlorine residuals (values shown in italics) at rapid mix effluent; chloramine (or total) residuals at other locations
2/5/01: Chlorine residuals (values shown in italics) at rapid mix effluent, GAC influent and effluent; chloramine residuals at other locations
[b]RM = Rapid mix
[c]ND = Not detected
[d]DS = Distribution system

Table 5. Water quality information at plant 4

	pH					Temperature (ºC)					Chlorine Residual (mg/L)				
Location	11/13/00	2/5/01	8/1/01	10/16/01	1/28/02	11/13/00	2/5/01	8/1/01	10/16/01	1/28/02	11/13/00	2/5/01	8/1/01	10/16/01	1/28/02
GAC inf.	6.2	5.5	6.1	6.0	NA	13.9	7	25.6	18.9	NA	2.6	1.4	1.5	0.9	NA
GAC eff.	6.2	5.5	6.0	6.0	NA	13.9	7	24.5	18.9	NA	0.6	0.8	0.4	0.4	NA
Plant eff.	7.2	6.8	6.9	7.2	NA	13.9	8	24.5	19.6	NA	1.1	1.2	1.2	1.2	NA
DS/ave.	7.0	6.5	6.9	7.2	NA	13.9	8	25.2	20.2	NA	1.8	1.0	0.8	1.0	NA
DS/max	6.8	6.5	6.9	7.0	NA	13.9	9	25.2	20.2	NA	1.2	0.5	0.9	0.8	NA
SDS/ave.	7.1	6.2	6.9	7.0	NA	13.9	9	24.5	20.2	NA	1.4	0.5	0.8	0.7	NA
SDS/max	7.1	6.2	6.9	7.0	NA	13.9	9	24.5	20.2	NA	1.1	0.5	0.8	0.4	NA

Data were also collected for total organic carbon (TOC) and ultraviolet (UV) absorbance (Table 6). The TOC ranged from 4.3 to 6.4 mg/L, and the UV absorbance from 0.090 to 0.187 cm^{-1}. At plants 3 and 4, coagulation removed 30-59 % of the TOC and GAC filtration removed another 4-23 %. At plant 3, GAC filtration was used to prevent taste-and-odor problems in the finished water and for the removal of other micropollutants, but it was not installed for DBP precursor (TOC) removal. The GAC is only regenerated once every three years at plant 3. At plants 3 and 4, coagulation, GAC filtration, and chlorination cumulatively reduced the UV absorbance by 67-84 %.

Table 6. TOC and UV removal at plants 3 and 4

Location	TOC (mg/L)	UV[a] (cm^{-1})	SUVA[b] (L/mg-m)	Removal/Unit (%)		Removal/Cumulative (%)	
				TOC	UV	TOC	UV
11/13/2000							
Raw water	4.37	0.091	2.08	---	---	---	---
Plant 3 GAC inf.	2.34	0.041	1.75	46%	55%	46%	55%
Plant 3 GAC eff.	2.2	0.028	1.27	6.0%	32%	50%	69%
Plant 4 GAC inf.	2.47	0.027	1.09	43%	70%	43%	70%
Plant 4 GAC eff.	2.31	0.029	1.26	6.5%	-7.4%	47%	68%
02/05/2001							
Raw water	6.44	0.187	2.90	---	---	---	---
Plant 3 GAC inf.	2.63	0.038	1.44	59%	80%	59%	80%
Plant 3 GAC eff.	2.46	0.033	1.34	6.5%	13%	62%	82%
Plant 4 GAC inf.	2.70	0.036	1.33	58%	81%	58%	81%
Plant 4 GAC eff.	2.59	0.033	1.27	4.1%	8.3%	60%	82%
08/01/2001							
Raw water	6.25	0.14	2.24	---	---	---	---
Plant 3 GAC inf.	2.63	0.034	1.29	58%	76%	58%	76%
Plant 3 GAC eff.	2.02	0.023	1.14	23%	32%	68%	84%
Plant 4 GAC inf.	3.24	0.03	0.93	48%	79%	48%	79%
Plant 4 GAC eff.	2.69	0.032	1.19	17%	-6.7%	57%	77%
10/16/2001							
Raw water	5.9	0.113	1.92	---	---	---	---
Plant 3 GAC inf.	2.87	0.036	1.25	51%	68%	51%	68%
Plant 3 GAC eff.	2.37	0.028	1.18	17%	22%	60%	75%
Plant 4 GAC inf.	4.13	0.047	1.14	30%	58%	30%	58%
Plant 4 GAC eff.	3.58	0.037	1.03	13%	21%	39%	67%
01/28/2002							
Raw water	4.27	0.090	2.11	---	---	---	---
Plant 3 GAC inf.	2.40	0.030	1.25	44%	67%	44%	67%
Plant 3 GAC eff.	2.23	0.029	1.30	7.1%	3.3%	48%	68%
Plant 4 GAC inf.	2.85	0.031	1.09	33%	66%	33%	66%
Plant 4 GAC eff.	2.45	0.029	1.18	14%	6.5%	43%	68%

[a]UV = Ultraviolet absorbance reported in units of "inverse centimeters" (APHA, 1998)
bSUVA (L/mg-m) = Specific ultraviolet absorbance = 100*UV (cm-1)/DOC (mg/L) or UV (m-1)/DOC (mg/L), where DOC = dissolved organic carbon, which typically = 90-95% TOC (used TOC values in calculating SUVA) (e.g., UV = 0.091/cm = 0.091/(0.01 m) = 9.1/m, DOC = 4.37 mg/L, SUVA = (9.1 m-1)/(4.37 mg/L) = 2.08 L/mg-m)

Table 7 shows other water quality parameters for the raw source water for plants 3 and 4. Note, that source water received a tremendous amount of rainfall the weekend before the August 2001 sampling, which may have diluted some of these water quality parameters.

Table 7. Miscellaneous water quality parameters in plants 3 and 4 raw water

Date	Bromide (mg/L)	Alkalinity (mg/L)	Ammonia (mg/L as N)
11/13/2000	0.058	69	0.07
02/05/2001	0.022	27	0.1
08/01/2001	0.05	49	0.08
10/16/2001	0.2	61	0.09
01/28/2002	0.023	38	0.12

Bromide was lowest in winter (0.02 mg/L) and highest in summer and fall (0.05-0.2 mg/L). The source water for plants 3 and 4 is a river, with intakes located 1.5 miles upstream of the confluence with another river. This area is influenced by the tides and is prone to flow reversal at the intakes. As much as 70 % of the source water can be contributed from the latter river, especially during low-flow conditions. Tidal influences were the source of bromide and should also have been a source of iodide.

The source water was relatively low in alkalinity. The addition of coagulant and chlorine depressed the pH of this low-alkalinity water to 5.5-6.3. Raw-water ammonia ranged from 0.07 to 0.12 mg/L as N.

DBPs

Tables 8-17 show results for the DBPs that were analyzed at the Metropolitan Water District of Southern California (MWDSC) for sampling periods 11/13/00, 2/5/01, 8/1/01, 10/16/01, and 1/28/02. Tables 18 (2/5/01), 19 (10/16/01), and 20 (10/16/01) show results for additional target DBPs that were analyzed at the University of North Carolina (UNC), which include halofuranones. Table 21 shows results from broadscreen DBP analyses conducted at the U.S. Environmental Protection Agency (USEPA) for sampling periods 11/13/00, 8/1/01, and 1/28/02.

Summary of tables for halogenated organic and other nonhalogenated organic DBPs

DBP Analyses (Laboratory)	11/13/00	2/5/01	8/1/01	10/16/01	1/28/02
Halogenated organic DBPs (MWDSC)	Tables 8-9	Tables 10-11	Tables 12-13	Tables 14-15	Tables 16-17
Additional target DBPs (UNC)		Table 18		Table 19	
Halogenated furanones (UNC)				Table 20	
Broadscreen analysis (USEPA)	Table 21		Table 21		Table 21

Table 8. DBP results at plant 3 (11/13/00)

11/13/2000	MRL[a]	Plant 3[b]								
Compound	µg/L	Raw	Rapid Mix	GAC Inf	GAC Eff	Plant Eff	SDS/Ave	SDS/Max	DS/Ave	DS/Max
Halomethanes										
Chloromethane	0.15	ND[d]		ND	ND	ND	ND		ND	
Bromomethane	0.20	ND		ND	ND	ND	ND		ND	
Bromochloromethane	0.14	ND		ND	ND	ND	ND		ND	
Dibromomethane	0.11	ND		ND	ND	ND	ND		ND	
Chloroform[e]	0.10	0.7	5	7	9	12	16	20	14	18
Bromodichloromethane[e]	0.10	0.7	4	9	9	13	17	19	15	19
Dibromochloromethane[e]	0.12	0.3	1	3	2	5	7	8	6	7
Bromoform[e]	0.10	ND	0.7	0.8	0.4	0.7	1	1	0.8	1
THM4[f]		2	11	20	20	31	41	48	36	45
Dichloroiodomethane	0.10	ND	NR[g]	2	1	2	2	NR	2	NR
Bromochloroiodomethane	0.50	ND	NR	NR	NR	NR	NR	NR	NR	NR
Dibromoiodomethane	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.59	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.53	ND	ND	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.22	ND	0.7	ND	ND	0.5	0.6	0.9	0.9	0.4
Carbon tetrachloride	0.06	ND		0.8	0.3	0.3	0.3		0.3	
Haloacetic acids										
Monochloroacetic acid[e]	2			ND	3.2	ND	4.2		3.9	
Monobromoacetic acid[e]	1			ND	ND	ND	ND		ND	
Dichloroacetic acid[e]	1			12	ND	6.7	6.9		6.4	
Bromochloroacetic acid[e]	1			7.1	ND	3.0	3.1		3.0	
Dibromoacetic acid[e]	1			1.2	ND	1.0	1.0		ND	
Trichloroacetic acid[e]	1			10	ND	6.0	5.6		5.6	
Bromodichloroacetic acid	1			3.3	ND	2.6	2.5		2.4	
Dibromochloroacetic acid	1			1.2	ND	1.1	1.0		1.1	
Tribromoacetic acid	2			ND	ND	ND	ND		ND	
HAA5[h]				24	3.2	14	18		16	
HAA9[i]				36	3.2	20	24		22	
DXAA[j]				21	ND	11	11		9.4	
TXAA[k]				15	ND	9.7	9.1		9.1	
Haloacetonitriles										
Chloroacetonitrile	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromoacetonitrile	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[e]	0.10	ND	0.5	0.9	0.2	1	2	2	1	2
Bromochloroacetonitrile[e]	0.10	ND	0.2	0.3	ND	0.9	1	1	0.8	1
Dibromoacetonitrile[e]	0.10	ND	ND	ND	ND	0.3	0.2	0.3	0.2	0.2
Trichloroacetonitrile[e]	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
Haloketones										
Chloropropanone	0.10	ND	0.2	0.3	ND	ND	0.3	0.3	0.1	0.2
1,1-Dichloropropanone[e]	0.10	ND	0.5	1	0.1	0.5	0.6	0.6	0.3	0.5
1,3-Dichloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	3	ND		ND	ND	ND	ND		ND	
1,1,1-Trichloropropanone[e]	0.10	ND	1	1	0.3	0.9	1	1	1	1
1,1,3-Trichloropropanone	0.10	ND	0.2	0.2	ND	ND	0.1	ND	ND	ND
1-Bromo-1,1-dichloropropanone	3	ND		<3[l]	ND	<3	ND		<3	
1,1,1-Tribromopropanone	3	ND		ND	ND	ND	ND		ND	
1,1,3-Tribromopropanone	3	ND		ND	ND	ND	ND		ND	
1,1,3,3-Tetrachloropropanone	0.10	ND	0.2	0.2	ND	0.2	0.1	0.1	0.1	0.1
1,1,3,3-Tetrabromopropanone	0.10	ND	0.1	ND	ND	ND	ND	ND	ND	ND

Table 8 (continued)

11/13/2000	MRL[a]	Plant 3[b]								
Compound	µg/L	Raw	Rapid Mix	GAC Inf	GAC Eff	Plant Eff	SDS/Ave	SDS/Max	DS/Ave	DS/Max
Haloacetaldehydes										
Dichloroacetaldehyde	0.16	0.1	0.8	2	0.2	0.8	1	1	0.6	2
Bromochloroacetaldehyde[m] Chloral hydrate[e,m]	0.20	ND	0.8	4	ND	2	4	4	2	4
Tribromoacetaldehyde	0.10	ND	0.2	0.2	ND	ND	0.1	0.2	ND	ND
Halonitromethanes										
Bromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	3	ND		ND	ND	ND	ND		ND	
Dibromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[e]	0.10	ND	ND	0.1	ND	ND	ND	0.1	ND	0.2
Miscellaneous Compounds										
Methyl ethyl ketone	1.90	ND		ND	ND	ND	ND		ND	
Methyl *tertiary* butyl ether	0.16	1.0		1.0	1.0	1.1	1.0		1.1	
Benzyl chloride	0.50	NR	NR	NR	NR	NR	NR	NR	NR	NR

[a]MRL = Minimum reporting level, which equals method detection limit (MDL) or lowest calibration standard or concentration of blank

[b]Plant 3 sampled at (1) raw water, (2) effluent of rapid mix, (3) GAC influent and (4) effluent, (5) plant effluent, (6) SDS testing of plant effluent held for average detention time and (7) held for maximum detention time, (8) DS at average detention time and (9) at maximum detention time.

[c]Plant 4 sampled at (1) GAC influent and (2) effluent, (3) plant effluent, (4) SDS testing of plant effluent held for average detention time and (5) held for maximum detention time, (6) DS at average detention time and (7) at maximum detention time.

[d]ND = Not detected at or above MRL

[e]DBP in the Information Collection Rule (ICR) (note: some utilities collected data for all 9 haloacetic acids for the ICR, but monitoring for only 6 haloacetic acids was required)

[f]THM4 = Sum of 4 THMs (chloroform, bromodichloromethane, dibromochloromethane, bromoform)

[g]NR = Not reported, due to interference problem on gas chromatograph or to problem with quality assurance

[h]HAA5 = Sum of 5 haloacetic acids (monochloro-, monobromo-, dichloro-, dibromo-, trichloroacetic acid)

[i]HAA9 = Sum of 9 haloacetic acids

[j]DXAA = Sum of dihaloacetic acids (dichloro-, bromochloro-, dibromoacetic acid)

[k]TXAA = Sum of trihaloacetic acids (trichloro-, bromodichloro-, dibromochoro-, tribromoacetic acid)

[l]<3: Concentration less than MRL of 3 µg/L

[m]Bromochloroacetaldehyde and chloral hydrate co-eulte; result = sum of 2 DBPs

Table 9. DBP results at plant 4 (11/13/00)

11/13/2000	MRL[a]	Plant 4[c]						
Compound	µg/L	GAC Inf	GAC Eff	Plant Eff	SDS/Ave	SDS/Max	DS/Ave	DS/Max
Halomethanes								
Chloromethane	0.15	ND	ND	ND	ND		ND	
Bromomethane	0.20	ND	ND	ND	ND		ND	
Bromochloromethane	0.14	ND	ND	ND	ND		ND	
Dibromomethane	0.11	ND	ND	ND	ND		ND	
Chloroform[e]	0.10	30	33	43	56	61	41	46
Bromodichloromethane[e]	0.10	17	21	28	33	37	24	27
Dibromochloromethane[e]	0.12	5	6	7	7	8	6	7
Bromoform[e]	0.10	1	1	1	0.9	0.9	1	0.9
THM4[f]		53	61	79	97	107	72	81
Dichloroiodomethane	0.10	1	1	1	1	NR	1	NR
Bromochloroiodomethane	0.50	NR	NR	NR	NR	NR	NR	NR
Dibromoiodomethane	0.10	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.59	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.53	ND	0.6	ND	ND	ND	ND	ND
Iodoform	0.22	0.5	0.3	2	2	2	2	2
Carbon tetrachloride	0.06	0.3	0.4	0.8	0.7		0.7	
Haloacetic acids								
Monochloroacetic acid[e]	2	7.7	12	6.4	11		5.1	
Monobromoacetic acid[e]	1	1.0	ND	ND	1.5		ND	
Dichloroacetic acid[e]	1	24	23	27	30		22	
Bromochloroacetic acid[e]	1	7.0	6.4	8.0	9.4		5.9	
Dibromoacetic acid[e]	1	1.0	ND	1.0	1.2		ND	
Trichloroacetic acid[e]	1	27	27	32	34		24	
Bromodichloroacetic acid	1	11	11	13	14		9.7	
Dibromochloroacetic acid	1	1.7	1.7	2.0	2.3		1.6	
Tribromoacetic acid	2	ND	ND	ND	ND		ND	
HAA5[h]		61	61	66	78		52	
HAA9[j]		81	81	89	103		69	
DXAA[j]		32	29	36	41		28	
TXAA[k]		40	40	46	50		36	
Haloacetonitriles								
Chloroacetonitrile	0.10	ND	ND	0.1	0.1	0.1	ND	0.1
Bromoacetonitrile	0.10	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[e]	0.10	5	5	5	5	6	5	5
Bromochloroacetonitrile[e]	0.10	1	1	1	2	2	1	1
Dibromoacetonitrile[e]	0.10	0.1	0.1	0.2	0.2	0.2	0.1	0.1
Trichloroacetonitrile[e]	0.10	0.2	0.2	0.1	ND	ND	0.1	0.1
Haloketones								
Chloropropanone	0.10	0.4	0.5	0.3	0.2	0.2	0.2	0.3
1,1-Dichloropropanone[e]	0.10	1	1	0.9	0.3	0.3	1	0.8
1,3-Dichloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	3	ND	ND	ND	ND		ND	
1,1,1-Trichloropropanone[e]	0.10	5	5	5	6	7	5	5
1,1,3-Trichloropropanone	0.10	0.3	0.3	0.2	0.2	0.2	0.4	0.3
1-Bromo-1,1-dichloropropanone	3	<3	<3	<3	<3		<3	
1,1,1-Tribromopropanone	3	ND	ND	ND	ND		ND	
1,1,3-Tribromopropanone	3	ND	ND	ND	ND		ND	
1,1,3,3-Tetrachloropropanone	0.10	0.6	0.8	0.4	0.4	0.4	0.7	0.4
1,1,3,3-Tetrabromopropanone	0.10	0.3	0.2	0.1	0.3	0.3	0.2	0.2

Table 9 (continued)

11/13/2000	MRL[a]	Plant 4[c]						
Compound	µg/L	GAC Inf	GAC Eff	Plant Eff	SDS/Ave	SDS/Max	DS/Ave	DS/Max
Haloacetaldehydes								
Dichloroacetaldehyde	0.16	4	5	3	2	3	3	3
Bromochloroacetaldehyde[m]								
Chloral hydrate[e,m]	0.20	12	13	14	18	22	15	15
Tribromoacetaldehyde	0.10	0.1	0.1	ND	ND	ND	ND	ND
Halonitromethanes								
Bromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	3	ND	ND	ND	ND		ND	
Dibromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[e]	0.10	0.2	0.2	0.2	0.2	0.3	0.2	0.2
Miscellaneous Compounds								
Methyl ethyl ketone	1.90	ND	ND	ND	ND		ND	
Methyl *tertiary* butyl ether	0.16	0.8	0.8	0.8	0.9		0.9	
Benzyl chloride	0.50	NR	NR	NR	NR	NR	NR	NR

Table 10. DBP results at plant 3 (2/5/01)

02/05/2001	MRL[a]	Plant 3[b]								
Compound	µg/L	Raw	Rapid Mix	GAC Inf	GAC Eff	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes										
Chloromethane	0.15	ND[d]		ND	ND	ND	ND		ND	
Bromomethane	0.20	ND		ND	ND	ND	ND		ND	
Bromochloromethane	0.14	ND		ND	ND	ND	ND		ND	
Dibromomethane	0.11	ND		ND	ND	ND	ND		ND	
Chloroform[e]	0.1	0.5	5.5	15	21	27	33	37	33	40
Bromodichloromethane[e]	0.1	ND	1.0	3.1	3.7	5.3	5.9	6.0	5.8	6.4
Dibromochloromethane[e]	0.10	ND	ND	0.4	0.6	0.8	0.8	0.9	0.9	0.9
Bromoform[e]	0.12	ND	ND	ND	0.1	0.1	0.3	0.3	0.3	0.3
THM4[f]		0.5	6.5	18	25	33	40	44	40	48
Dichloroiodomethane	0.25	ND	NR[g]	0.29	0.27	0.30	0.31	NR	0.26	NR
Bromochloroiodomethane	0.20	ND	NR	ND	ND	ND	ND	NR	ND	NR
Dibromoiodomethane	0.60	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.51	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.56	ND	ND	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.54	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.06	ND		ND	ND	ND	ND		ND	
Tribromochloromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids										
Monochloroacetic acid[e]	2			3.6	ND	2.3	2.8		2.6	
Monobromoacetic acid[e]	1			ND	ND	ND	ND		ND	
Dichloroacetic acid[e]	1			25	4.2	11	12		11	
Bromochloroacetic acid[e]	1			1.7	ND	1.2	1.2		1.2	
Dibromoacetic acid[e]	1			ND	ND	ND	ND		ND	
Trichloroacetic acid[e]	1			28	15	19	21		19	
Bromodichloroacetic acid	1			2.4	1.3	1.9	1.9		1.8	
Dibromochloroacetic acid	1			ND	ND	ND	ND		ND	
Tribromoacetic acid	2			ND	ND	ND	ND		ND	
HAA5[h]				57	19	32	36		33	
HAA9[i]				61	21	35	39		36	
DXAA[j]				27	4.2	12	13		12	
TXAA[k]				30	16	21	23		21	
Haloacetonitriles										
Chloroacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[e]	0.10	ND	0.6	2.4	1.6	2.2	2.4	2.4	2.4	2.5
Bromochloroacetonitrile[e]	0.1	ND	ND	0.2	ND	0.2	0.2	0.2	0.2	0.3
Dibromoacetonitrile[e]	0.17	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trichloroacetonitrile[e]	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Haloketones										
Chloropropanone	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloropropanone[e]	0.11	ND	1.1	0.9	0.5	0.6	1.0	1.1	1.1	1.2
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	N/A[n]	NR		NR	NR	NR	NR		NR	
1,3-Dibromopropanone	N/A	NR		NR	NR	NR	NR		NR	
1,1,1-Trichloropropanone[e]	0.10	ND	1.6	3.1	2.4	2.5	2.7	2.6	2.4	2.4
1,1,3-Trichloropropanone	0.10	ND	0.3	0.2	0.2	0.2	0.2	0.2	ND	0.2
1-Bromo-1,1-dichloropropanone	N/A	NR		NR	NR	NR	NR		NR	
1,1,1-Tribromopropanone	N/A	NR		NR	NR	NR	NR		NR	
1,1,3-Tribromopropanone	N/A	NR		NR	NR	NR	NR		NR	
1,1,3,3-Tetrachloropropanone	0.12	ND	0.4	0.7	0.5	0.4	0.6	0.4	0.2	0.4
1,1,1,3-Tetrachloropropanone	N/A	NR		NR	NR	NR	NR		NR	
1,1,3,3-Tetrabromopropanone	0.58	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table 10 (continued)

02/05/2001	MRL[a]	Plant 3[b]								
Compound	µg/L	Raw	Rapid Mix	GAC Inf	GAC Eff	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloacetaldehydes										
Dichloroacetaldehyde	0.16	ND	0.8	2	1	1	1	1	2	2
Bromochloroacetaldehyde	0.1	ND	ND	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Chloral hydrate[e]	0.1	ND	1.0	3.0	1.8	2.7	3.8	3.6	3.4	3.6
Tribromoacetaldehyde	0.1	ND	0.2	0.2	0.1	ND	ND	ND	ND	ND
Halonitromethanes										
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	N/A	NR		NR	NR	NR	NR		NR	
Bromochloronitromethane	N/A	NR		NR	NR	NR	NR		NR	
Dibromonitromethane	0.12	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[e]	0.1	ND	0.4	0.8	0.2	0.3	0.4	0.5	0.5	0.6
Miscellaneous Compounds										
Methyl ethyl ketone	1.9	ND		ND	ND	ND	ND		ND	
Methyl *tertiary* butyl ether	0.16	0.4		0.5	0.5	0.4	0.5		0.4	
Benzyl chloride	2	ND	ND	ND	ND	ND	ND	ND	ND	ND

[n]N/A = Not applicable

Table 11. DBP results at plant 4 (2/5/01)

02/05/2001	MRL[a]	Plant 4[c]						
Compound	µg/L	GAC Inf	GAC Eff	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes								
Chloromethane	0.15	ND	ND	ND	ND		ND	
Bromomethane	0.20	ND	ND	ND	ND		ND	
Bromochloromethane	0.14	ND	ND	ND	ND		ND	
Dibromomethane	0.11	ND	ND	ND	ND		ND	
Chloroform[e]	0.1	24	27	29	33	33	36	42
Bromodichloromethane[e]	0.1	3.3	3.8	4.3	4.7	4.7	5.3	6.1
Dibromochloromethane[e]	0.10	0.5	0.5	0.7	0.7	0.7	0.8	0.9
Bromoform[e]	0.12	0.1	ND	0.1	0.1	0.3	0.1	ND
THM4[f]		28	31	34	39	38	42	49
Dichloroiodomethane	0.25	0.27	0.25	0.29	0.28	NR	0.29	NR
Bromochloroiodomethane	0.20	ND	ND	ND	ND	NR	ND	NR
Dibromoiodomethane	0.60	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.51	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.56	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.54	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.06	ND	ND	ND	ND		ND	
Tribromochloromethane	0.1	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids								
Monochloroacetic acid[e]	2	5.1	5.5	4.7	5.7		6.3	
Monobromoacetic acid[e]	1	ND	ND	ND	ND		ND	
Dichloroacetic acid[e]	1	32	31	25	25		28	
Bromochloroacetic acid[e]	1	1.9	1.9	1.7	1.7		1.9	
Dibromoacetic acid[e]	1	ND	ND	ND	ND		ND	
Trichloroacetic acid[e]	1	33	35	35	35		38	
Bromodichloroacetic acid	1	3.5	3.6	3.3	3.6		4.6	
Dibromochloroacetic acid	1	1.0	1.0	ND	ND		ND	
Tribromoacetic acid	2	ND	ND	ND	ND		ND	
HAA5[h]		70	72	65	66		72	
HAA9[i]		77	78	70	71		79	
DXAA[j]		34	33	27	27		30	
TXAA[k]		38	40	38	39		43	
Haloacetonitriles								
Chloroacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[e]	0.10	2.6	2.8	2.7	2.8	2.8	3.2	3.4
Bromochloroacetonitrile[e]	0.1	0.2	0.2	0.2	0.3	0.3	0.3	0.4
Dibromoacetonitrile[e]	0.17	ND	ND	ND	ND	ND	ND	ND
Trichloroacetonitrile[e]	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Haloketones								
Chloropropanone	0.5	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloropropanone[e]	0.11	1.0	1.0	0.9	1.0	1.0	1.0	1.0
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	N/A	NR	NR	NR	NR		NR	
1,3-Dibromopropanone	N/A	NR	NR	NR	NR		NR	
1,1,1-Trichloropropanone[e]	0.10	3.2	3.3	3.1	3.2	3.3	3.7	4.0
1,1,3-Trichloropropanone	0.10	0.3	0.3	0.2	0.3	0.2	0.3	0.2
1-Bromo-1,1-dichloropropanone	N/A	NR	NR	NR	NR		NR	
1,1,1-Tribromopropanone	N/A	NR	NR	NR	NR		NR	
1,1,3-Tribromopropanone	N/A	NR	NR	NR	NR		NR	
1,1,3,3-Tetrachloropropanone	0.12	0.5	0.6	0.6	0.5	0.5	0.6	0.5
1,1,1,3-Tetrachloropropanone	N/A	NR	NR	NR	NR		NR	
1,1,3,3-Tetrabromopropanone	0.58	ND	ND	ND	ND	ND	ND	ND

Table 11 (continued)

02/05/2001	MRL[a]	Plant 4[c]						
Compound	µg/L	GAC Inf	GAC Eff	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloacetaldehydes								
Dichloroacetaldehyde	0.16	2	3	2	2	2	2	2
Bromochloroacetaldehyde	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Chloral hydrate[e]	0.1	3.2	3.6	4.5	4.4	4.7	6.9	7.5
Tribromoacetaldehyde	0.1	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes								
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	N/A	NR	NR	NR	NR		NR	
Bromochloronitromethane	N/A	NR	NR	NR	NR		NR	
Dibromonitromethane	0.12	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[e]	0.1	0.8	0.8	0.6	0.6	0.6	0.7	0.7
Miscellaneous Compounds								
Methyl ethyl ketone	1.9	ND	ND	ND	ND		ND	
Methyl *tertiary* butyl ether	0.16	0.5	0.4	0.5	0.5		0.5	
Benzyl chloride	2	ND	ND	ND	ND	ND	ND	ND

Table 12. DBP results at plant 3 (8/1/01)

08/01/2001	MRL[a]	Plant 3[b]								
Compound	µg/L	Raw	Rapid Mix	GAC Inf	GAC Eff	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes										
Chloromethane	0.2	ND[d]		0.3	ND	ND	ND		ND	
Bromomethane	0.2	ND		ND	ND	ND	ND		ND	
Bromochloromethane	0.5	ND		ND	ND	ND	ND		ND	
Dibromomethane	0.5	ND		ND	ND	ND	ND		ND	
Chloroform[e]	0.1	0.2	3	8	14	16	19	18	19	NR[g]
Bromodichloromethane[e]	0.1	0.1	0.9	4	5	7	8	7	8	NR
Dibromochloromethane[e]	0.1	ND	0.2	0.8	0.6	2	2	2	2	NR
Bromoform[e]	0.11	ND	ND	ND	ND	0.3	0.3	0.2	0.4	0.5
THM4[f]		0.3	4.1	13	20	25	28	27	29	NR
Dichloroiodomethane	0.5	ND	NR	<0.5[o]	ND	ND	ND	ND	ND	NR
Bromochloroiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibromoiodomethane	0.52	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.2	ND		ND	ND	ND	ND		ND	
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids										
Monochloroacetic acid[e]	2			3.9	ND	2.2	ND		2.3	
Monobromoacetic acid[e]	1			1.2	ND	ND	ND		ND	
Dichloroacetic acid[e]	1			25	ND	6.4	8.7		7.3	
Bromochloroacetic acid[e]	1			6.5	1.6	2.7	3.2		3.1	
Dibromoacetic acid[e]	1			1.1	ND	1.0	1.0		ND	
Trichloroacetic acid[e]	1			16	ND	2.2	2.3		2.2	
Bromodichloroacetic acid	1			4.6	ND	1.5	1.4		1.4	
Dibromochloroacetic acid	1			1.2	ND	ND	ND		ND	
Tribromoacetic acid	2			ND	ND	ND	ND		ND	
HAA5[h]				47	ND	12	12		12	
HAA9[i]				60	2	16	17		16	
DXAA[j]				33	2	10	13		10	
TXAA[k]				22	ND	3.7	3.7		3.6	
Haloacetonitriles										
Chloroacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[e]	0.10	ND	0.6	4	0.1	0.9	1	1	2	2
Bromochloroacetonitrile[e]	0.1	ND	0.1	0.8	ND	0.7	0.8	0.8	0.9	1
Dibromoacetonitrile[e]	0.14	ND	ND	0.2	ND	0.6	0.7	0.5	0.8	0.8
Trichloroacetonitrile[e]	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodichloroacetonitrile	0.5	ND		ND	ND	ND				
Dibromochloroacetonitrile	0.5	ND		ND	ND	ND				
Tribromoacetonitrile	0.5	ND		ND	ND	ND				
Haloketones										
Chloropropanone	0.1	ND	ND	0.1	0.1	0.1	0.1	0.1	0.3	0.3
1,1-Dichloropropanone[e]	0.10	ND	0.9	2	0.2	0.4	1	1	0.8	1
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloropropanone[e]	0.1	ND	1	2	0.2	0.8	0.5	0.2	0.8	0.4
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	0.1	ND	ND	0.5	ND	0.2	ND	ND	ND	ND
1,1,1-Tribromopropanone	0.29	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3-Tribromopropanone	0.14	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrachloropropanone	0.1	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
1,1,1,3-Tetrachloropropanone	0.10	*ND*	*ND*	*2*[p]	*1*[p]	*0.6*[p]	*ND*	*ND*	*ND*	*ND*
1,1,3,3-Tetrabromopropanone	0.1	ND	ND	0.1	0.2	0.3	ND	ND	ND	ND

Table 12 (continued)

08/01/2001	MRL[a]	Plant 3[b]								
Compound	µg/L	Raw	Rapid Mix	GAC Inf	GAC Eff	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloacetaldehydes										
Dichloroacetaldehyde	0.1	ND	0.8	4	0.9	1	3	3	2	4
Bromochloroacetaldehyde	0.1	ND	ND	2	ND	ND	0.5	ND	0.4	0.5
Chloral hydrate[e]	0.1	*ND*[p]	*ND*[p]	*3*[p]	*0.6*[p]	*2*[p]	*2*[p]	*2*[p]	*2*[p]	*2*[p]
Tribromoacetaldehyde	0.1	*ND*[p]	*ND*[p]	*1*[p]	*ND*[p]	*ND*[p]	*ND*[p]	*ND*[p]	*ND*[p]	*ND*[p]
Halonitromethanes										
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromochloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[e]	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodichloronitromethane	0.5	ND		ND	ND	ND				
Dibromochloronitromethane	0.5	ND		ND	ND	ND				
Bromopicrin	2.0	ND		ND	ND	ND				
Miscellaneous Compounds										
Methyl ethyl ketone	0.5	28		12	15	5	5		2	
Methyl *tertiary* butyl ether	0.2	1		1	1	1	1		0.9	
1,1,2,2-Tetrabromo-2-chloroethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzyl chloride	0.25	ND	NR	ND	ND	ND	ND	NR	ND	NR

[o]<0.5: Detected by SPE-GC/MS, but below MRL for SPE-GC/MS

[p]Low spike recoveries for 1,1,1,3- and 1,1,3,3-tetrachloropropanone and for chloral hydrate and tribromoacetaldehyde.

Table 13. DBP results at plant 4 (8/1/01)

08/01/2001	MRL[a]	Plant 4[c]						
Compound	µg/L	GAC Inf	GAC Eff	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes								
Chloromethane	0.2	ND	ND	ND	ND		ND	
Bromomethane	0.2	ND	ND	ND	ND		ND	
Bromochloromethane	0.5	ND	ND	ND	ND		ND	
Dibromomethane	0.5	ND	ND	ND	ND		ND	
Chloroform[e]	0.1	22	27	22	27	27	27	25
Bromodichloromethane[e]	0.1	7	9	8	9	10	9	9
Dibromochloromethane[e]	0.1	1	1	1	1	2	2	2
Bromoform[e]	0.11	ND	ND	ND	ND	ND	ND	0.1
THM4[f]		30	37	31	38	39	38	36
Dichloroiodomethane	0.5	ND	ND	ND	ND	NR	0.5	NR
Bromochloroiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND
Dibromoiodomethane	0.52	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.1	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.5	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.2	ND	ND	ND	ND		ND	
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids								
Monochloroacetic acid[e]	2	20	16	8.2	7.8		8.1	
Monobromoacetic acid[e]	1	ND	ND	ND	ND		ND	
Dichloroacetic acid[e]	1	56	25	24	25		26	
Bromochloroacetic acid[e]	1	8.7	4.5	4.5	4.9		5.1	
Dibromoacetic acid[e]	1	ND	ND	ND	ND		ND	
Trichloroacetic acid[e]	1	68	49	29	31		30	
Bromodichloroacetic acid	1	12	8.7	6.8	7.3		7.0	
Dibromochloroacetic acid	1	1.9	1.3	1.3	1.2		1.2	
Tribromoacetic acid	2	ND	ND	ND	ND		ND	
HAA5[h]		144	90	61	64		64	
HAA9[i]		167	105	74	77		77	
DXAA[j]		65	30	29	30		31	
TXAA[k]		82	59	37	40		38	
Haloacetonitriles								
Chloroacetonitrile	0.1	0.3	0.4	0.3	0.3	0.3	0.3	0.3
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[e]	0.10	10	10	6	8	8	8	8
Bromochloroacetonitrile[e]	0.1	1	1	1	1	1	1	1
Dibromoacetonitrile[e]	0.14	0.8	0.3	0.4	0.4	0.5	0.4	0.4
Trichloroacetonitrile[e]	0.1	ND	ND	ND	ND	ND	ND	ND
Bromodichloroacetonitrile	0.5	ND	ND	ND				ND
Dibromochloroacetonitrile	0.5	ND	ND	ND				ND
Tribromoacetonitrile	0.5	ND	ND	ND				ND
Haloketones								
Chloropropanone	0.1	0.1	0.2	0.1	0.2	0.2	0.2	0.2
1,1-Dichloropropanone[e]	0.10	3	2	0.9	1	0.8	0.8	1
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	0.10	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloropropanone[e]	0.1	8	7	4	6	6	6	5
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	0.1	0.7	0.7	0.4	0.5	0.4	0.3	0.1
1,1,1-Tribromopropanone	0.29	ND	ND	ND	ND	ND	ND	ND
1,1,3-Tribromopropanone	0.14	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrachloropropanone	0.1	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
1,1,1,3-Tetrachloropropanone	0.10	*2*[p]	*1*[p]	*0.7*[p]	*1*[p]	*ND*	*0.7*[p]	*0.2*[p]
1,1,3,3-Tetrabromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND

Table 13 (continued)

08/01/2001	MRL[a]	Plant 4[c]						
Compound	µg/L	GAC Inf	GAC Eff	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloacetaldehydes								
Dichloroacetaldehyde	0.1	8	4	3	3	3	5	5
Bromochloroacetaldehyde	0.1	2	0.4	0.4	0.3	0.3	0.3	0.4
Chloral hydrate[e]	0.1	*16*[p]	*6*[p]	*6*[p]	*4*[p]	*4*[p]	*7*[p]	*11*[p]
Tribromoacetaldehyde	0.1	*2*[p]	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
Halonitromethanes								
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND
Bromochloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND
Dibromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[e]	0.1	ND	ND	ND	ND	ND	0.2	0.2
Bromodichloronitromethane	0.5	ND	ND	ND				ND
Dibromochloronitromethane	0.5	ND	ND	ND				ND
Bromopicrin	2.0	ND	ND	ND				ND
Miscellaneous Compounds								
Methyl ethyl ketone	0.5	24	23	ND	0.5		0.6	
Methyl *tertiary* butyl ether	0.2	2	2	1	1		0.9	
1,1,2,2-Tetrabromo-2-chloroethane	0.1	ND	ND	ND	ND	ND	ND	ND
Benzyl chloride	0.25	ND	ND	ND	ND	NR	ND	NR

[e]DBP in the Information Collection Rule (ICR) (note: some utilities collected data for all 9 haloacetic acids for the ICR, but monitoring for only 6 haloacetic acids was required)

[p]Low spike recoveries for 1,1,1,3- and 1,1,3,3-tetrachloropropanone and for chloral hydrate and tribromoacetaldehyde.

Table 14. DBP results at plant 3 (10/16/01)

10/16/2001	MRL[a]	Plant 3[b]								
Compound	µg/L	Raw	Rapid Mix	GAC Inf	GAC Eff	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes										
Chloromethane	0.2	ND[d]		ND	ND	ND	ND		ND	
Bromomethane	0.2	ND		ND	ND	ND	ND		ND	
Bromochloromethane	0.5	ND		ND	ND	ND	ND		ND	
Dibromomethane	0.5	ND		ND	ND	ND	ND		ND	
Chloroform[e]	0.1	ND	1	8	12	18	19	20	16	23
Bromodichloromethane[e]	0.1	0.2	2	13	14	24	26	27	24	36
Dibromochloromethane[e]	0.1	ND	0.8	7	6	11	12	14	10	22
Bromoform[e]	0.25	ND	0.2	2	0.8	2	3	2	4	3
THM4[f]		0.2	4	30	33	55	60	63	54	84
Dichloroiodomethane	0.5	ND	NR[g]	ND	ND	ND	0.8	NR	0.5	NR
Bromochloroiodomethane	0.5	ND	NR	ND	ND	ND	ND	NR	ND	NR
Dibromoiodomethane	0.52	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.1	ND	ND	ND	ND	ND	ND	ND	NR	NR
Carbon tetrachloride	0.2	ND		ND	ND	ND	ND		ND	
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids										
Monochloroacetic acid[e]	2			ND	ND	ND	ND		ND	
Monobromoacetic acid[e]	1			ND	ND	ND	ND		ND	
Dichloroacetic acid[e]	1			14	ND	4.6	4.7		3.4	
Bromochloroacetic acid[e]	1			7.8	ND	3.4	3.6		4.2	
Dibromoacetic acid[e]	1			3.5	ND	2.6	2.6		3.0	
Trichloroacetic acid[e]	1			9.8	ND	1.2	1.4		1.4	
Bromodichloroacetic acid	1			8.2	ND	3.3	3.4		2.4	
Dibromochloroacetic acid	1			3.2	ND	2.0	2.1		1.7	
Tribromoacetic acid	2			ND	ND	ND	ND		ND	
HAA5[h]				27	ND	8.4	8.7		7.8	
HAA9[i]				47	ND	17	18		16	
DXAA[j]				25	ND	11	11		11	
TXAA[k]				21	ND	6.5	6.9		5.5	
Haloacetonitriles										
Chloroacetonitrile	0.2	ND	NR	0.5	ND	0.3	0.4	NR	0.4	NR
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[e]	0.1	ND	0.5	2	0.2	0.7	0.8	0.9	1	2
Bromochloroacetonitrile[e]	0.1	ND	0.4	2	ND	1	2	2	2	2
Dibromoacetonitrile[e]	0.1	ND	0.5	2	0.1	0.7	0.7	0.8	1	1
Trichloroacetonitrile[e]	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodichloroacetonitrile	0.5	ND		ND	ND	ND				
Dibromochloroacetonitrile	0.5	ND		ND	ND	ND				
Tribromoacetonitrile	0.90	ND		ND	ND	ND				
Haloketones										
Chloropropanone	0.1	ND	0.3	0.5	0.4	0.6	0.5	0.6	0.4	0.5
1,1-Dichloropropanone[e]	0.10	ND	0.7	1	0.2	0.4	0.4	0.4	0.3	0.4
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	0.1	ND	ND	0.4	ND	0.1	ND	0.1	ND	ND
1,1,1-Trichloropropanone[e]	0.1	ND	0.6	1	0.2	0.5	0.5	0.5	0.2	0.2
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	0.1	ND	0.5	1	ND	0.4	0.2	0.1	ND	ND
1,1,1-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrachloropropanone	0.1	ND	0.5	2	ND	0.4	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	0.10	ND	ND	0.4	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table 14 (continued)

10/16/2001	MRL[a]	Plant 3[b]								
Compound	µg/L	Raw	Rapid Mix	GAC Inf	GAC Eff	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloacetaldehydes										
Dichloroacetaldehyde	0.22	ND	0.9	4	0.2	0.7	1	1	1	2
Bromochloroacetaldehyde	0.5	ND	ND	2	ND	ND	1	1	1	2
Chloral hydrate[e]	0.1	ND	0.3	4	0.3	0.7	1	2	0.7	1
Tribromoacetaldehyde	0.1	ND	ND	1	ND	ND	0.1	ND	ND	ND
Halonitromethanes										
Chloronitromethane	0.1	ND	0.2	0.3	ND	ND	ND	0.1	NR	NR
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	0.2	0.2
Bromochloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[e]	0.1	ND	ND	0.1	ND	ND	ND	ND	ND	0.2
Bromodichloronitromethane	0.5	ND		0.5	ND	ND				
Dibromochloronitromethane	0.5	ND		0.6	ND	0.5				
Bromopicrin	0.5	ND		ND	ND	ND				
Miscellaneous Compounds										
Methyl ethyl ketone	0.5	0.6		3	ND	ND	ND		ND	
Methyl *tertiary* butyl ether	0.2	1		1	1	1	1		0.9	
1,1,2,2-Tetrabromo-2-chloroethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzyl chloride	0.25	ND	NR	ND	ND	ND	ND	NR	ND	NR

Table 15. DBP results at plant 4 (10/16/01)

10/16/2001	MRL[a]	Plant 4[c]						
Compound	µg/L	GAC Inf	GAC Eff	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes								
Chloromethane	0.2	ND	ND	ND	ND		ND	
Bromomethane	0.2	ND	ND	ND	ND		ND	
Bromochloromethane	0.5	ND	ND	ND	ND		ND	
Dibromomethane	0.5	ND	ND	ND	ND		ND	
Chloroform[e]	0.1	26	30	34	34	48	60	69
Bromodichloromethane[e]	0.1	27	32	34	36	45	64	68
Dibromochloromethane[e]	0.1	10	11	13	14	18	32	37
Bromoform[e]	0.25	1	1	2	2	1	3	2
THM4[f]		64	74	83	86	112	159	176
Dichloroiodomethane	0.5	ND	0.7	0.8	0.9	NR	1	NR
Bromochloroiodomethane	0.5	ND	ND	ND	ND	NR	ND	NR
Dibromoiodomethane	0.52	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.1	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.1	ND	ND	ND	ND	ND	NR	NR
Carbon tetrachloride	0.2	ND	ND	ND	ND		ND	
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids								
Monochloroacetic acid[e]	2	2.5	ND	ND	ND		2.3	
Monobromoacetic acid[e]	1	1.2	ND	ND	ND		1.2	
Dichloroacetic acid[e]	1	23	14	17	17		15	
Bromochloroacetic acid[e]	1	15	7.5	7.2	7.3		12	
Dibromoacetic acid[e]	1	3.3	1.5	2.8	2.9		4.1	
Trichloroacetic acid[e]	1	25	22	20	20		17	
Bromodichloroacetic acid	1	18	15	12	12		12	
Dibromochloroacetic acid	1	5.5	4.4	3.8	3.9		4.3	
Tribromoacetic acid	2	ND	ND	ND	ND		ND	
HAA5[h]		55	38	40	40		40	
HAA9[i]		94	64	63	63		68	
DXAA[j]		41	23	27	27		31	
TXAA[k]		49	41	36	36		33	
Haloacetonitriles								
Chloroacetonitrile	0.2	0.9	0.9	0.9	0.9	NR	1	NR
Bromoacetonitrile	0.1	ND	0.1	0.2	0.1	0.1	ND	ND
Dichloroacetonitrile[e]	0.1	6	6	5	5	7	8	7
Bromochloroacetonitrile[e]	0.1	2	2	2	2	3	4	4
Dibromoacetonitrile[e]	0.1	2	1	0.6	1	0.9	2	2
Trichloroacetonitrile[e]	0.1	0.1	ND	0.1	ND	ND	ND	ND
Bromodichloroacetonitrile	0.5	ND	ND	ND				
Dibromochloroacetonitrile	0.5	ND	ND	ND				
Tribromoacetonitrile	0.90	ND	ND	ND				
Haloketones								
Chloropropanone	0.1	0.3	0.3	0.4	0.4	0.5	0.3	0.3
1,1-Dichloropropanone[e]	0.1	2	2	1	1	0.3	0.3	0.6
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	0.1	0.2	0.1	ND	ND	ND	ND	ND
1,1,1-Trichloropropanone[e]	0.1	3	3	3	3	3	2	1
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	0.1	2	1	0.9	1	0.7	ND	ND
1,1,1-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1,3-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrachloropropanone	0.1	1	0.4	0.3	0.3	0.2	ND	ND
1,1,1,3-Tetrachloropropanone	0.1	0.2	0.3	0.1	0.1	0.1	ND	ND
1,1,3,3-Tetrabromopropanone	0.5	ND	ND	ND	ND	ND	ND	ND

Table 15 (continued)

10/16/2001	MRL[a]	Plant 4[c]						
Compound	µg/L	GAC Inf	GAC Eff	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloacetaldehydes								
Dichloroacetaldehyde	0.22	5	5	3	4	4	2	2
Bromochloroacetaldehyde	0.5	2	2	1	1	2	1	1
Chloral hydrate[e]	0.1	9	9	7	8	12	15	8
Tribromoacetaldehyde	0.1	0.1	0.1	ND	ND	0.1	ND	ND
Halonitromethanes								
Chloronitromethane	0.1	0.4	0.4	0.2	0.2	ND	NR	NR
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	0.1	ND	ND	ND	ND	ND	0.2	0.2
Bromochloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND
Dibromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[e]	0.1	0.1	0.2	0.2	0.2	0.2	ND	0.2
Bromodichloronitromethane	0.5	ND	ND	ND				
Dibromochloronitromethane	0.5	ND	ND	ND				
Bromopicrin	0.5	ND	ND	ND				
Miscellaneous Compounds								
Methyl ethyl ketone	0.5	3	2	1	2		2	
Methyl *tertiary* butyl ether	0.2	0.8	1	1	1		1	
1,1,2,2-Tetrabromo-2-chloroethane	0.5	ND	ND	ND	ND	ND	ND	ND
Benzyl chloride	0.25	ND	ND	ND	ND	NR	ND	NR

Table 16. DBP results at plant 3 (1/28/02)

01/28/2002	MRL[a]	Plant 3[b]								
Compound	µg/L	Raw	Rapid Mix	GAC Inf	GAC Eff	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes										
Chloromethane	0.2	ND[d]		ND	ND	ND	ND		ND	
Bromomethane	0.2	ND		ND	ND	ND	ND		ND	
Bromochloromethane	0.5	ND		ND	ND	ND	ND		ND	
Dibromomethane	0.5	ND		ND	ND	ND	ND		ND	
Chloroform[e]	0.2	ND	NR[g]	20	16	*20*[q]	NR	NR	NR	NR
Bromodichloromethane[e]	0.2	ND	NR	4	6	7	8	NR	10	NR
Dibromochloromethane[e]	0.5	ND	NR	2	3	4	5	NR	4	NR
Bromoform[e]	0.5	ND	NR	ND	0.6	0.6	0.6	NR	0.7	NR
THM4[f]		ND	NR	26	26	*32*	NR	NR	NR	NR
Dichloroiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromochloroiodomethane	0.5	ND	NR	ND	ND	ND	ND	NR	ND	NR
Dibromoiodomethane	0.5	ND	NR	ND	ND	ND	ND	NR	ND	NR
Chlorodiiodomethane	0.1	ND	ND	ND	ND	ND	ND	ND	NR	ND
Bromodiiodomethane	0.52	ND	ND	ND	ND	ND	ND	ND	NR	ND
Iodoform	1.0	ND	NR	ND	ND	ND	ND	NR	ND	NR
Carbon tetrachloride	0.2	ND		ND	ND	ND	ND		ND	
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids										
Monochloroacetic acid[e]	2			ND	ND	2.5	2.8		2.7	
Monobromoacetic acid[e]	1			ND	ND	ND	ND		ND	
Dichloroacetic acid[e]	1			19	4.3	7.8	7.6		9.3	
Bromochloroacetic acid[e]	1			2.6	ND	1.6	1.5		5.2	
Dibromoacetic acid[e]	1			ND	ND	ND	ND		ND	
Trichloroacetic acid[e]	1			20	9.8	13	12		13	
Bromodichloroacetic acid	1			5.6	2.7	4.4	4.0		1.5	
Dibromochloroacetic acid	1			2.0	1.2	1.6	1.4		2.8	
Tribromoacetic acid	2			ND	ND	ND	ND		ND	
HAA5[h]				39	14	23	22		25	
HAA9[i]				49	18	31	29		35	
DXAA[j]				22	4.3	9.4	9.1		15	
TXAA[k]				28	14	19	17		17	
Haloacetonitriles										
Chloroacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	NR	ND
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	NR	ND
Dichloroacetonitrile[e]	1	ND	NR	3	1	1	NR	NR	NR	NR
Bromochloroacetonitrile[e]	0.1	ND	NR	0.5	0.2	0.3	0.4	NR	1	0.7
Dibromoacetonitrile[e]	0.1	ND	ND	ND	ND	<0.5[o]	<0.5	ND	<0.5	0.2
Trichloroacetonitrile[e]	0.5	ND	NR	ND	ND	ND	ND	NR	ND	NR
Bromodichloroacetonitrile	0.5	ND		ND	ND	ND				
Dibromochloroacetonitrile	0.5	ND		ND	ND	ND				
Tribromoacetonitrile	0.95	ND		ND	ND	ND				
Haloketones										
Chloropropanone	0.1	ND	0.1	0.3	0.3	0.3	0.3	0.4	NR	0.3
1,1-Dichloropropanone[e]	0.10	ND	0.4	1	0.7	0.7	0.6	0.2	1	NR
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	NR	ND
1,1-Dibromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	NR	ND
1,1,1-Trichloropropanone[e]	0.5	ND	ND	2	1	1	1	NR	1	NR
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	NR	ND
1-Bromo-1,1-dichloropropanone	1.0	ND	NR	1	ND	ND	<1[r]	NR	ND	NR
1,1,1-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	NR	ND
1,1,3-Tribromopropanone	0.1	*0.1*	ND	*0.2*	*0.1*	ND	*0.1*	ND	NR	*0.1*
1,1,3,3-Tetrachloropropanone	0.10	ND	ND	*0.2*	ND	ND	ND	ND	NR	*0.2*
1,1,1,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	NR	ND
1,1,3,3-Tetrabromopropanone	N/A	NR	NR	NR	NR	NR	NR	NR	NR	NR

Table 16 (continued)

01/28/2002	MRL[a]	Plant 3[b]								
Compound	µg/L	Raw	Rapid Mix	GAC Inf	GAC Eff	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloacetaldehydes										
Dichloroacetaldehyde	0.98	ND	0.6	3	1	ND	ND	ND	NR	3
Bromochloroacetaldehyde	0.5	ND	ND	ND	ND	ND	ND	ND	NR	ND
Chloral hydrate[e]	0.1	0.3	0.2	3	0.8	0.9	0.9	ND	NR	4
Tribromoacetaldehyde	0.1	ND	ND	ND	ND	ND	ND	ND	NR	ND
Halonitromethanes										
Chloronitromethane	N/A	ND		ND	ND	ND	ND		ND	
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	NR	ND
Dichloronitromethane	0.10	ND	ND	ND	ND	ND	ND	ND	NR	0.2
Bromochloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	NR	ND
Dibromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[e]	0.1	ND	ND	0.5	ND	ND	ND	ND	<0.5	1
Bromodichloronitromethane	0.5	ND		0.5	ND	0.6				
Dibromochloronitromethane	0.5	ND		ND	ND	ND				
Bromopicrin	0.5	ND		ND	ND	ND				
Miscellaneous Compounds										
Methyl ethyl ketone	0.5	ND		ND	ND	ND	ND		ND	
Methyl *tertiary* butyl ether	0.2	0.6		0.6	0.6	0.6	0.7		0.7	
1,1,2,2-Tetrabromo-2-chloroethane	2.5	ND	NR	ND	ND	ND	ND	NR	ND	NR
Benzyl chloride	0.25	ND	NR	ND	ND	ND	ND	NR	ND	NR

[q]Results in italics tentative due to problems with quality assurance

[r]<1: Detected by SPE-GC/MS, but below MRL for SPE-GC/MS

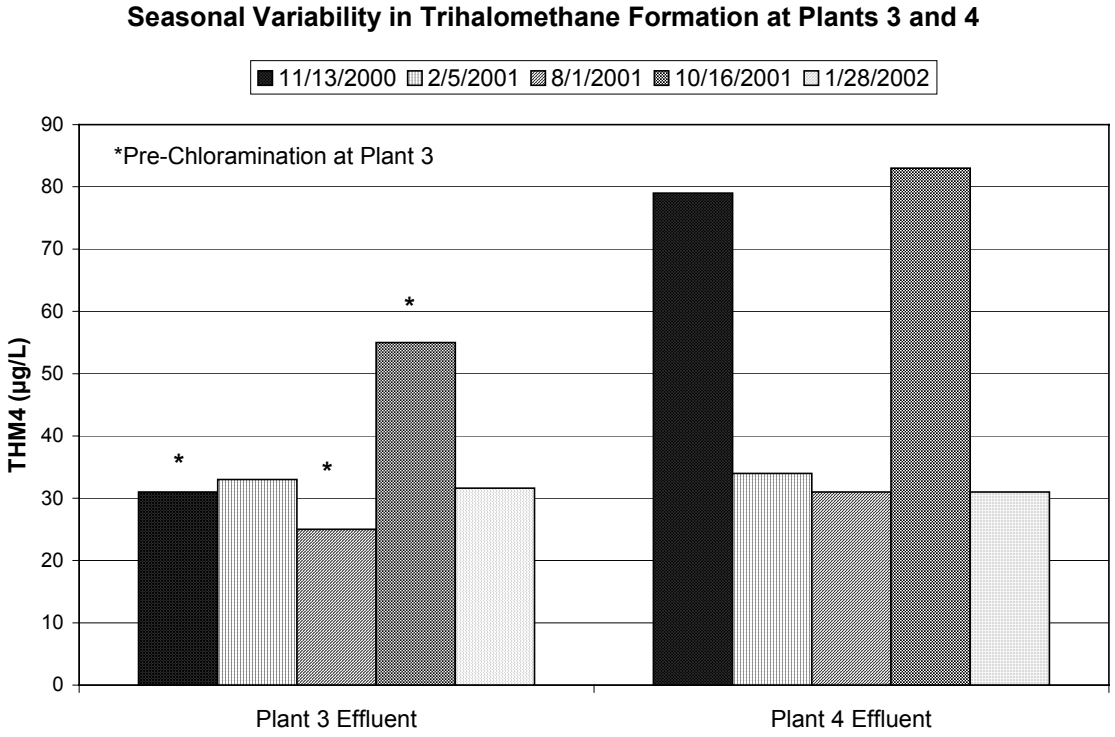
Table 17. DBP results at plant 4 (1/28/02)

01/28/2002	MRL[a]	Plant 4[c]						
Compound	µg/L	GAC Inf	GAC Eff	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes								
Chloromethane	0.2	ND	ND	ND	ND		ND	
Bromomethane	0.2	ND	ND	ND	ND		ND	
Bromochloromethane	0.5	ND	ND	ND	ND		ND	
Dibromomethane	0.5	ND	ND	ND	ND		ND	
Chloroform[e]	0.2	*20*	*20*	*20*	NR	NR	NR	NR
Bromodichloromethane[e]	0.2	9	6	8	8	NR	11	NR
Dibromochloromethane[e]	0.5	3	2	3	2	NR	5	NR
Bromoform[e]	0.5	ND	ND	ND	ND	NR	ND	NR
THM4[f]		*32*	*28*	*31*	NR	NR	NR	NR
Dichloroiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND
Bromochloroiodomethane	0.5	ND	ND	ND	ND	NR	ND	NR
Dibromoiodomethane	0.5	ND	ND	ND	ND	NR	ND	NR
Chlorodiiodomethane	0.1	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.52	ND	ND	ND	ND	ND	ND	ND
Iodoform	1.0	ND	ND	ND	ND	NR	ND	NR
Carbon tetrachloride	0.2	ND	ND	ND	ND		ND	
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids								
Monochloroacetic acid[e]	2	2.3	2.6	ND	ND		2.5	
Monobromoacetic acid[e]	1	ND	ND	1.0	ND		ND	
Dichloroacetic acid[e]	1	21	21	17	16		19	
Bromochloroacetic acid[e]	1	3.3	3.2	2.6	2.4		3.5	
Dibromoacetic acid[e]	1	ND	ND	ND	ND		ND	
Trichloroacetic acid[e]	1	26	28	21	21		24	
Bromodichloroacetic acid	1	6.8	6.9	5.8	5.8		5.3	
Dibromochloroacetic acid	1	2.8	2.5	1.9	1.8		ND	
Tribromoacetic acid	2	ND	ND	ND	ND		ND	
HAA5[h]		49	52	39	37		46	
HAA9[i]		62	64	49	47		54	
DXAA[j]		24	24	20	18		23	
TXAA[k]		36	37	29	29		29	
Haloacetonitriles								
Chloroacetonitrile	0.1	0.3	ND	ND	ND	ND	0.3	0.3
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[e]	1	4	3	2	NR	NR	NR	NR
Bromochloroacetonitrile[e]	0.1	0.8	0.6	0.6	0.8	0.2	1	2
Dibromoacetonitrile[e]	0.1	0.3	ND	ND	<0.5	ND	0.3	0.4
Trichloroacetonitrile[e]	0.5	ND	ND	ND	ND	NR	ND	NR
Bromodichloroacetonitrile	0.5	ND	ND	ND			ND	
Dibromochloroacetonitrile	0.5	ND	ND	ND			ND	
Tribromoacetonitrile	0.95	ND	ND	ND			ND	
Haloketones								
Chloropropanone	0.1	0.3	0.4	0.4	0.4	0.4	0.4	0.2
1,1-Dichloropropanone[e]	0.1	2	1	0.7	0.5	0.8	0.6	0.5
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloropropanone[e]	0.5	4	3	3	3	NR	3	NR
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	1.0	<1	<1	<1	1	NR	ND	NR
1,1,1-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND
1,1,3-Tribromopropanone	0.1	*0.3*	*0.2*	ND	ND	ND	*0.1*	*0.1*
1,1,3,3-Tetrachloropropanone	0.10	*0.1*	ND	ND	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrabromopropanone	N/A	NR	NR	NR	NR	NR	NR	NR

Table 17 (continued)

01/28/2002	MRL[a]	Plant 4[c]						
Compound	µg/L	GAC Inf	GAC Eff	Plant Eff	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloacetaldehydes								
Dichloroacetaldehyde	0.98	2	3	1	1	1	1	1
Bromochloroacetaldehyde	0.5	ND	ND	ND	ND	ND	ND	ND
Chloral hydrate[e]	0.1	9	5	2	2	3	10	17
Tribromoacetaldehyde	0.1	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes								
Chloronitromethane	N/A	ND	ND	ND	ND		ND	
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.2
Bromochloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND
Dibromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[e]	0.1	0.6	0.4	ND	ND	ND	0.7	1
Bromodichloronitromethane	0.5	0.6	0.6	0.5			0.7	
Dibromochloronitromethane	0.5	ND	ND	ND			ND	
Bromopicrin	0.5	ND	ND	ND			ND	
Miscellaneous Compounds								
Methyl ethyl ketone	0.5	ND	ND	ND	ND		ND	
Methyl *tertiary* butyl ether	0.2	0.6	0.7	0.6	0.7		0.7	
1,1,2,2-Tetrabromo-2-chloroethane	2.5	ND	ND	ND	ND	NR	ND	NR
Benzyl chloride	0.25	ND	ND	ND	ND	NR	ND	NR

Figure 4



Halomethanes. Figure 4 shows the seasonal variability in THM formation at plants 3 and 4. The sum of the four regulated THMs (THM4) ranged from 31 to 83 µg/L in the plant 4 effluent. The highest formation was in October 2001 when the bromide level was the highest. Note, during most sampling events, plant 4 effluent represented a blend of plant 4 and plant 3 waters. For example, in August 2001, the plant 4 effluent had 31 µg/L THM4. Based on a plant 4 flow of 11 mgd--with 37 µg/L THM4 in the GAC effluent--and the addition of 4.2 mgd of plant 3 GAC effluent--with 20 µg/L THM4--the theoretical THM4 for the plant 4 effluent was 32 µg/L. Because the plant 4 distribution system had a free chlorine residual, THM formation increased to 38-39 µg/L.

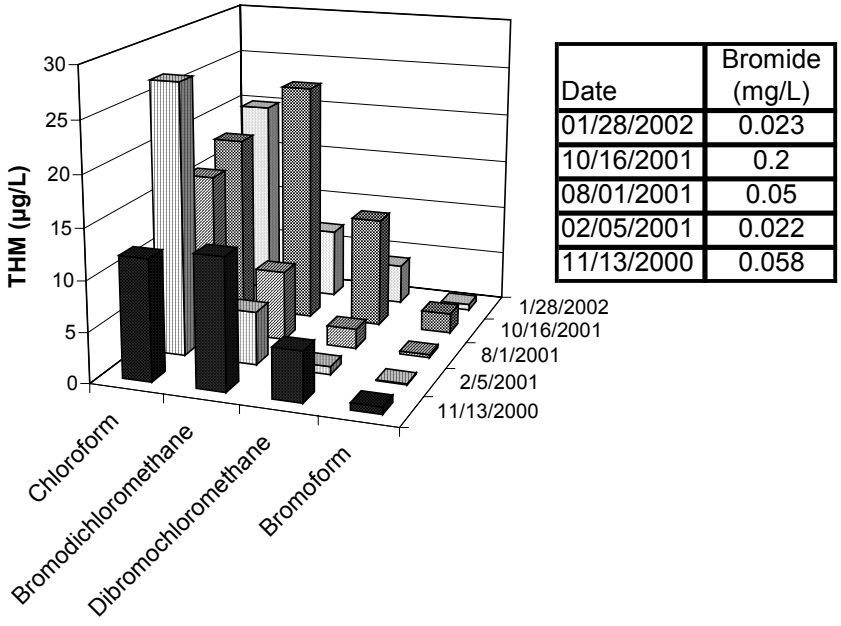
THM4 ranged from 25 to 55 µg/L in the plant 3 effluent. Pre-chloramination at plant 3 was more effective at minimizing THM formation in November 2000 than in October 2001, most likely due to the difference in bromide concentrations between these two periods (0.06 versus 0.2 mg/L, respectively). Pre-chloramination was not required in February 2001, as the water temperature (7-10ºC) and bromide (0.02 mg/L) were relatively low during this time period. Thus, pre-chloramination was used at plant 3 at the times of the year in which THM formation would be too high with pre-chlorination (e.g., summer and fall).

Figure 5 shows the impact of bromide on THM speciation in plant 3 effluent. In October 2001, when the bromide level was the highest, there was the greatest shift in speciation to brominated THMs. In February 2001 and January 2002, when the bromide concentration was the lowest, chloroform was the major THM species formed.

In terms of iodinated THMs, dichloroiodomethane was typically detected in some of the samples each quarter. When detected, the concentration of this iodinated THM ranged from 0.25 to 2 µg/L. In November 2000, bromodiiodomethane and iodoform were also detected in selected samples. Dichloroiodomethane and/or bromochloroiodomethane were also found using broadscreen-gas chromatography/mass spectrometry (GC/MS) methods (carried out by the USEPA) in finished water from plant 3 and plant 4.

Figure 5

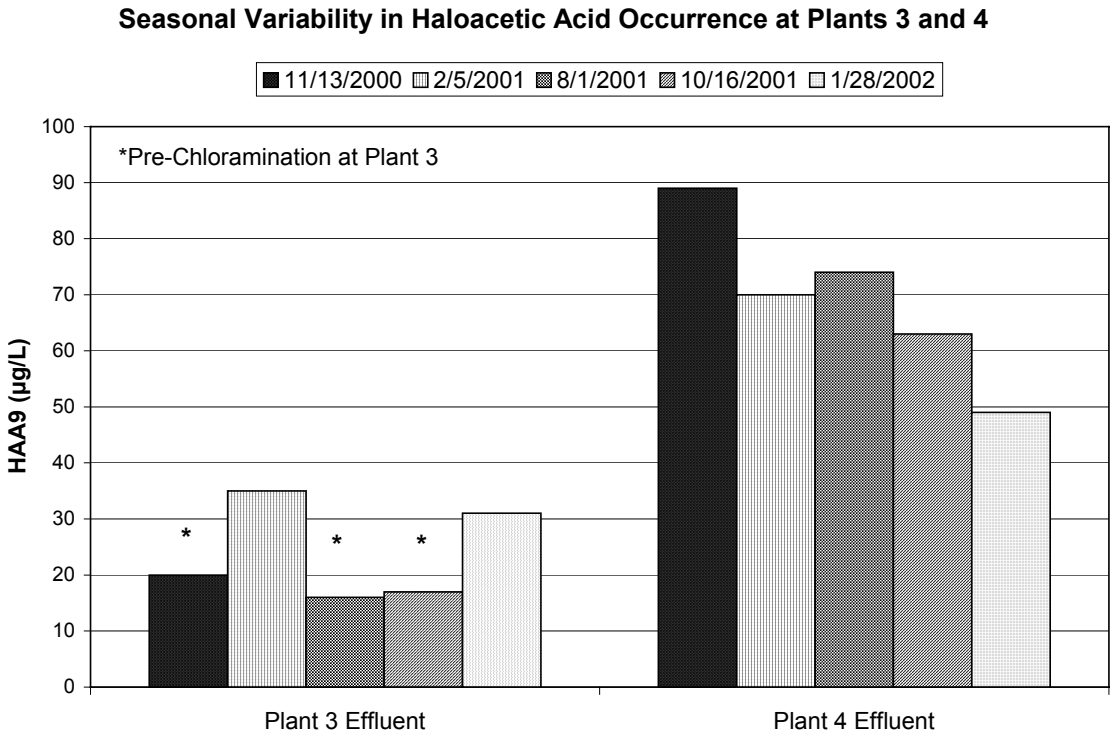
Impact of Bromide on Trihalomethane Speciation in Plant 3 Effluent



Date	Bromide (mg/L)
01/28/2002	0.023
10/16/2001	0.2
08/01/2001	0.05
02/05/2001	0.022
11/13/2000	0.058

Haloacids. Figure 6 shows the seasonal variability in haloacetic acid (HAA) occurrence at plants 3 and 4. The sum of the five regulated HAAs (HAA5) ranged from 39 to 66 µg/L in the plant 4 effluent. The sum of all nine species (HAA9) ranged from 49 to 89 µg/L. The plant 4 effluent typically represented a blend of plant 4 and plant 3 waters. For example, in August 2001, the plant 4 effluent had 61 µg/L HAA5 and 74 µg/L HAA9. Based on a plant 4 flow of 11 mgd before the addition of 4.2 mgd of plant 3 GAC effluent, the theoretical HAA5 and HAA9 for the plant 4 effluent was 65 and 76 µg/L, respectively. HAA5 and HAA9 were 8.4-32 and 17-35 µg/L, respectively, in the plant 3 effluent. The highest HAA occurrence in the plant 3 effluents was during the winter.

Figure 6



At plant 3, the concentration of HAA9 in the GAC influent was 36-61 µg/L, whereas the level in the GAC effluent ranged from not detected (ND) to 21 µg/L. Figure 7 shows that when the water temperature was warmer, HAAs were effectively removed, whereas when the water was colder, the removal of dihalogenated HAAs (DXAAs) was somewhat diminished and the removal of trihalogenated HAAs (TXAAs) was significantly impacted. GAC can provide a medium for biological activity, which can result in the control of HAAs. Other research has demonstrated that HAAs can be removed by GAC filtration, presumably by biodegradation processes within the filter bed (Singer et al., 1999). In another study, DXAAs were found to be much better biodegraded than TXAAs in a distribution system with no disinfectant residual, and the removal effectiveness was significantly impacted by water temperature (Baribeau et al., 2000).

In contrast, HAAs were typically not removed during GAC filtration at plant 4 (Figure 8), and when they were the percentage removed was much less than at plant 3. At plant 3, GAC was used in a post-filtration contactor, whereas at plant 4 GAC was used as a filter media in wood tub filters. In addition, there was little to no disinfectant residual in the plant 3 GAC effluents, whereas there was a free chlorine residual in the plant 4 GAC effluents. The operational use of GAC was different at the two plants.

Figure 7

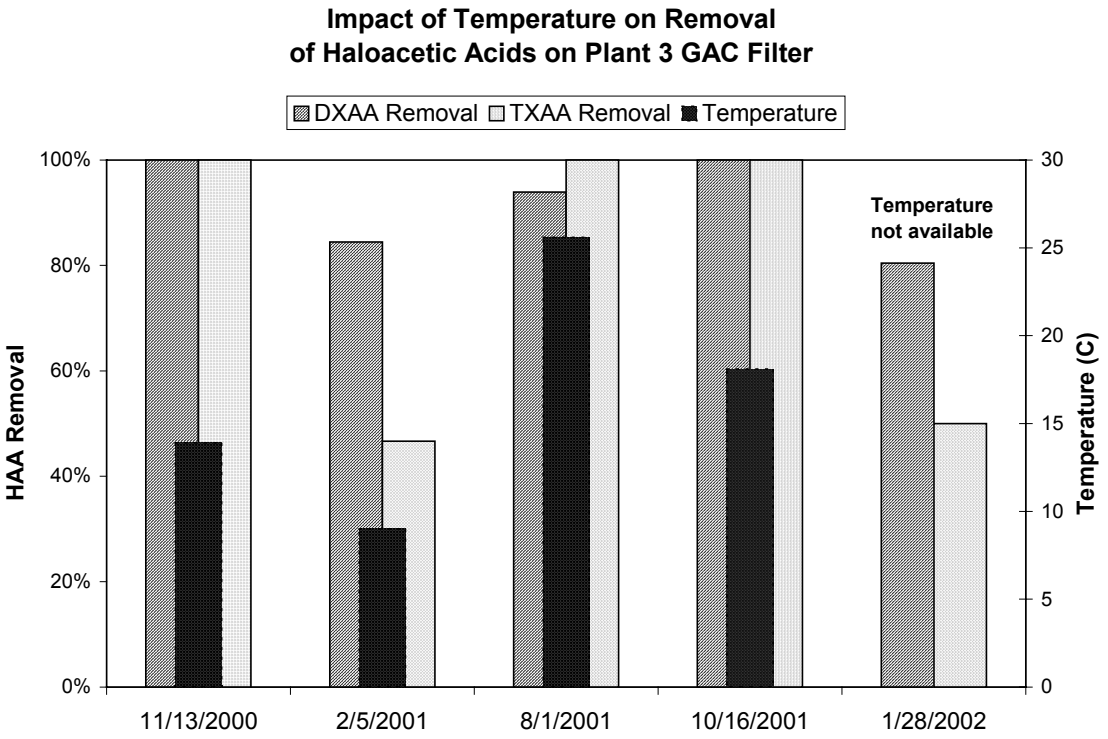


Figure 8

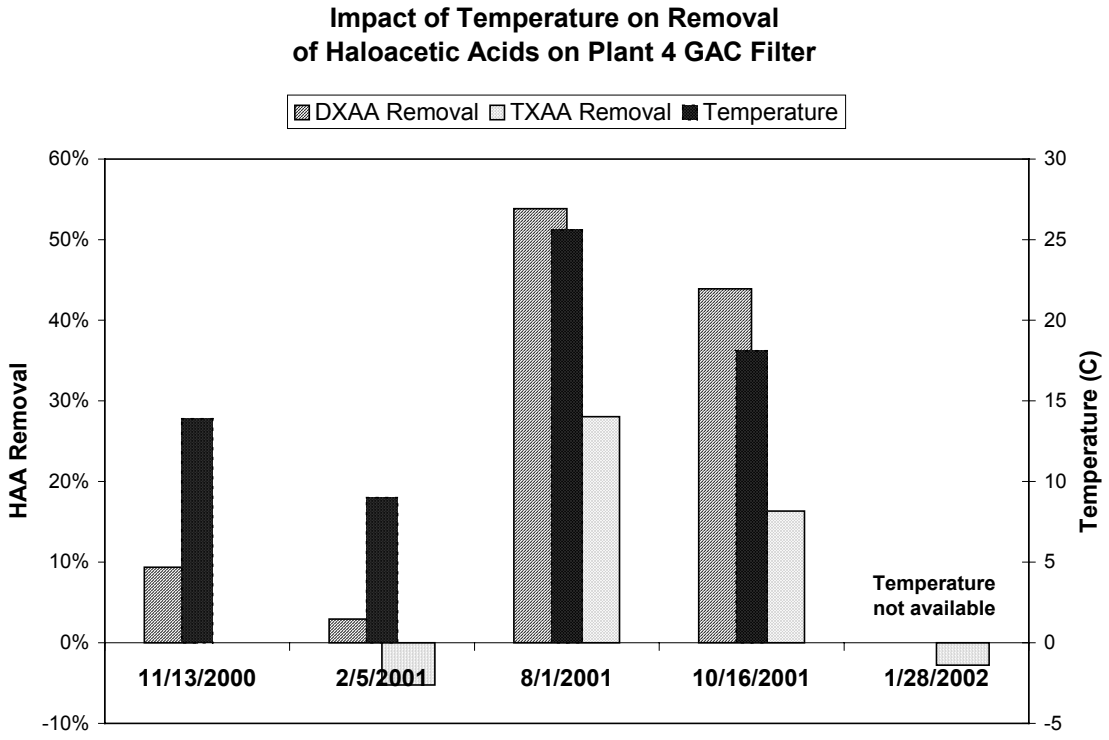


Figure 9 shows how HAAs were reformed during post-GAC chlorination, whereas THMs—which were not removed during GAC filtration—increased in formation through the treatment process. The levels of HAAs formed during post-GAC chlorination were less than what was initially formed by pre-chlor(am)ination. Because the HAAs were effectively removed by GAC during the warmer months, HAA occurrence in the plant effluent was primarily from the post-GAC chlorination. Alternatively, during the colder months, HAAs in the plant effluent were from a combination of HAAs not removed by GAC and that formed during post-GAC chlorination. Thus, HAA occurrence in the plant effluent was higher in the winter at plant 3.

Figure 9

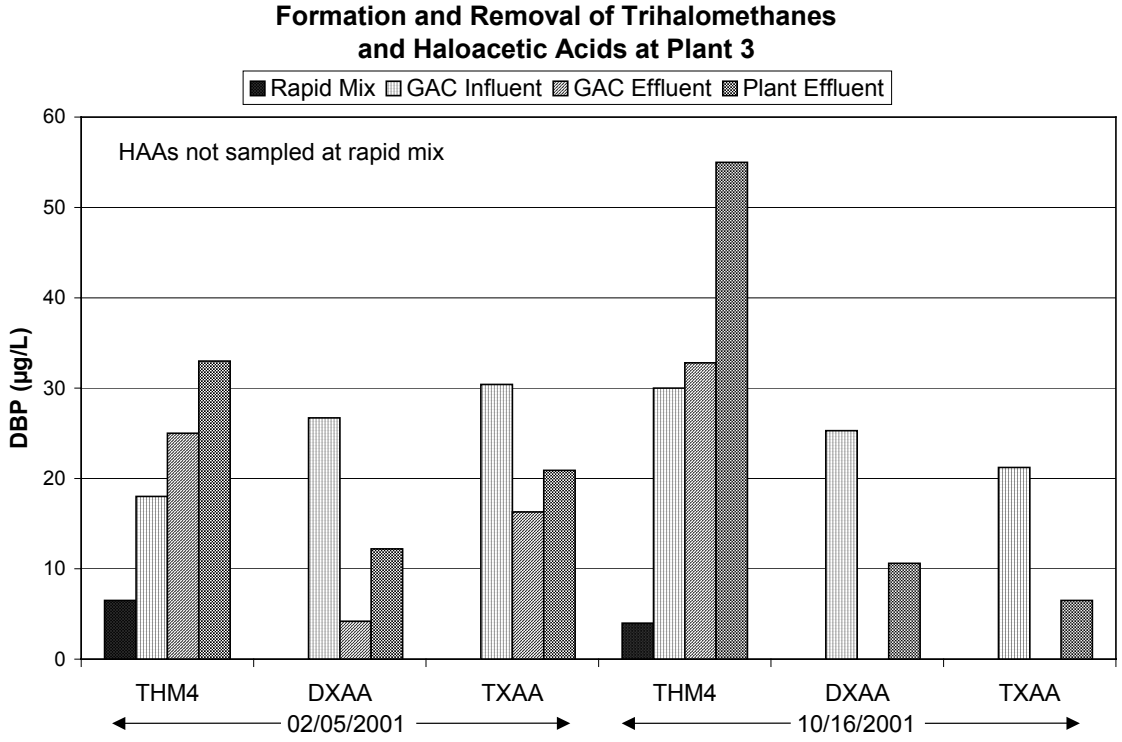
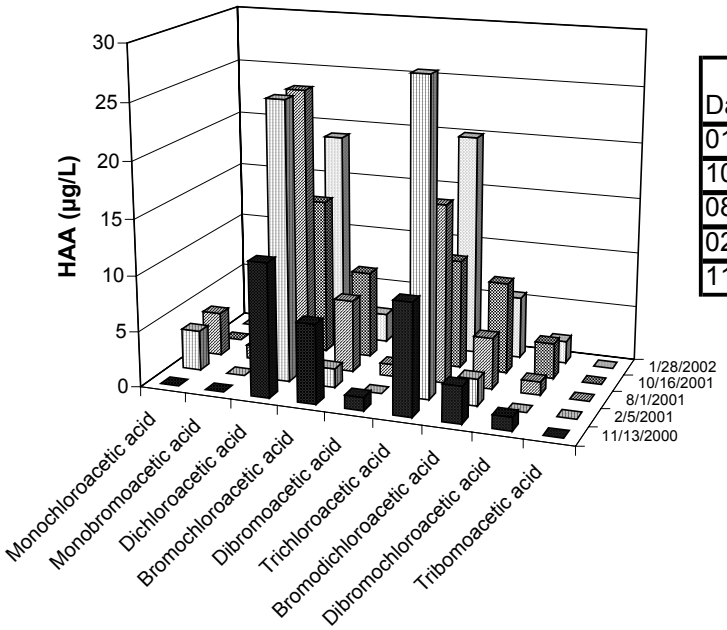


Figure 10 shows the impact of bromide on HAA speciation in the plant 3 GAC influent. In October 2001, when the bromide level was the highest, there was the greatest shift in speciation to brominated HAAs. In February 2001 and January 2002, when the bromide concentration was the lowest, dichloro- and trichloroacetic acid were the major HAA species formed.

Figure 10

Impact of Bromide on Haloacetic Acid Speciation in Plant 3 GAC Influent

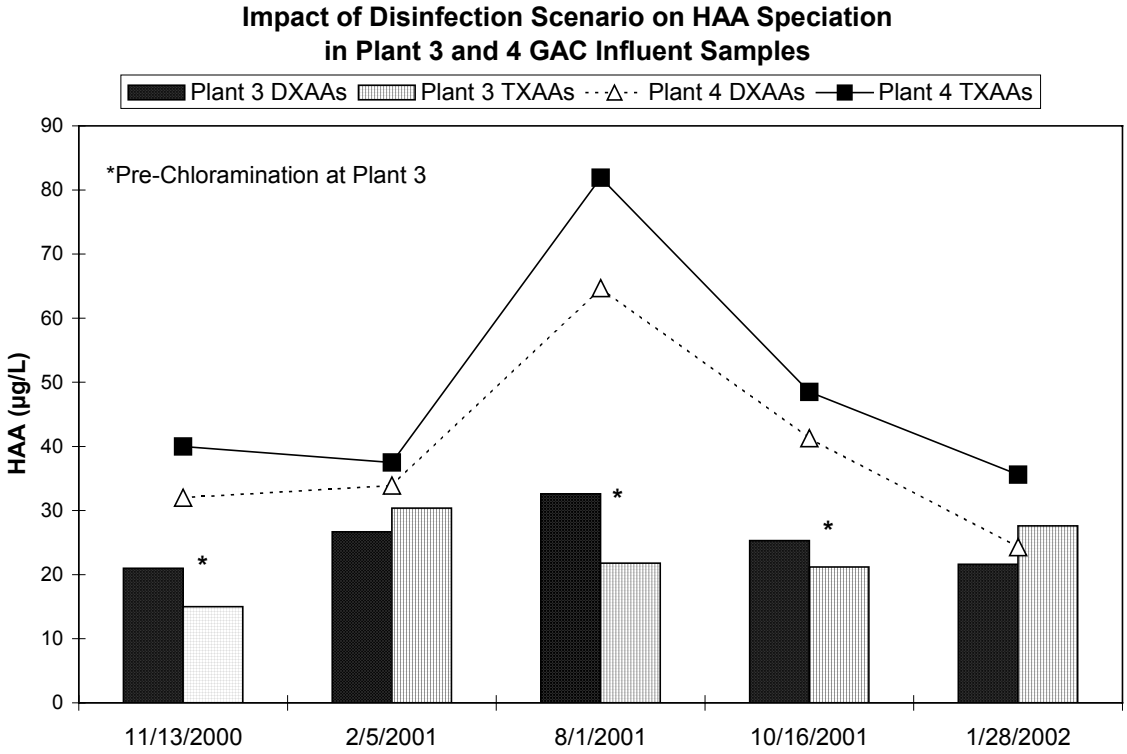


Date	Bromide (mg/L)
01/28/2002	0.023
10/16/2001	0.2
08/01/2001	0.05
02/05/2001	0.022
11/13/2000	0.058

Figure 11 shows the impact of disinfection scenario on HAA speciation in plants 3 and 4 GAC influent samples. At plant 4, pre-chlorination resulted in the formation of more TXAAs than DXAAs. Likewise, Cowman and Singer (1996) found that the TXAAs were the dominant HAA species in their study during chlorination. At plant 3, during pre-chloramination, DXAAs were formed to a higher extent than the TXAAs. Krasner and co-workers (1996) found that chloramines minimized the formation of THMs and TXAAs better than that of DXAAs. Likewise, Cowman and Singer (1996) found that DXAAs were the principal HAA species formed from chloramination.

February 2001 results from UNC also show the presence of another target halo-acid, 3,3-dichloropropenoic acid, at levels of 1.5 and 0.9 µg/L, respectively, in finished waters from plant 3 and plant 4 (Table 18). 3,3-Dichloropropenoic acid, as well as trichloropropenoic acid, was also identified in broadscreen GC/MS analyses carried out by the USEPA.

Figure 11



Haloacetonitriles. In other research, haloacetonitriles (HANs) have been found to be produced at approximately one-tenth the level of the THMs (on a weight basis) (Krasner et al., 1989). In the latter study, the 25th and 75th percentile ratios of HANs to THMs were 0.065 and 0.147, respectively. The HAN to THM relationship had originally been established between dichloroacetonitrile (DCAN) and chloroform (trichloromethane [TCM]) (Oliver, 1983).

Figure 12 shows that DCAN formation in GAC influent samples at plants 3 and 4 was equal to or higher than one-tenth the level of chloroform. A linear regression of the data, except for the August 2001 data that were atypical, indicated that DCAN was ~17 % of the level of chloroform. This value was somewhat higher than the 75th percentile ratio observed by Krasner and colleagues (1989).

In these samples, the pH ranged from 5.5 to 6.2. In other research, THM formation has been shown to be lower at acidic pH and DCAN formation has been higher at acidic pH, whereas dichloroacetic acid (DCAA) formation was found to be relatively insensitive to pH (Stevens et al., 1989). Figure 13 shows the relationship between DCAN and DCAA formation for these samples. A linear regression of the data, including the August 2001 samples, indicated that DCAN was ~18 % of the level of DCAA. These results suggest that the pH of chlorination within plants 3 and 4 was, in part, impacting the relative formation of DCAN, chloroform, and DCAA.

Figure 12

Dichloroacetonitrile (DCAN) Formation as a Function of Chloroform (TCM) Formation in Plants 3 and 4 GAC Influent Samples

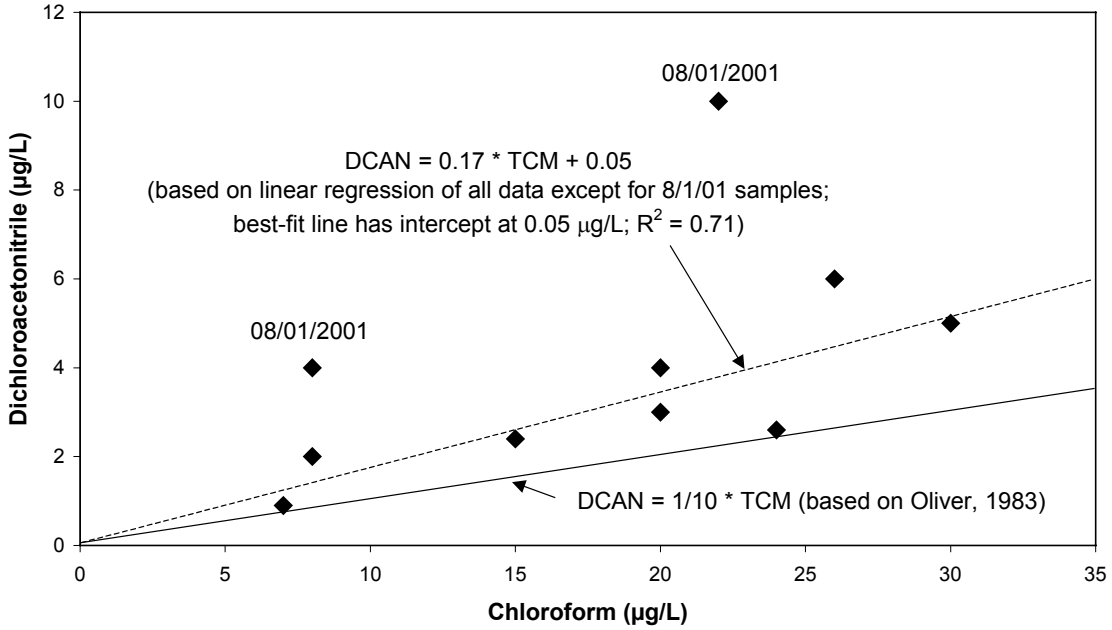
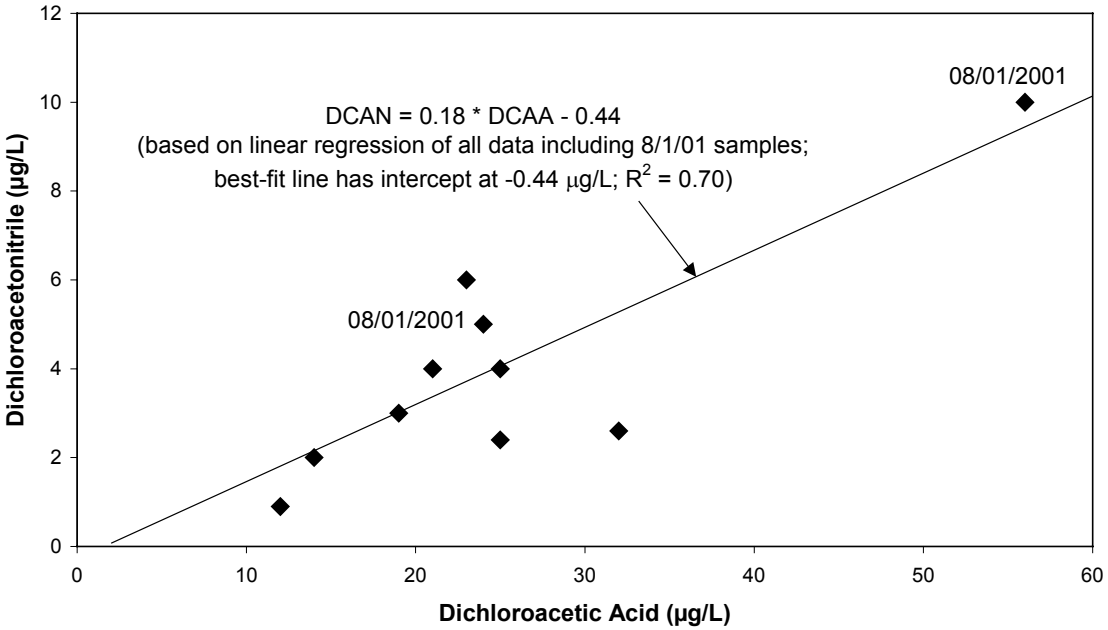


Figure 13

Dichloroacetontrile (DCAN) Formation as a Function of Dichloroacetic Acid (DCAA) Formation in Plants 3 and 4 GAC Influent Samples



DCAN was 0.9-4 and 0.1-1.6 µg/L in the plant 3 GAC influent and effluent, respectively. Figure 14 shows that the concentration of DCAN was significantly reduced in passing through the GAC when the water temperature was warm. DCAN was 2.6-10 and 2.8-10 µg/L in the plant 4 GAC influent and effluent, respectively. The level of DCAN was generally unchanged in passing through the plant 4 GAC filters (Figure 14). Likewise, the brominated analogues of DCAN were reduced in concentration in passing through the plant 3 GAC filter when the water temperature was warm, whereas the plant 4 GAC filters had no significant impact. Similar to the HAAs, the plant 3 GAC filter resulted in a significant reduction in the concentration of the HANs, and the phenomenon was temperature sensitive, whereas the plant 4 GAC filter did not significantly reduce the concentration of the HANs.

Figure 15 shows the impact of bromide on HAN speciation in plant 3 GAC influent. In October 2001, when the bromide level was the highest, there was the greatest shift in speciation to brominated HANs. In February 2001 and January 2002, when the bromide concentration was the lowest, DCAN was the major HAN species formed.

The plant 4 effluent typically represented a blend of plant 4 and plant 3 waters. For example, in August 2001, the plant 4 effluent had 6 µg/L DCAN. Based on a plant 4 flow of 11 mgd before the addition of 4.2 mgd of plant 3 GAC effluent, the theoretical DCAN concentration for the plant 4 effluent was 7 µg/L.

Finally, sub-µg/L levels of one of the EPA study HANs (i.e., chloroacetonitrile) were detected in selected samples. Broadscreen GC/MS analyses also revealed the presence of tribromoacetonitrile in one sample (finished water from plant 3, November 2000).

Haloketones. Figure 16 shows the impact of bromide on haloketone (HK) speciation in plants 3 and 4 GAC influent samples. Specifically, the two HK species in the Information Collection Rule (ICR) (1,1-dichloro- and 1,1,1-trichloropropanone) were evaluated along with two brominated analogues included in the EPA DBP study (1,1-dibromo- and 1-bromo-1,1-dichloropropanone). In October 2001, when the bromide level was the highest, there was an increase in the formation of both of these brominated HKs when compared to the August 2001 sampling, which was accompanied by decreases in the concentrations of the corresponding chlorinated species.

In addition to the formation of selected brominated species, other EPA study HKs (e.g., chloro-, 1,1,3-trichloro-, 1,1,3,3-tetrachloro-, and 1,1,1,3-tetrachloropropanone) were detected in selected samples. Furthermore, pentachloropropanone and hexachloropropanone were detected at plants 3 and 4 in November 2000, August 2001, and January 2002 by the USEPA using broadscreen-GC/MS methods.

Figure 14

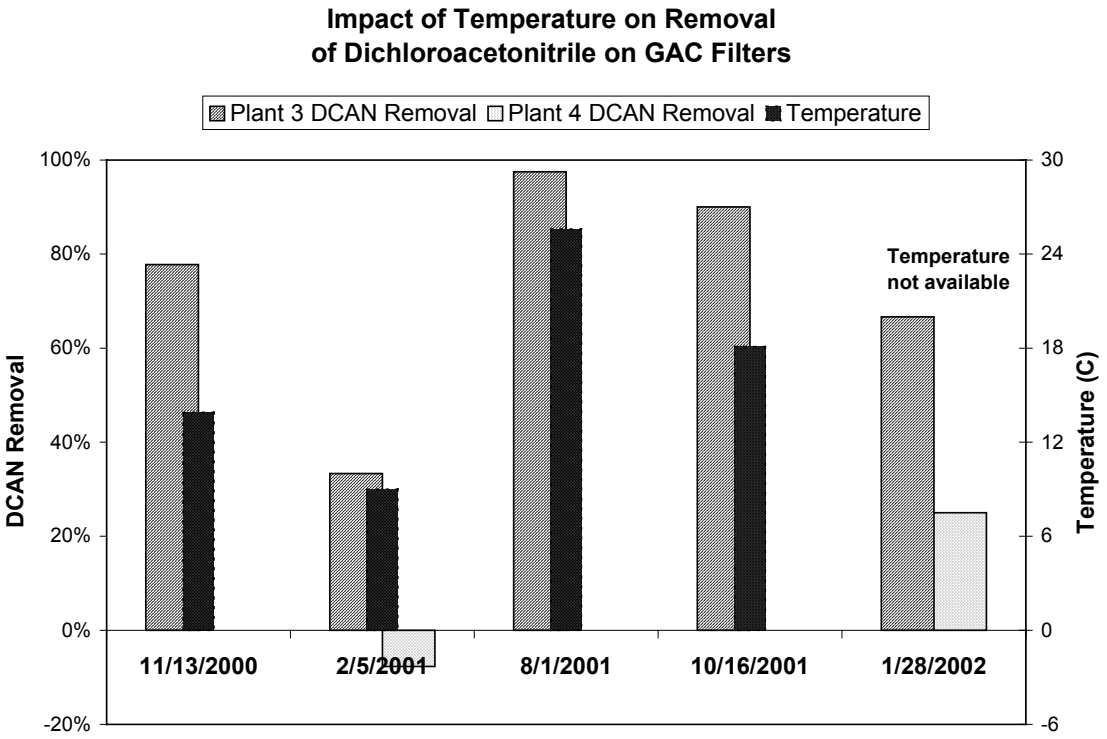
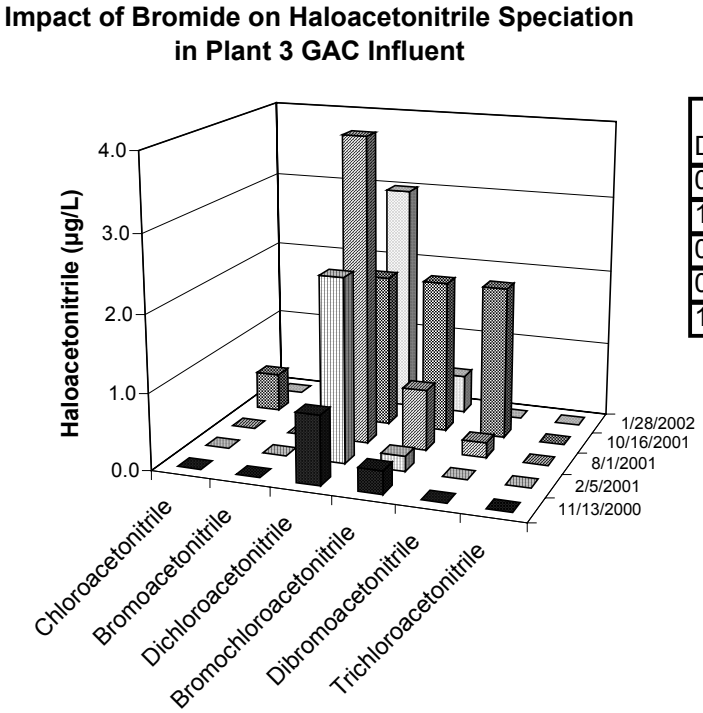


Figure 15



Date	Bromide (mg/L)
01/28/2002	0.023
10/16/2001	0.2
08/01/2001	0.05
02/05/2001	0.022
11/13/2000	0.058

Figure 16. Impact of bromide on haloketone speciation in plants 3 and 4 GAC influent samples: bromide = 0.05 and 0.2 mg/L on 8/1/01 and 10/16/01, respectively.

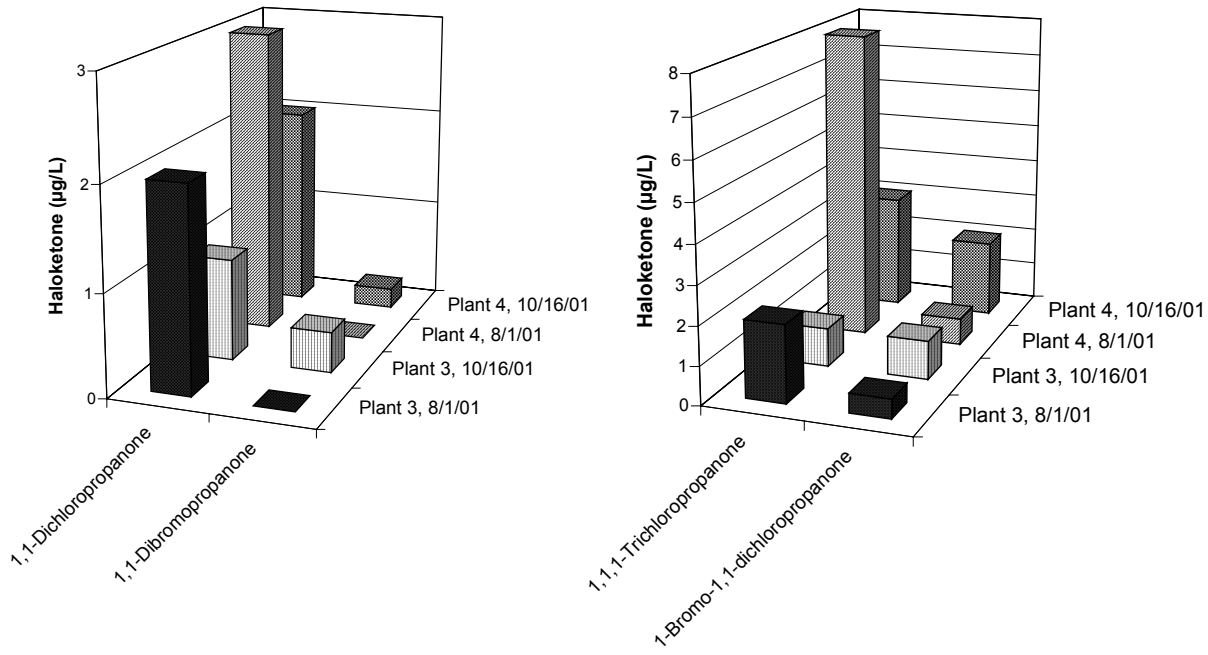


Figure 17 shows that the concentrations of 1,1-dichloro- and 1,1,1-trichloropropanone were significantly reduced in passing through the GAC when the water temperature was warm. The levels of these two HKs were generally unchanged in passing through the plant 4 GAC filters (Figure 18). Likewise, many of the EPA DBP study HKs were reduced in concentration in passing through the plant 3 GAC filter when the water temperature was warm, whereas the plant 4 GAC filters had no significant impact. Similar to the HAAs, the plant 3 GAC filter resulted in a significant reduction in the concentration of many of the HKs, and the phenomenon was temperature sensitive, whereas the plant 4 GAC filter did not significantly reduce the concentration of the HKs.

Figure 19 shows how most HKs that were reduced in concentration in the plant 3 GAC filter were reformed during post-GAC chlorination, whereas chloropropanone—which was not removed during GAC filtration—increased somewhat in concentration through the treatment process. The levels of HKs formed during post-GAC chlorination were less than what was initially formed by pre-chlor(am)ination.

Figure 17

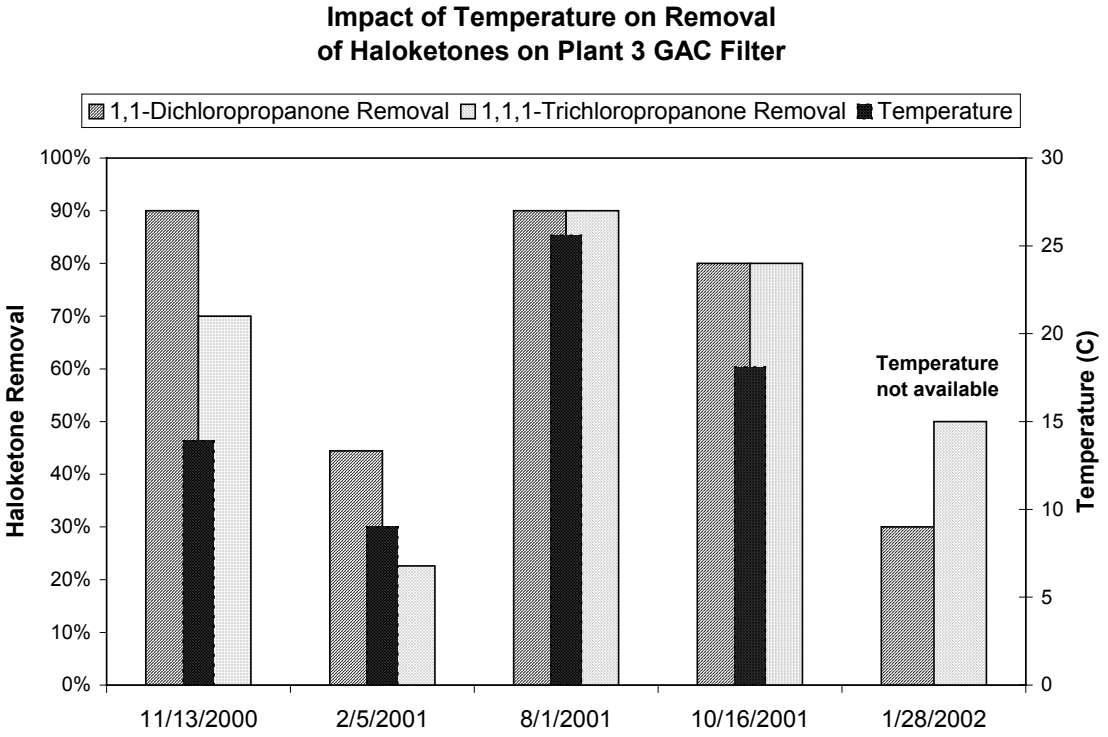


Figure 18

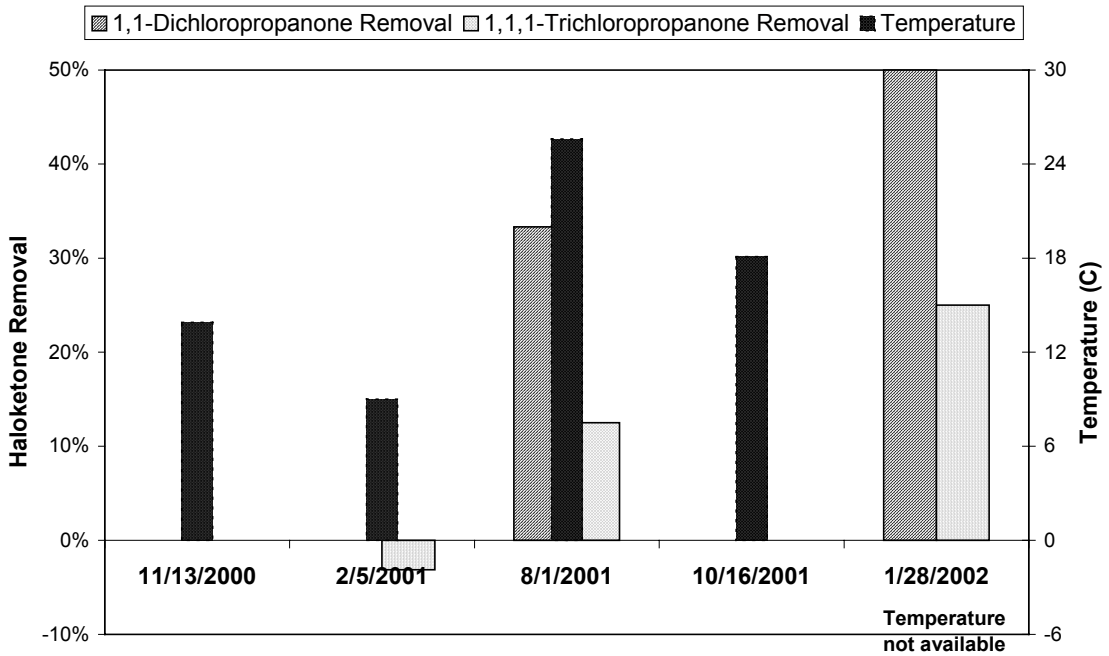
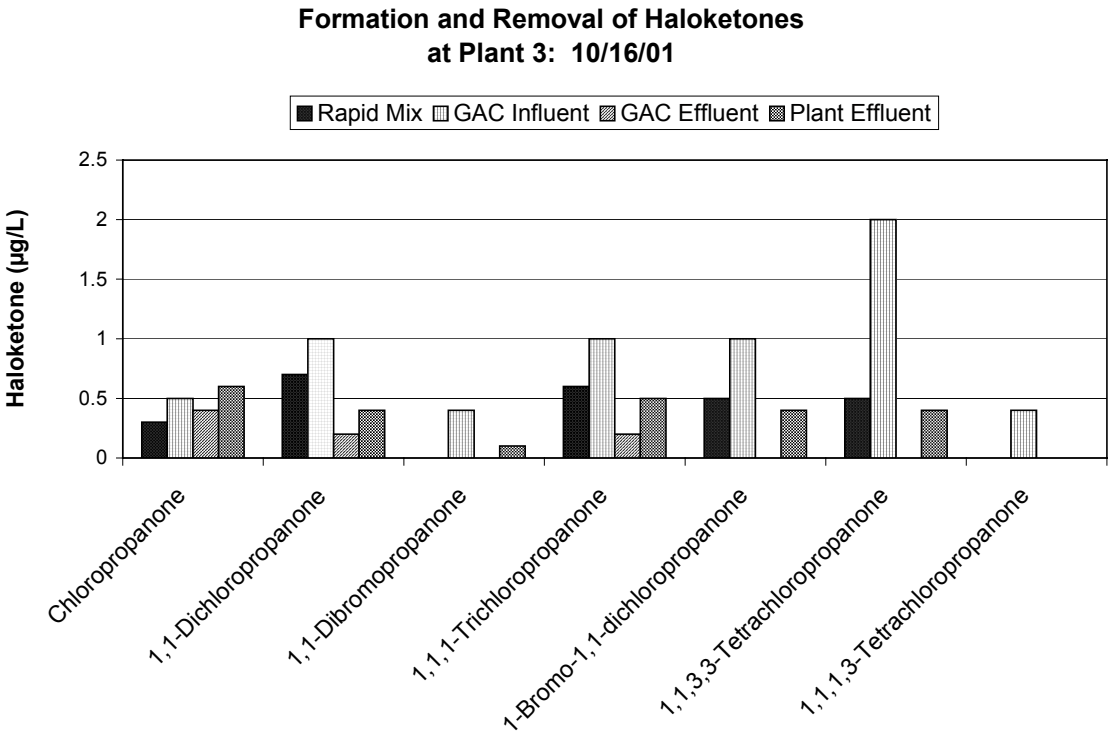


Figure 19

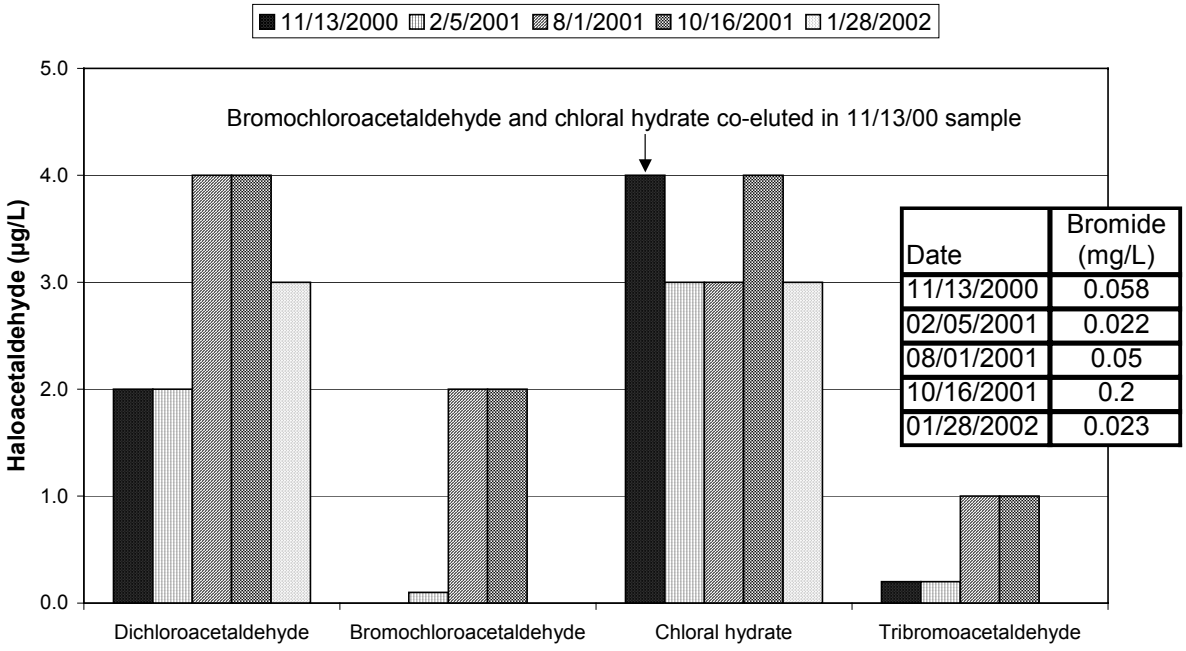


Haloacetaldehydes. Figure 20 shows the impact of bromide on haloacetaldehyde speciation in the plant 3 GAC influent. Note, the results for chloral hydrate in November 2000 represented the sum of the concentrations of chloral hydrate and bromochloroacetaldehyde, as these two DBPs co-eluted with the originally used GC method. In October 2001, when the bromide level was the highest, there was a significant formation of bromochloro- and tribromoacetaldehyde. In August 2001, there was also a significant formation of these two brominated haloacetaldehydes. Although the bromide concentration was lower in August, the higher water temperature combined with the bromide probably contributed to the formation of these brominated DBPs in that month. In February 2001 and January 2002, when the bromide concentration was the lowest, both brominated species were formed at very low levels or were not detected. In addition, another brominated aldehyde (2-bromo-2-methylpropanal) was detected at plant 3 in November 2000 by the USEPA using broad-screen GC/MS methods.

Figure 21 shows the impact of disinfection scenario on haloacetaldehyde speciation in plants 3 and 4 GAC influent samples. At plant 4, pre-chlorination resulted in the formation of more trihalogenated acetaldehydes than dihalogenated acetaldehydes. At plant 3, during pre-chloramination, dihalogenated acetaldehydes were typically formed to a higher extent than the trihalogenated acetaldehydes. Note, because bromochloroacetaldehyde results in November 2000 were included in the chloral hydrate (trichloroacetaldehyde) results due to co-elution on the GC, the speciation in that month could not be properly resolved.

Figure 20

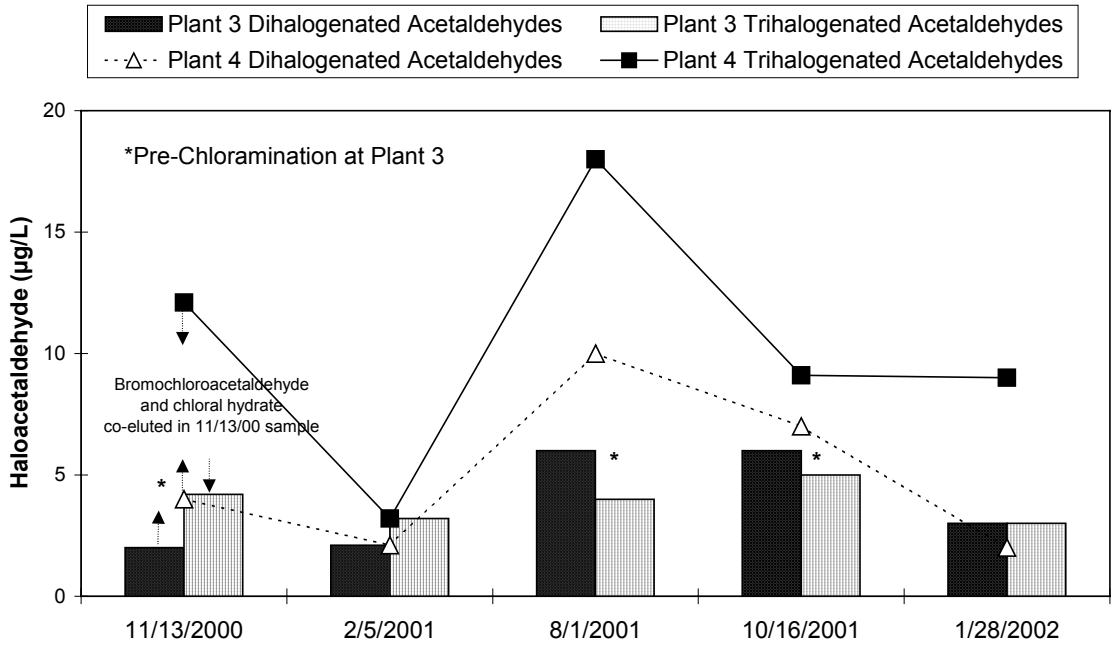
Impact of Bromide on Haloacetaldehyde Speciation in Plant 3 GAC Influent



Date	Bromide (mg/L)
11/13/2000	0.058
02/05/2001	0.022
08/01/2001	0.05
10/16/2001	0.2
01/28/2002	0.023

Figure 21

Impact of Disinfection Scenario on Haloacetaldehyde Speciation In Plants 3 and 4 GAC Influent Samples



Young and colleagues (1995) observed that chloral hydrate production was minimized by chloramination, whereas the formation of DCAN was similar during chlorination and chloramination, and where DCAN was produced from the reaction of chloramines with reaction by-products such as dichloroacetaldehyde. The relative formation of di- and trihalogenated acetaldehydes with pre-chlorination versus pre-chloramination was similar to that observed for DXAAs and TXAAs (Figure 11).

Figure 22 shows that the concentrations of dichloroacetaldehyde and chloral hydrate were significantly reduced in passing through the GAC when the water temperature was warm. The levels of these two haloacetaldehydes were generally unchanged in passing through the plant 4 GAC filters (Figure 23). Likewise, the brominated haloacetaldehydes were reduced in concentration in passing through the plant 3 GAC filter when the water temperature was warm, whereas the plant 4 GAC filters typically had no significant impact. Similar to the HAAs, the plant 3 GAC filter resulted in a significant reduction in the concentration of the haloacetaldehydes, and the phenomenon was temperature sensitive, whereas the plant 4 GAC filter typically did not significantly reduce the concentration of the haloacetaldehydes.

Figure 22

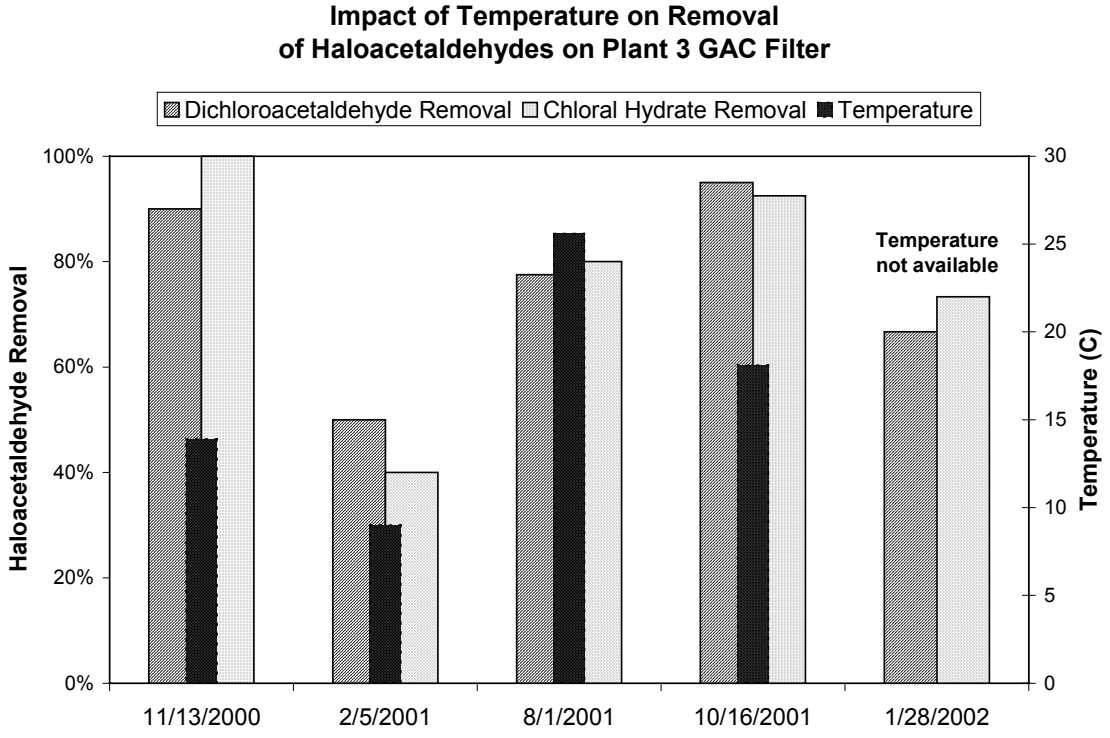


Figure 23

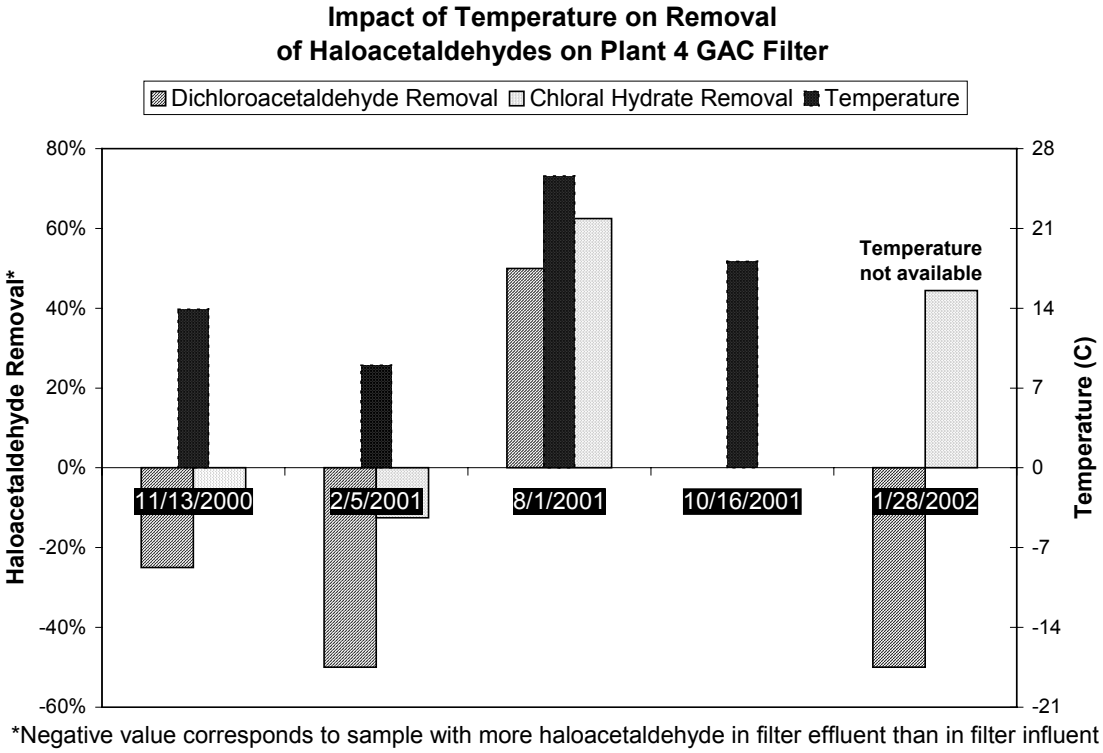
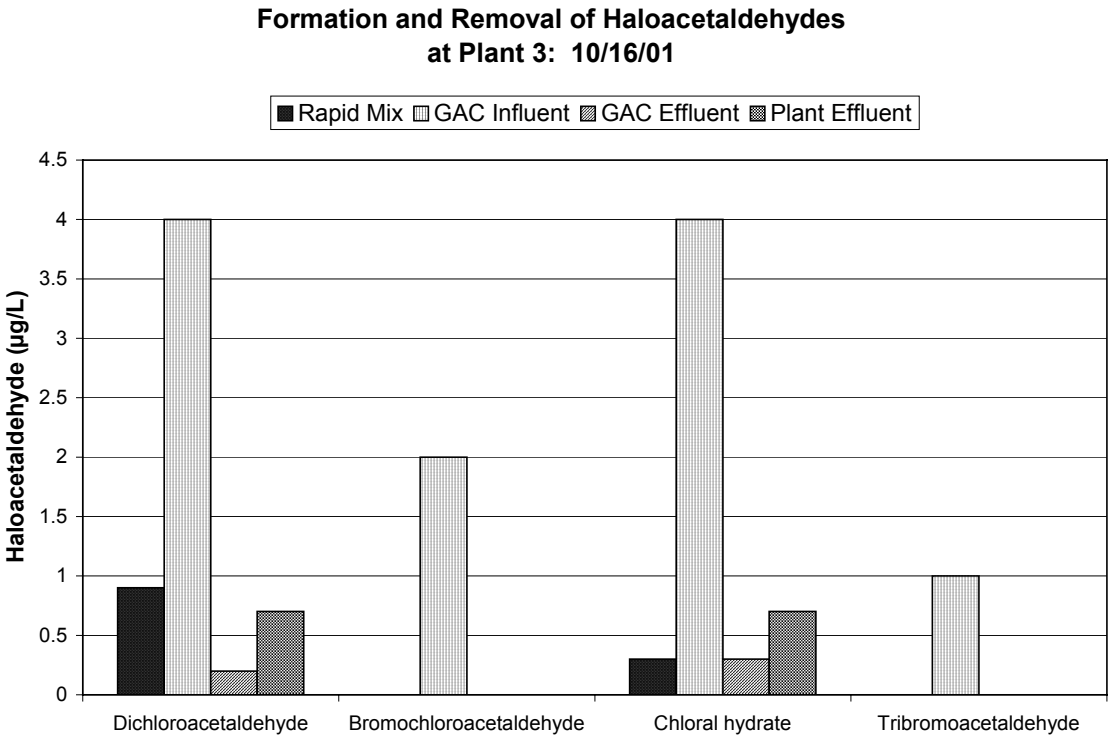


Figure 24 shows how some of the haloacetaldehydes were reformed during post-GAC chlorination at plant 3. The levels of haloacetaldehydes formed during post-GAC chlorination were less than what was initially formed by pre-chlor(am)ination.

Broadscreen analyses carried out at the USEPA also revealed the presence of four haloaldehydes that were not among the targeted list (Table 21). These are tentatively identified as 2-bromo-2-methylpropanal, iodobutanal, dichloropropenal, and 4-chloro-2-butenal. The identification of iodobutanal represents the first time that an iodinated aldehyde has been identified as a DBP. This compound was not present in the mass spectral library databases, but high resolution electron ionization (EI) mass spectrometry confirmed the empirical formula assignment of C_4H_7OI (molecular weight of 198). An exact isomer assignment for this molecule was not possible from the MS data obtained.

Figure 24



Halonitromethanes. Sub-µg/L levels of chloropicrin (trichloronitromethane) were detected in selected samples. Dichloronitromethane was detected in selected samples in October 2001 and in January 2002. Brominated analogues of chloropicrin were detected in the plant 3 GAC influent in October 2001 when the bromide concentration was the highest (Figure 25). Because the occurrence of these DBPs were typically at or near their minimum reporting levels (MRLs), it was not possible to study their fate through the GAC filters on most sample dates. However, the data from February 2001 (Figure 26) suggest that chloropicrin was removed during GAC filtration at plant 3, not plant 4, even though the water temperature was relatively cold. Dichloronitromethane was also detected in finished water in August 2001 using broadscreen GC/MS techniques.

Figure 25

Impact of Bromide on Halonitromethane Speciation in Plant 3 GAC Influent: Bromide = 0.02 and 0.2 mg/L on 1/28/02 and 10/16/01, Respectively

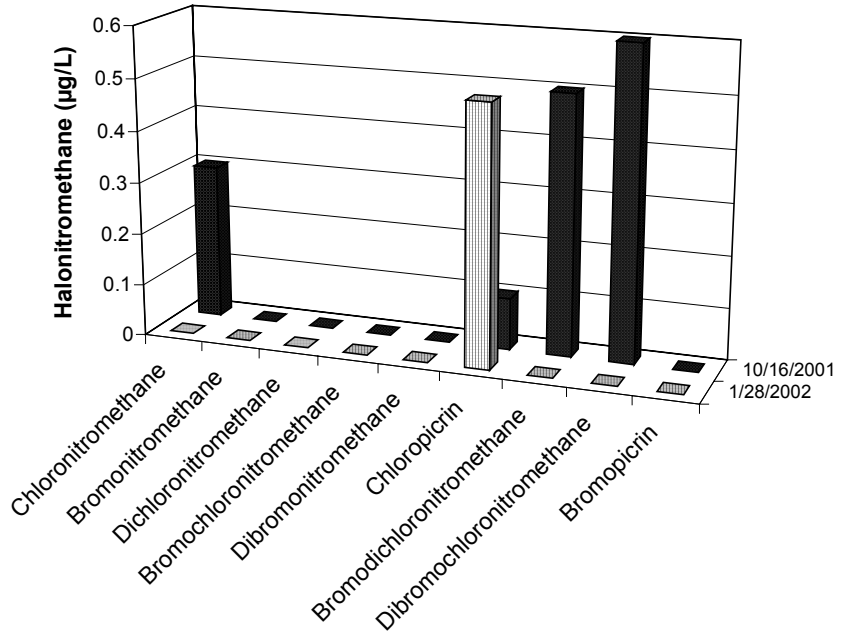
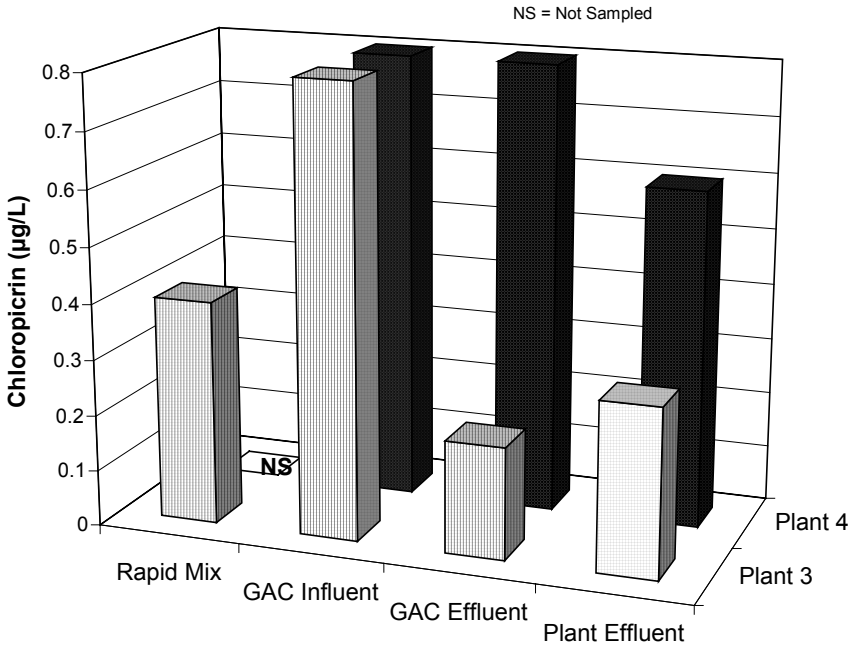


Figure 26

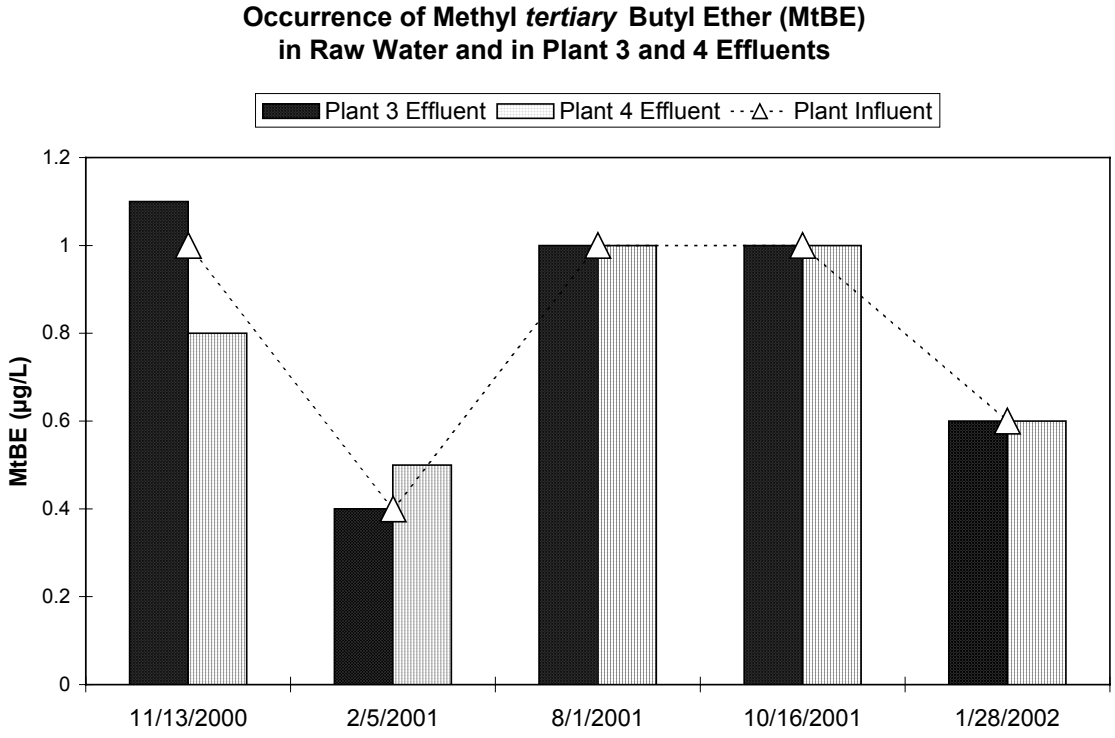
Formation and Removal of Chloropicrin at Plants 3 and 4: 2/5/01



Volatile Organic Compounds (VOCs). Carbon tetrachloride, which is a VOC and a possible DBP, was detected (0.3-0.8 µg/L) at both plants in November 2000, but was not found in the raw water (MRL = 0.06 µg/L). As mentioned in a previous chapter, carbon tetrachloride has been detected by some utilities in gaseous chlorine cylinders (EE&T, 2000), due to imperfections in the manufacturing process or improper cleaning procedures.

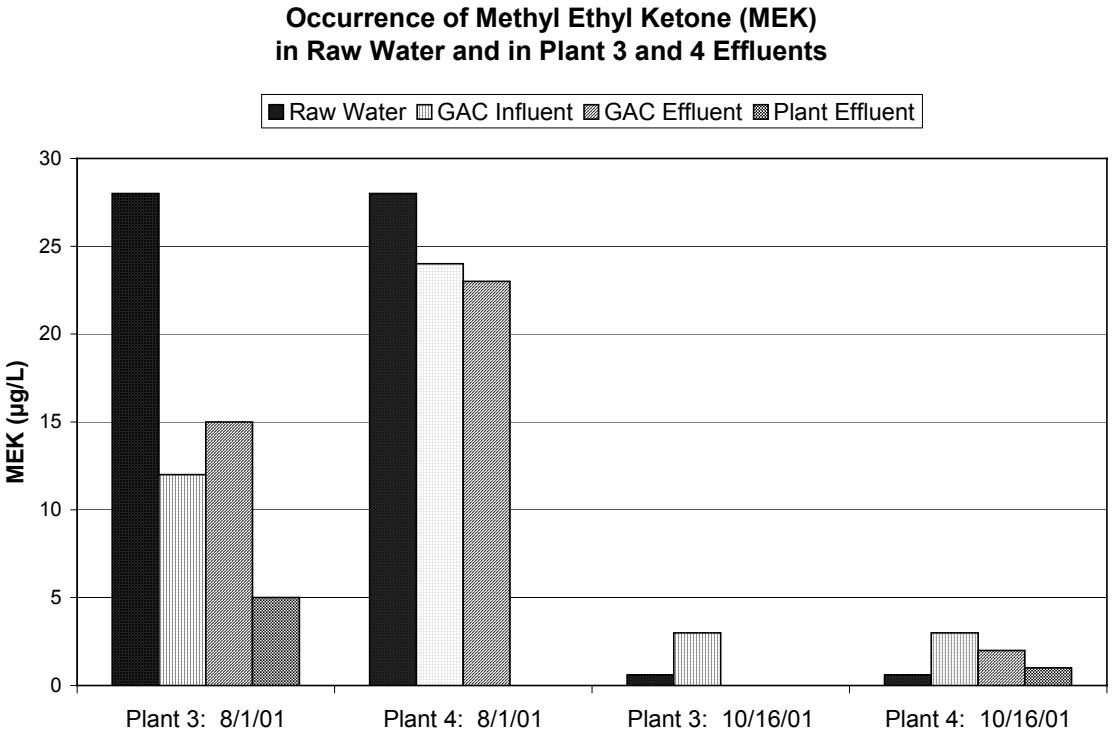
Methyl *tertiary* butyl ether (MtBE) was detected in the raw water on all of the sample dates, with concentrations of 0.4 to 1 µg/L (Figure 27). The level of MtBE was unchanged through either treatment plant. GAC at plant 3 did not remove MtBE. MtBE is a VOC (e.g., a gasoline additive), not a DBP, but is of concern due to widespread contamination of source waters.

Figure 27



Methyl ethyl ketone (MEK) was detected in the raw water on August 1, 2001 at a concentration of 28 µg/L (Figure 28). The level of MEK decreased through both treatment plants. MEK is an industrial solvent. The tremendous amount of rainfall the weekend before the sampling may have contributed to the presence of this solvent in the raw water (e.g., due to runoff). MEK was detected in the raw water on October 16, 2001 at 0.6 µg/L. After pre-chlor(am)ination, the level of MEK was 3 µg/L. MEK is also a DBP (an oxidation by-product). MEK was removed on the plant 3 GAC in October 2001, but only a small percentage of it was removed on the plant 4 GAC. MEK is a carbonyl, and various carbonyls have been shown to be biodegradable on biologically active filters (Krasner et al., 1993).

Figure 28



Halogenated Furanones. Table 20 presents data for 3-chloro-4-(dichloromethyl)-5-hydroxy-2[5H]-furanone, otherwise known as MX; (E)-2-chloro-3-(dichloromethyl)-4-oxobutenoic acid, otherwise known as EMX; and mucochloric acid (MCA), which can be found as a closed *ring* or in an *open* form. In October 2001, MX was detected at 0.18 µg/L (180 ng/L) in the finished water of plant 3 (which used chlorine-chloramine disinfection), which was higher than levels reported in a survey of Australian waters (<90 ng/L) (Simpson and Hayes, 1998). However, water quality and treatment/disinfection schemes may be different in Australia than in the United States. In particular, regulatory requirements in Australia are significantly different than in the United States. Subsequently, MX levels dropped in the distribution system to 0.013 µg/L (13 ng/L). EMX levels were 0.10 µg/L in the finished water, but dropped to 0.03 µg/L in the distribution system. Mucochloric acid (*ring* form) was 0.53 µg/L in the GAC influent and 0.05 µg/L in the GAC effluent. Likewise, the *open* form of mucochloric acid was 0.11 and 0.014 µg/L in the GAC influent and effluent, respectively. Similar to that of many other DBPs in this study, MCA (*ring* and *open* forms) was removed on the biologically-active GAC filters. MCA (*ring* form) was partially re-formed at 0.13 µg/L in the finished water, and its concentration remained steady at 0.12 µg/L in the distribution system. The *open* form of mucochloric acid was re-formed in the finished water (0.03 µg/L) and continued to increase in the distribution system (0.16 µg/L). The concentrations of MCA *ring* and *open* forms were qualitative, due to sample matrix co-elutants on the GC column. Due to the relatively high level of bromide in the source water (0.2 mg/L), brominated MX analogs (BMXs) would be expected; however, they were not analyzed for in these samples.

Plant 4, which used chlorine disinfection (applied both to the raw and filtered waters), showed much lower levels of MX (0.015 µg/L) in the finished water, but higher levels (0.02 µg/L) in the chlorinated distribution system. Only a small amount of EMX was detected in finished water from plant 4 (0.011 µg/L), which decreased to below detection in the distribution system. Mucochloric acid levels (both *ring* and *open* forms) were higher in the finished water from plant 4 (0.71 and 0.19 µg/L) than in plant 3 (0.13 and 0.03 µg/L), which contributed to total levels of MX analogs being higher in plant 4 (Figure 29). At plant 4, spent GAC filters were not effective in removing the MX analogues initially formed. This is similar to what was observed for many other DBPs in this study.

Other Halogenated DBPs. A few additional halogenated DBPs were also detected. UNC methods detected dichloroacetamide at 1.2 µg/L in finished water from plant 3 in February 2001 (Table 18). Dichloroacetamide was also observed in the distribution system (2.1 µg/L, plant 3) in October 2001 (Table 19). In addition, broadscreen GC/MS analyses revealed the presence of trichlorophenol and trichlorobenzene-1,2-diol (Table 21) in plant 3 water pre-treated with chlorine (January 2002). These halo-phenols were not observed in the corresponding raw, untreated water, and were not detected in the plant effluent.

Non-Halogenated DBPs. Targeted non-halogenated DBPs observed included trans-2-hexenal (plant 4, February 2001) (Table 18) and dimethylglyoxal (plant 4, October 2001) (Table 19). Levels were 0.7 and 1.4 µg/L, respectively. Several carboxylic acids were also identified as DBPs using broadscreen GC/MS analysis (Table 21). Many carboxylic acids are also seen in the raw, untreated water. However, many were also judged to be formed as DBPs, as their levels increased substantially (2-3X) in the treated waters versus the raw, untreated waters.

Table 18. Additional target DBP results (µg/L) at plants 3 and 4 (2/5/01)

2/5/01	Plant 3[a] Cl_2/NH_2Cl						Plant 4 Cl_2				
Compound	Raw	FI	FE	PE	DS	SDS	FI	FE	PE	DS	SDS
Monochloroacetaldehyde	0	0.4	0.3	0.4	0.3	0.3	1.9	2.2	0.5	0.5	0.4
Dichloroacetaldehyde	0	4.7	2.9	4.3	3.8	3.7	3.9	3.8	3.5	3.6	3.6
Bromochloroacetaldehyde	0	0.5	0.5	0.7	0.3	0.5	0.9	0.6	0.8	0.6	0.5
3,3-Dichloropropenoic acid	0	0.7	0.5	1.5	0.4	1.6	1.0	0.6	0.9	0.9	1.2
Bromochloromethylacetate	0	0	0	0	0	0	0	0	0	0	0
Dichloroacetamide	0	0	0	1.2	1.0	1.9	0	0	0.5	0.4	0.6
TOX (µg/L as Cl^-)	0.6	105.1	47.4	87.3	88.0	110.1	127.6	31.8	188.3	154.9	138.5
Cyanoformaldehyde	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
5-Keto-1-hexanal	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6-Hydroxy-2-hexanone	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Dimethylglyoxal	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
trans-2-Hexenal	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.7	0.7	0.6

[a]Treatment plant sampled at (1) raw water, (2) GAC filter influent (FI), (3) GAC filter effluent (FE), (4) finished water at plant effluent (PE), (5) distribution system (DS) at average detention time, and (6) simulated distribution system (SDS) at maximum detection time.

Table 19. Additional target DBP results (µg/L) at plants 3 and 4 (10/16/01)

10/16/01	Plant 3[a] Cl_2/NH_2Cl						Plant 4 Cl_2				
Compound	Raw	FI	FE	PE	DS	SDS	FI	FE	PE	DS	SDS
Monochloroacetaldehyde	0	1.2	0	0	0.5	0.6	1.9	0.4	0.4	0.5	0.6
Dichloroacetaldehyde	0	5.1	0.5	0.5	1.2	1.6	5.4	4.2	4.4	4.8	6.1
Bromochloroacetaldehyde	0	3.1	0	0	0.9	1.5	1.1	1.5	1.8	2.0	2.8
3,3-Dichloropropenoic acid	0	0	0	0	0	0	0	0	0	0	0
Bromochloromethylacetate	0	0	0	0	0	0	0	0	0	0	0
Dichloroacetamide	0	1.8	0.2	0	2.1	4.8	0	0	0	0	0
TOX (µg/L as Cl^-)	29.1	216.0	82.3	161.0	162.0	141.0	291.0	278.0	278.0	257.0	323.0
Cyanoformaldehyde	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
5-Keto-1-hexanal	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6-Hydroxy-2-hexanone	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Dimethylglyoxal	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	1.4	1.6	2.4
trans-2-Hexenal	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

[a]Treatment plant sampled at (1) raw water, (2) GAC filter influent (FI), (3) GAC filter effluent (FE), (4) finished water at plant effluent (PE), (5) distribution system (DS) at average detention time, and (6) simulated distribution system (SDS) at maximum detection time.

Table 20. Halogenated furanone results (µg/L) at plants 3 and 4 (10/16/01)

10/16/01	Plant 3[a] Cl_2/NH_2Cl					Plant 4 Cl_2			
Compound	Raw	FI	FE	PE	DS	FI	FE	PE	DS
MX	<0.02	0.03	<0.02	0.18	<0.02 (0.013)	0.05	<0.02	<0.02 (0.015)	0.02
EMX	<0.02	<0.02	0.05	0.10	0.03	<0.02	0.02	<0.02 (0.011)	<0.02
Mucochloric acid (ring)	<0.02	0.53	0.05	0.13	0.12	0.86	1.00	0.71	0.47
Mucochloric acid (open)	<0.02	0.11	<0.02 (0.014)	0.03	0.16	0.25	0.13	0.19	0.14

[a]Treatment plant sampled at (1) raw water, (2) GAC filter influent (FI), (3) GAC filter effluent (FE), (4) finished water at plant effluent (PE), and (5) distribution system (DS) at average detention time. Value in parenthesis is less than the MRL.

Figure 29. Halogenated furanones.

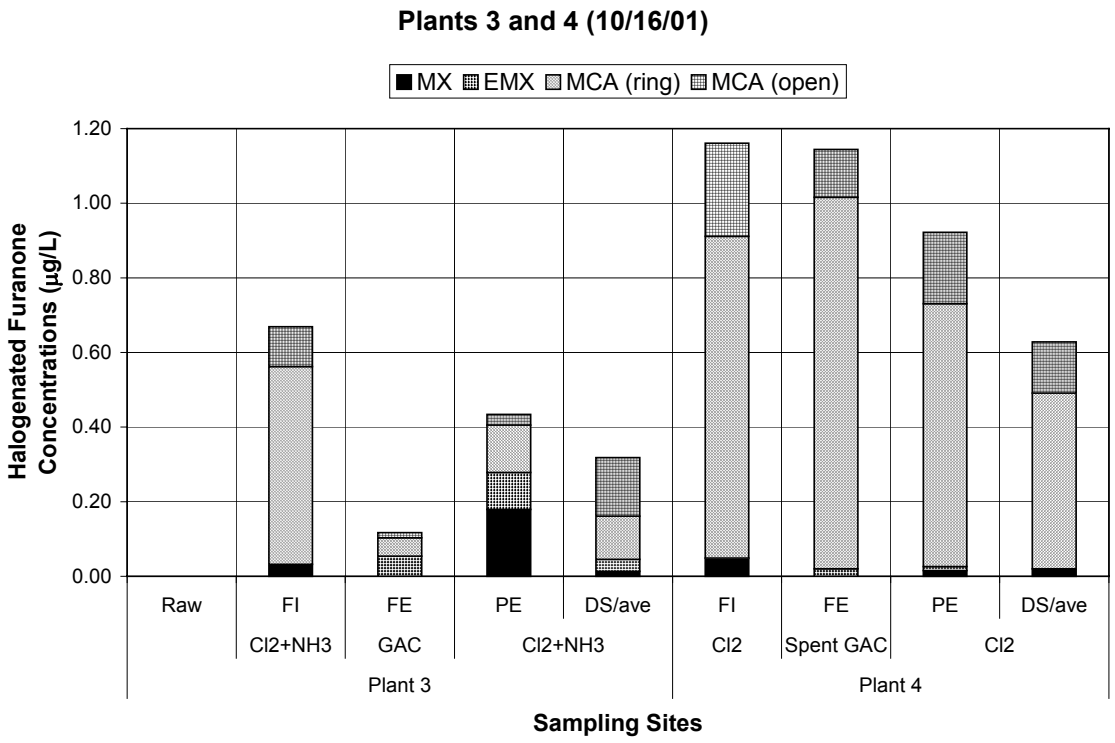


Table 21. Occurrence of other DBPs[a] at plants 3 and 4

	11/13/00	8/1/01		1/28/02	
Compound	Plant 3 Cl_2/NH_2Cl	Plant 3 Cl_2/NH_2Cl	Plant 4 Cl_2	Plant 3 Pre- Cl_2	Plant 3 Cl_2/NH_2Cl
Halomethanes					
Bromodichloromethane	x	-	x	x	x
Dibromochloromethane	x	x	x	x	x
Bromoform	x	x	x	x	x
Dichloroiodomethane	x	x	x	-	-
Bromochloroiodomethane	x	-	-	x	-
Haloacids					
Dichloroacetic acid	x	x	x	-	-
Bromochloroacetic acid	x	-	x	-	-
Dibromoacetic acid	x	x	-	-	-
Trichloroacetic acid	x	x	x	x	x
3,3-Dichloropropenoic acid	-	x	x	-	-
Trichloropropenoic acid	-	x	x	-	x
Haloacetonitriles					
Dichloroacetonitrile	x	x	x	x	-
Bromochloroacetonitrile	x	x	x	x	x
Dibromoacetonitrile	x	x	x	x	-
Tribromoacetonitrile	x	-	-	-	-
Haloaldehydes					
Dichloroacetaldehyde	x	x	x	x	x
Trichloroacetaldehyde	-	x	x	-	-
2-Bromo-2-methylpropanal	x	x	x	x	x
Iodobutanal[c]	x	-	-	-	-
Dichloropropenal[c]	-	x	x	-	-
4-Chloro-2-butenal	-	-	-	x	x
Haloketones					
1,1-Dichloropropanone	x	-	x	x	x
1,1,1-Trichloropropanone	x	x	x	x	x
1-Bromo-1,1-dichloropropanone	x	-	x	-	-
1,1,3,3-Tetrachloropropanone	x	x	x	x	x
Pentachloropropanone	x	x	x	x	x
Hexachloropropanone	x	-	x	x	-
Halonitromethanes					
Dichloronitromethane	-	x	x	-	-
Miscellaneous Halogenated DBPs					
Trichlorophenol	-	-	-	x	-
Trichlorobenzene-1,2-diol	-	-	-	x	-

Table 21 (continued)

	11/13/00	8/1/01		1/28/02	
Compound	Plant 3 Cl_2/NH_2Cl	Plant 3 Cl_2/NH_2Cl	Plant 4 Cl_2	Plant 3 Pre- Cl_2	Plant 3 Cl_2/NH_2Cl
Non-halogenated DBPs					
3-Methylbutanoic acid	-	-	x	-	-
Pentanoic acid	x	-	-	-	-
Hexanoic acid	x	-	-	-	-
Heptanoic acid	x	-	-	-	-
Octanoic acid	x	-	-	-	x
Nonanoic acid	-	-	-	-	x
Decanoic acid	-	-	-	-	x
Dodecanoic acid	-	-	x	-	x
Tetradecanoic acid	-	-	-	-	x
Pentadecanoic acid	-	-	-	-	x
Hexadecanoic acid	x	-	-	-	x
Octadecanoic acid	-	x	-	-	-
Butanedioic acid	-	-	-	-	x
Pentanedioic acid	-	-	-	-	x
Hexanedioic acid	-	-	-	-	x
Octanedioic acid	-	-	-	-	x
Decanedioic acid	-	-	-	-	x
Undecanedioic acid	-	-	-	-	x

[a]DBPs detected by broadscreen gas chromatography/mass spectrometry (GC/MS) technique.
[b]Compounds listed in italics were confirmed through the analysis of authentic standards; haloacids and non-halogenated carboxylic acids identified as their methyl esters.
[c]Exact isomer not known.

SDS Testing. Because plant 3 used chloramines, most DBPs were found to be relatively stable in concentration in the distribution system and in SDS testing. Because plant 4 used free chlorine, THMs and some of the other DBPs were found to increase in concentration in the distribution system and in SDS testing. Figure 30 shows that there was an increase in THM formation—especially for the bromochloro species—during the maximum detention time (140-hr) SDS test of the plant 3 effluent in October 2001 when the bromide level was the highest. However, the formation of the THMs increased by a much higher amount during SDS testing of the plant 4 effluent.

Figure 31 shows the formation and stability of the HANs in SDS testing in October 2001. Although DCAN can undergo base-catalyzed hydrolysis (Stevens et al., 1989), DCAN was stable (and continued to form) in SDS testing at plants 3 and 4, as the pH was 7.0-7.4. The other HANs, including chloroacetonitrile (an EPA study DBP), were stable during this SDS testing.

Figure 32 shows the formation and stability of the haloketones in SDS testing in October 2001. Stevens and colleagues (1989) found 1,1,1-trichloropropanone to be more sensitive to pH than DCAN. In the SDS testing, it did degrade over time. In addition, its brominated analogue 1-bromo-1,1-dichloropropanone, as well as 1,1,3,3-tetrachloropropanone, were detected in the plant effluent samples but not in the SDS testing. Alternatively, chloropropanone was stable during this SDS testing.

Figure 30

Formation of Trihalomethanes in Simulated Distribution System (SDS) Testing (10/16/01): Chloramine and Chlorine Residuals in Plants 3 and 4 SDS Tests, Respectively; Average and Maximum Detention Times of 77 and 140 hr, Respectively

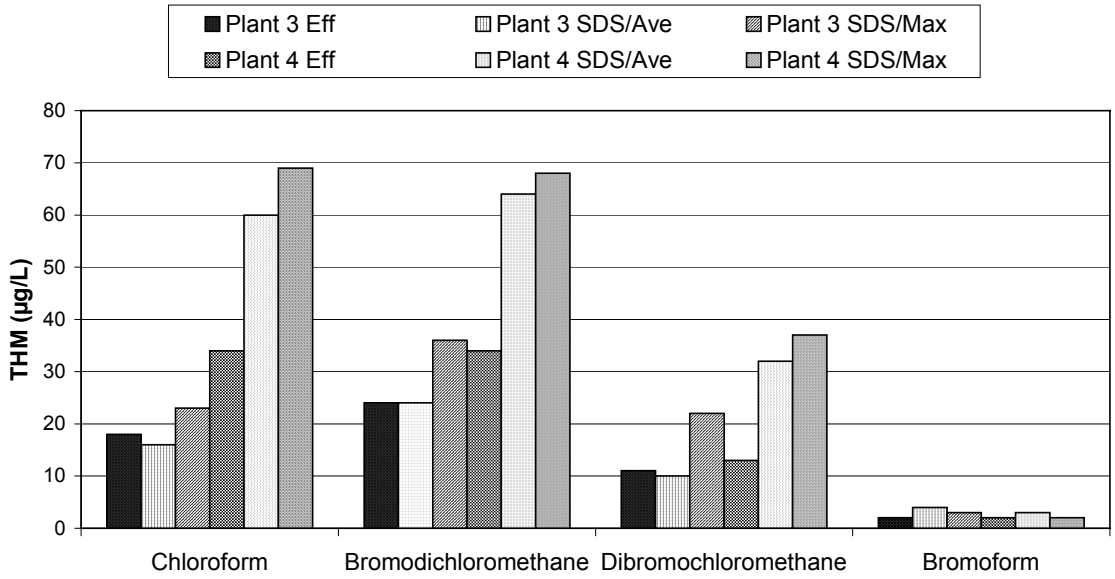
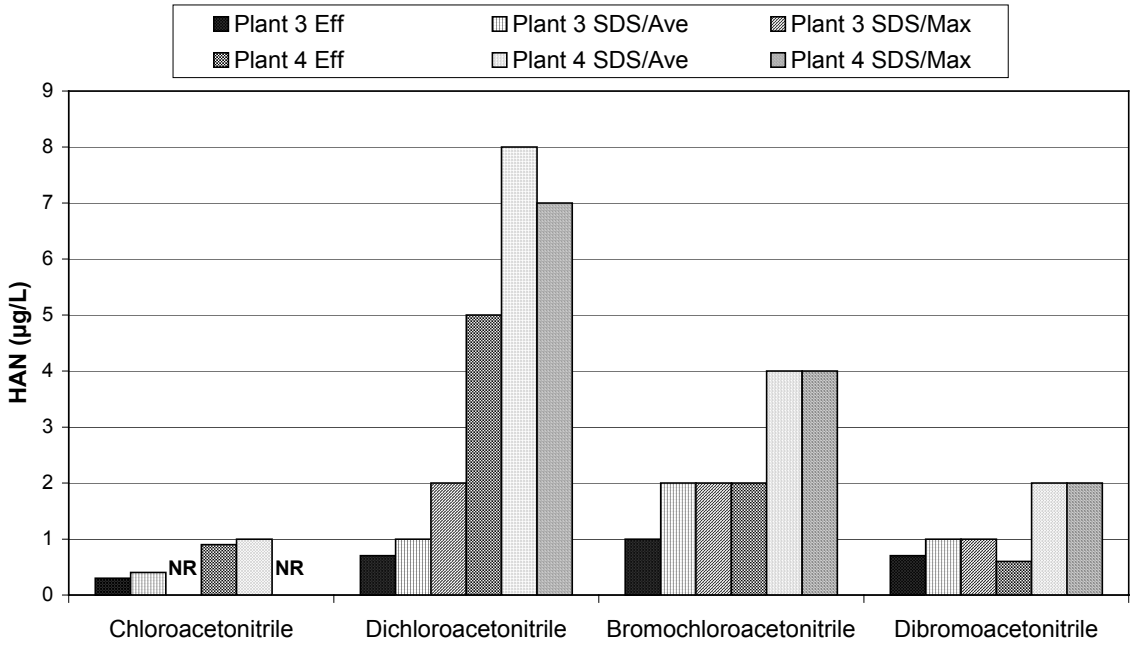


Figure 31

Formation and Stability of Haloacetonitriles in SDS Testing (10/16/01)



NR = Not reported

Figure 33 shows the formation and stability of the haloacetaldehydes in SDS testing in October 2001. Chloral hydrate can also undergo base catalyzed hydrolysis (Stevens et al., 1989). In the SDS testing of the chlorinated water from plant 4, it initially increased in formation and then was somewhat degraded at maximum detention time. Many non-THM DBPs are known to simultaneously form and degrade in a chlorinated distribution system. Alternatively, dichloro- and bromochloroacetaldehyde were stable during this SDS testing.

Figure 32

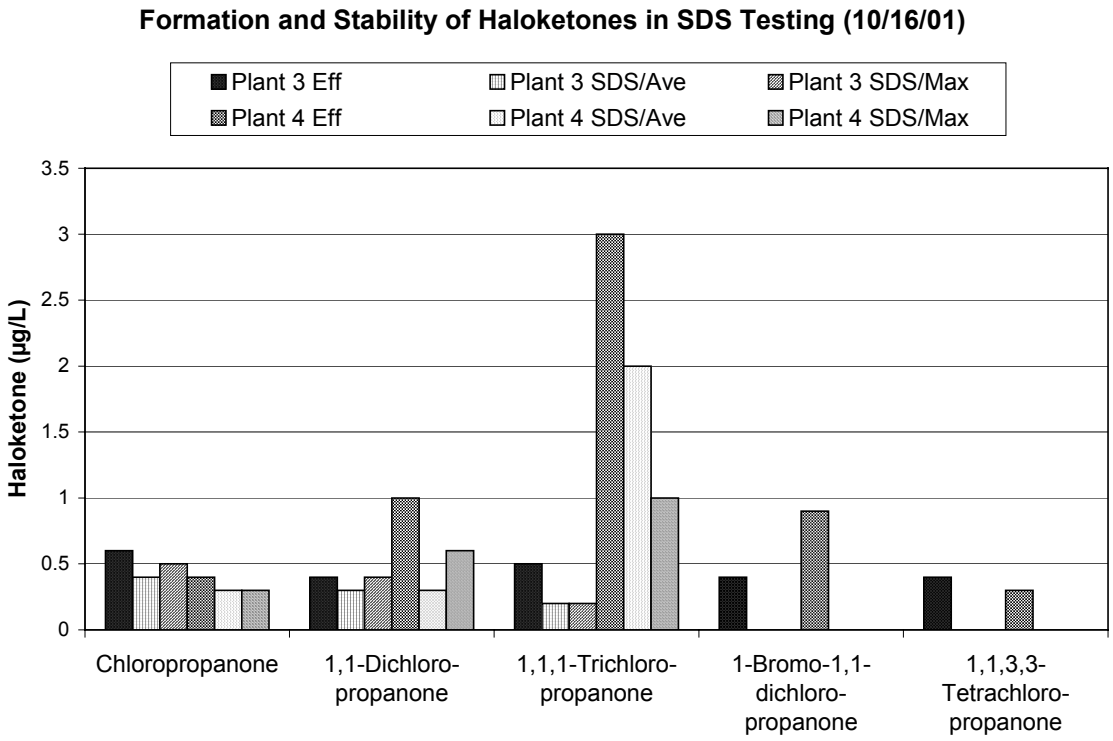
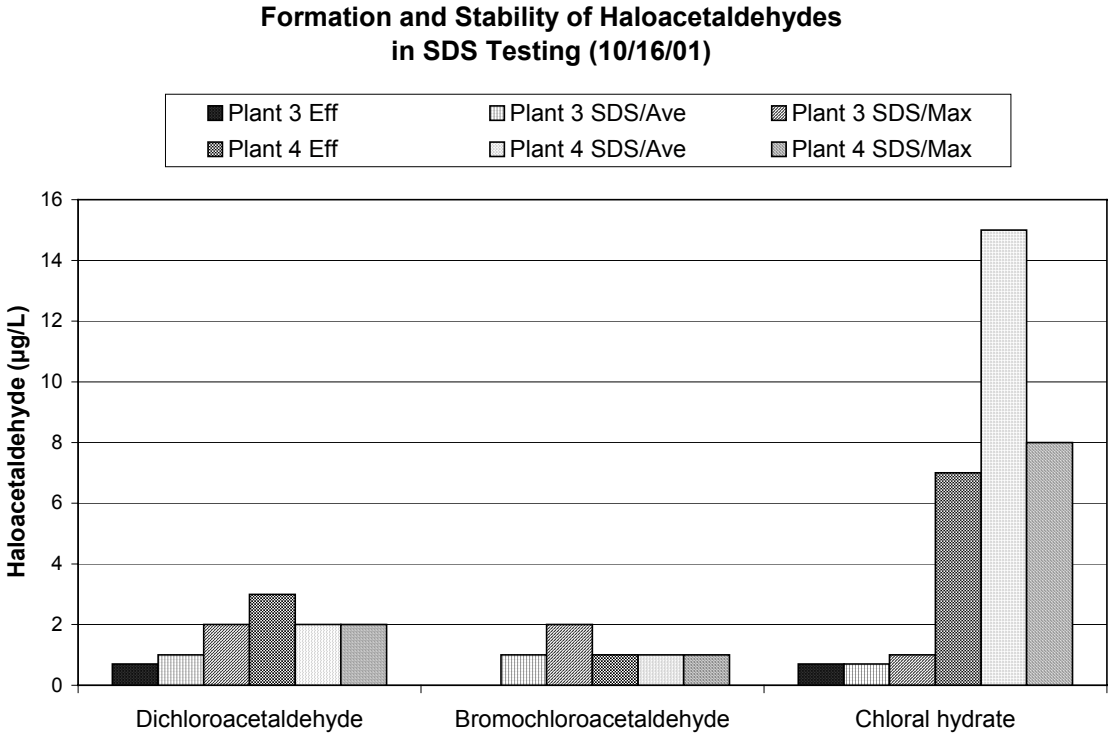


Figure 33



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EPA REGIONS 5 AND 7: PLANTS 9 AND 10

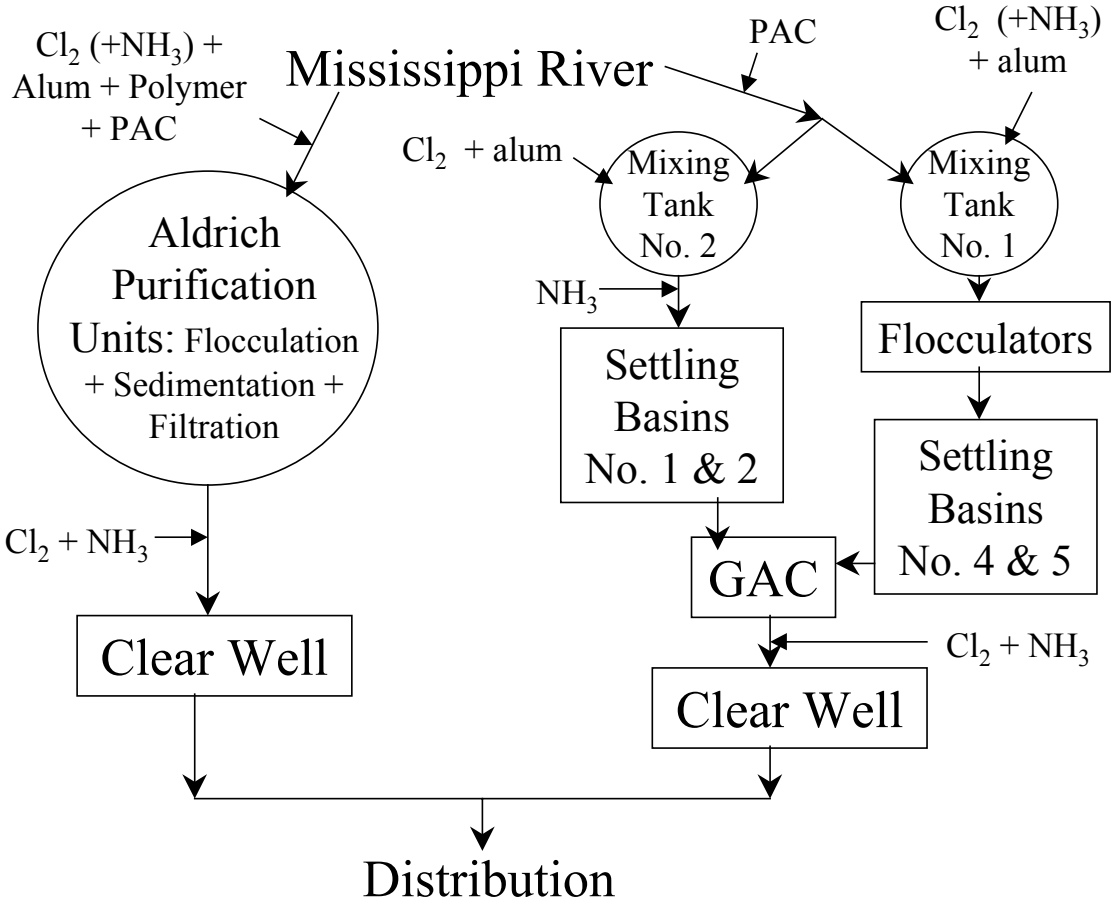
Plant Operations and Sampling

The Mississippi River is the source of water for many drinking-water-treatment plants (WTPs). Plant 10 (in EPA Region 5) treated water from the Mississippi River. In addition, plant 9 (in EPA Region 7) treated water from the Mississippi River; however, the water that was treated at plant 9 was a combination of water from the Mississippi River and another river that flowed into the Mississippi. On January 10, 2001, April 9, 2001, August 27 or September 5, 2001, November 26, 2001, and February 25, 2002, plant 10 and plant 9 were sampled.

Plant 10 had two different treatment trains (Figure 1):

- One train consisted of Aldrich purification units. Chlorine, alum, polymer, and powdered activated carbon (PAC) were added to the raw water. The water underwent flocculation, sedimentation, and filtration. Chlorine and ammonia were added to the filtered water to form chloramines in January and April 2001. Alternatively, chlorine and ammonia were both added to the raw water in November 2001 and February 2002 to form chloramines. During the September 2001 sampling, plant 10 used chlorine only. Many utilities that use chloramines switch back to the use of chlorine only once per year to control the growth of nitrifying bacteria in the distribution system.

Figure 1. Schematic of treatment process at plant 10



- The other train at plant 10 consisted of conventional treatment. PAC was applied to the raw water. Then within this train, there were parallel treatment basins:
  - Chlorine and alum were added at mixing tank number 2. Ammonia (to form chloramines) was added immediately after the mixing tank in January 2001, April 2001, and February 2002, but not during the September 2001 sampling. The water underwent sedimentation in basins 1 and 2. Basins 1 and 2 were out of service for repairs in November 2001.
  - (The raw water for basins 4 and 5 was a mixture of water from the two intakes, one for the Aldrich purification units and the other for the conventional treatment train.) Chlorine and alum were added at mixing tank number 1. No ammonia was added to this portion of the conventional train in January, April or September 2001. Alternatively, chlorine and ammonia were both added at mixing tank number 1 in November 2001 and February 2002 to form chloramines. Chlorinated (or chloraminated) water underwent flocculation and sedimentation (in basins number 4 and 5).
  - The water from all four settling basins was then filtered through granular activated carbon (GAC) filters. The GAC was operated for taste-and-odor control and not for the removal of DBP precursors. Chlorine and ammonia (to form chloramines) was added to the filtered water in January 2001, April 2001, November 2001, and February 2002, but not during the September 2001 sampling, when only chlorine was added.

At plant 9 (Figure 2), initially, the water underwent pretreatment with polymer addition. Then the water was lime softened. The softened water was then chlorinated and treated with ferric sulfate [$Fe_2(SO_4)_3$] in the conditioning chamber. At the end of the conditioning chamber, ammonia was added to form chloramines. The water then passed through a series of settling basins. PAC was added to the effluent of basin #6. The water was then treated with additional ferric sulfate, polymer, chlorine, and ammonia. Finally, the water underwent filtration.

Plant 10 was sampled at the following locations:

<u>Aldrich Purification Units Train</u>

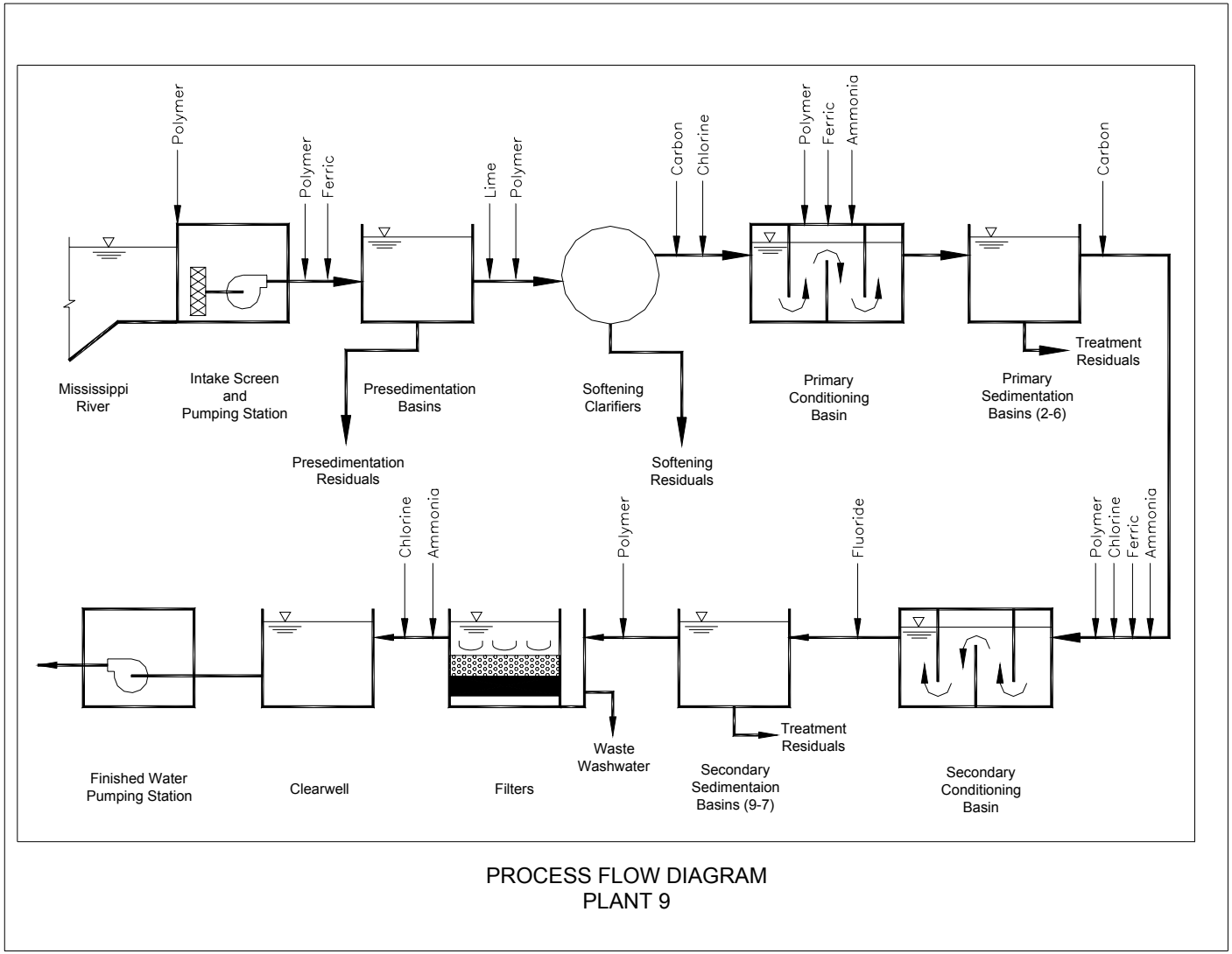
(1) raw water
(2) the filter effluent (January 2001 only)
(3) the clearwell effluent

<u>Conventional Treatment Train</u>

(4) raw water
(5) the effluent of basins 4 and 5
(6) the effluent of basins 1 and 2 (except for November 2001)
(7) the filter effluent
(8) the clearwell effluent (January 2001 only)

<u>Combined Plant</u>

(9) the finished water



PROCESS FLOW DIAGRAM
PLANT 9

Figure 2. Plant 9 water treatment plant

In addition, finished water from the point of entry was collected and simulated distribution system (SDS) testing was conducted for average and maximum detention times for that time of year (Table 1). In November 2001, a separate SDS sample at maximum detention time was prepared for the University of North Carolina (UNC), which used water from the clearwell of the conventional treatment train. Furthermore, the distribution system was sampled at one to two locations, one representing an average detention time and the other representing a maximum detention time (January 2001 only).

Plant 9 was sampled at the following locations:

(1) raw water
(2) softened water
(3) water from the primary conditioner
(4) the effluent of basin #6
(5) the filter influent
(6) and the finished water

In addition, finished water was collected and SDS testing was conducted for average and maximum detention times for that time of year (Table 1). Furthermore, the distribution system was sampled at two locations, one representing an average detention time and the other representing a maximum detention time.

Table 1. SDS holding times at Mississippi River WTPs

Sample	1/10/01	4/9/01	8/27 or 9/5/01	11/26/01	2/25/02
Plant 10 average detention time	4 hr	4 hr	4 hr	4 hr	4 hr
Plant 10 maximum detention time	5 days	5 days	5 days	5 days	5 days
Plant 9 average detention time	3 days	3 days	2 days	2 days	2 days
Plant 9 maximum detention time	6 days	6 days	3 days	4 days	3 days

On the day of sampling, information was collected on the operations at each plant (Tables 2-3).

Table 2. Operational information at plant 10

Parameter	1/10/01	4/9/01	9/5/01	11/26/01	2/25/02
Aldrich Purification Units Train					
Plant flow for this train (mgd)	8	8	11	10	8
Chlorine dose at plant influent (mg/L as Cl_2)	10	17	16	10	9.7
Ammonia dose at plant influent (mg/L as NH_3-N)	0	0	0	2.0	1.7
Alum dose at plant influent (mg/L)	96	96	35	60.4	76.6
Polymer dosage at plant influent (mg/L)	3.7	3.5	2.1[a]	2.0	3.5
PAC dosage at plant influent (mg/L)	1	1.8	0.5	1.2	3.0
Permanganate dose at plant influent (mg/L)	0	0	2.2	0	0
Chlorine dose at combined filter eff. (mg/L as Cl_2)	2	1.6	3.6	0.8	0
NH_3 dose at combined filter eff. (mg/L as NH_3-N)	0.6	0.8	0	0.8	0
Conventional Treatment Train					
PAC dosage at intake (mg/L)	1	1	0.7	0	0
Permanganate dose at intake (mg/L)	0	0	2.0	0	1.7

Table 2 (continued)

Parameter	1/10/01	4/9/01	9/5/01	11/26/01	2/25/02
Train for Basins 1 and 2					
Plant flow for these basins (mgd)	10	11	11	0	8
Chlorine dose at mixing tank no. 2 (mg/L as Cl_2)	6	6	6.7	---	7.5
NH_3 dose immediately after mixing tank no. 2 (mg/L as NH_3-N)	1	1	0	---	1.5
Alum dose at mixing tank number 2 (mg/L)	54	50	53.2	---	51
Train for Basins 4 and 5					
Plant flow for these basins (mgd)	22	20.6	25.8	27.5	20.0
Chlorine dose at mixing tank no. 1 (mg/L as Cl_2)	6	14	9.1	4.9	5.7
NH_3 dose at mixing tank no. 1 (mg/L as NH_3-N)	0	0	0	0.9	1.2
Alum dose at mixing tank number 1 (mg/L)	54	50	45.6	55.4	51
Polymer dosage at mixing tank number 1 (mg/L)	0	1.1	0	0	0
Combined Conventional Treatment Train					
GAC filter loading rate (gpm/sq ft)	NA[b]	2	2	2	2
GAC empty bed contact time (min)	NA	5.6	5.6	5.6	5.6
Chlorine dose at combined filter eff. (mg/L as Cl_2)	2	3	3.6	3.7	1.9
NH_3 dose at combined filter eff. (mg/L as NH_3-N)	0.6	0.6	0	0.7	0.5

[a]At intake
[b]NA = Not available

Table 3. Operational information at plant 9

Parameter	1/10/01	4/9/01	8/27/01	11/26/01	2/25/02
Plant flow (mgd)	122	88-94	82	70	84
Polymer dosage at plant influent (mg/L)	1.0	3.0	2.0	2.0	2.5
Lime dosage in softening basins (mg/L)	108	77	101	101	103
Chlorine dose at cond. chamber (mg/L as Cl_2)	2.52	2.3	2.88	2.16	2.0
$Fe_2(SO_4)_3$ dose at conditioning chamber (mg/L)	6.8	6.8	8.6	3.4	3.4
Polymer dosage at conditioning chamber (mg/L)	0.5	1.5	1.0	1.0	1.0
NH_3 dose at end of cond. chamber (mg/L as NH_3-N)	1.44	1.2	1.92	1.68	1.6
PAC dosage at Basin 6 effluent (mg/L)	2.4	6.0	6.0	1.2	1.2[a]
$Fe_2(SO_4)_3$ dose at influent to Basin 9 (mg/L)	8.6	6.8	6.8	3.4	0
Polymer dosage at influent to Basin 9 (mg/L)	1.0	0.4	0.4	0.4	0
Chlorine dose at influent to Basin 9 (mg/L as Cl_2)	1.92	2.9	2.4	2.16	2.3
Ammonia dose at inf. to Basin 9 (mg/L as NH_3-N)	1.44	1.6	1.92	1.8	1.8
Chlorine dose at clearwell effluent (mg/L as Cl_2)	0	0	0.24	0	0
Ammonia dose at clearwell eff. (mg/L as NH_3-N)	0	0	0.12	0	0

[a]PAC dosage at Basin 1 influent

Water Quality

On the day of sampling, information was collected on water quality at each plant (Tables 4-5). Data were collected for total organic carbon (TOC) and ultraviolet (UV) absorbance (Tables 6-7). The raw water in January 2001, April 2001, summer (August or September) 2001, November 2001, and February 2002 at plant 10 was somewhat higher in TOC than at plant 9 (4.0-5.9 versus 3.4-5.0 mg/L). Nonetheless, both utilities had a moderate loading of DBP precursors.

At plant 10, in the Aldrich purification units in January 2001, April 2001, September 2001, November 2001, and February 2002, 14-32 % of the TOC and 18-47 % of the UV was removed. At plant 10, in the conventional treatment train in January 2001, April 2001, September 2001, November 2001, and February 2002, coagulation removed 17-27 % of the TOC and filtration removed another 2-17 %. The overall TOC removal in the conventional treatment train was 28-34 %. In addition, the overall UV removal in the conventional treatment train was 41-62 %.

At plant 9, in April 2001, August 2001, November 2001, and February 2002, softening removed 19-28 % of the TOC, whereas in January 2001 no TOC was initially removed during the softening process. At plant 9, with downstream coagulation and filtration, the overall TOC removal on these three sample dates was 17-34 %. In addition, the overall UV removal was 11-45 %.

Tables 8-9 show the values of miscellaneous other water quality parameters in the raw water at plant 10 and plant 9, respectively. The raw water in January 2001, April 2001, summer (August or September) 2001, November 2001, and February 2002 at plant 9 was higher in bromide than at plant 10 (0.06-0.36 versus 0.05-0.08 mg/L). Nonetheless, both utilities had a moderate loading of inorganic DBP precursors.

Table 4. Water quality information at plant 10

	pH					Temperature (ºC)					Disinfectant Residual[a] (mg/L)				
Location	1/10/01	4/9/01	9/5/01	11/26/01	2/25/02	1/10/01	4/9/01	9/5/01	11/26/01	2/25/02	1/10/01	4/9/01	9/5/01	11/26/01	2/25/02
Aldrich Purification Units Train															
Raw water	8.01	8.32	8.21	8.5	8.67	1.5	13.1	28.1	13.3	7.5	---	---	---	---	---
Filter eff.	7.67	7.51	7.39	7.8	7.84	2.7	14.7	29.8	14.2	8.2	1.3	2.4	*2.1*	5.4	5.0
Clearwell	7.56	7.50	7.60	7.6	7.70	---	14.9	28.4	13.5	9.5	3.7	4.2	*4.0*	5.6	4.9
Conventional Treatment Train															
Raw water	8.03	8.38	8.33	8.5	8.68	0.7	13.3	28.0	14.7	6.4	---	---	---	---	---
Basins 4&5	7.38	7.36	7.24	7.8	7.79	0.3	14.0	29.2	16.1	5.8	*1.9*	*3.3*	*2.4*	3.3	5.3
Basins 1&2	7.49	7.47	7.22	NS	7.80	0.4	14.1	27.4	NS	5.6	4.7	4.1	*0.7*	NS	3.9
Filter eff.	7.37	7.37	7.16	7.6	7.75	3.5	14.7	28.3	13.2	6.1	0.3[b]	0.2[b]	*0.4*	0.4	1.1
Clearwell	7.45	7.54	7.70	7.5	7.64	2.6	15.0	28.0	13.1	7.9	3.2	3.6	*3.4*	3.8	3.6
Combined Plant															
Finished	7.48	7.41	7.68	7.5	7.69	3.0	14.4	27.5	12.3	6.5	3.7	3.7	*3.5*	3.4	3.6
DS[c]/ave	7.53	7.48	7.54	7.4	7.38	2.4	13.1	26.4	13.5	7.4	2.4	3.3	*3.1*	3.1	3.0
DS/max	7.47	NS[d]	NS	NS	NS	10.4	NS	NS	NS	NS	1.7	NS	NS	NS	NS
SDS/ave	7.51	7.46	7.63	7.5	7.65	2.9	14.8	27.6	12.2	6.3	3.5	3.5	*2.9*	3.2	3.0
SDS/max	7.52	7.39	7.56	7.5	7.57	2.5	15.3	26.4	11.8	5.6	2.9	1.8	*0.3*	0.9	2.3
SDS/max for UNC	---	---	---	7.5	---	---	---	---	11.5	---	---	---	---	1.0	---

[a]Chlorine residuals (values shown in italics) at Basins 4 & 5 effluent in January and April 2001, and all sample locations in September 2001; chloramine residuals at other locations.
[b]GAC filters removed chlorine.
[c]DS = Distribution system
[d]NS = Not sampled

Table 5. Water quality information at plant 9

	pH					Temperature (ºC)					Disinfectant Residual[a] (mg/L)				
Location	1/10/01	4/9/01	8/27/01	11/26/01	2/25/02	1/10/01	4/9/01	8/27/01	11/26/01	2/25/02	1/10/01	4/9/01	8/27/01	11/26/01	2/25/02
Raw	8.10	8.00	8.64	8.26	8.24	1.1	14.4	28.3	12.8	8.3	---	---	---	---	---
Softened	9.97	10.2	9.82	10.1	9.37	1.5	14.4	27.0	13.3	8.6	---	---	---	---	---
1º cond.	9.74	9.85	9.66	9.97	9.35	1.4	15.6	26.9	13.3	8.6	*1.60*	*1.50*	*1.10*	2.20	1.60
Basin #6	9.66	9.68	9.76	9.65	9.32	2.2	15.6	26.1	13.3	9.4	1.60	1.10	0.95	1.50	1.55
Filter inf.	9.21	9.31	9.34	9.39	9.12	2.2	15.6	26.7	14.4	9.8	2.50	2.25	2.25	2.65	2.60
Finished	9.59	9.70	9.23	9.35	9.12	1.4	15.6	27.2	13.3	8.9	2.45	2.25	2.40	2.65	2.60
DS/ave	9.74	9.35	9.15	9.10	9.23	3.7	18.9	28.0	13.1	9.8	2.45	2.15	2.25	2.30	2.55
DS/max	9.48	9.33	9.38	9.20	9.28	4.0	18.9	28.4	13.2	9.8	2.40	2.15	2.10	2.20	2.40
SDS/ave	9.18	9.26	9.19	9.36	8.93	8.9	16.0	24.4	15.6	7.8	2.45	2.20	2.20	2.40	2.45
SDS/max	9.09	9.26	9.29	9.38	8.9	6.7	16.5	25.0	13.9	7.2	2.35	2.10	2.10	2.30	2.4

[a]Chlorine residuals (values shown in italics) at primary (1º) conditioner in January, April, and August 2001; chloramine residuals at other locations.

Table 6. TOC and UV removal at plant 10

Location	TOC (mg/L)	UV[a] (cm^{-1})	SUVA[b] (L/mg-m)	Removal/Unit (%)		Removal/Cumulative (%)	
				TOC	UV	TOC	UV
01/10/2001							
Aldrich Raw	4.83	0.113	2.34	---	---	---	---
Aldrich Filter Eff.	3.57	0.063	1.76	26%	44%	26%	44%
Conventional Raw	5.11	0.127	2.49	---	---	---	---
Basins 4 & 5 Eff.	4.12	0.057	1.38	19%	55%	19%	55%
Basins 1 & 2 Eff.	4.04	0.079	1.96	21%	38%	21%	38%
Combined Filter Eff.[c]	3.42	0.053	1.55	17%	7.0%	33%	58%
04/09/2001							
Aldrich Raw	4.01	0.093	2.32	---	---	---	---
Aldrich Clearwell Eff.	2.86	0.051	1.78	29%	45%	29%	45%
Conventional Raw	4.22	0.103	2.44	---	---	---	---
Basins 4 & 5 Eff.	3.08	0.035	1.14	27%	66%	27%	66%
Basins 1 & 2 Eff.	3.11	0.053	1.70	26%	49%	26%	49%
Combined Filter Eff.	3.03	0.039	1.29	1.6%	-11%	28%	62%
09/05/2001							
Aldrich Raw	5.45	0.148	2.72	---	---	---	---
Aldrich Clearwell Eff.	4.68	0.078	1.67	14%	47%	14%	47%
Conventional Raw	5.87	0.152	2.59	---	---	---	---
Basins 4 & 5 Eff.	4.39	0.066	1.50	25%	57%	25%	57%
Basins 1 & 2 Eff.	4.89	0.075	1.53	17%	51%	17%	51%
Combined Filter Eff.	4.22	0.067	1.59	3.9%	-1.5%	28%	56%
11/26/2001							
Aldrich Raw	4.98	0.122	2.45	---	---	---	---
Aldrich Clearwell Eff.	3.64	0.100	2.75	27%	18%	27%	18%
Conventional Raw	5.04	0.127	2.52	---	---	---	---
Basins 4 & 5 Eff.	4.0	0.089	2.23	21%	30%	21%	30%
Basins 1 & 2 Eff.	NS	NS	---	---	---	---	---
Combined Filter Eff.	3.43	0.070	2.04	14%	21%	32%	45%
02/25/2002							
Aldrich Raw	4.52	0.099	2.19	---	---	---	---
Aldrich Clearwell Eff.	3.08	0.075	2.44	32%	24%	32%	24%
Conventional Raw	4.91	0.111	2.26	---	---	---	---
Basins 4 & 5 Eff.	3.67	0.083	2.26	25%	25%	25%	25%
Basins 1 & 2 Eff.	3.57	0.072	2.02	27%	35%	27%	35%
Combined Filter Eff.	3.24	0.065	2.01	12%	22%	34%	41%

[a]UV = Ultraviolet absorbance reported in units of "inverse centimeters" (APHA, 1998)

[b]SUVA (L/mg-m) = Specific ultraviolet absorbance = 100*UV (cm^{-1})/DOC (mg/L) or UV (m^{-1})/DOC (mg/L), where DOC = dissolved organic carbon, which typically = 90-95% TOC (used TOC values in calculating SUVA) (e.g., UV = 0.113/cm = 0.113/(0.01 m) = 11.3/m, DOC = 4.83 mg/L, SUVA = (11.3 m^{-1})/(4.83 mg/L) = 2.34 L/mg-m)

[c]Removal/unit compared to basins 4 & 5 effluent

Table 7. TOC and UV removal at plant 9

Location	TOC (mg/L)	UV[a] (cm^{-1})	SUVA[b] (L/mg-m)	Removal/Unit (%)		Removal/Cumulative (%)	
				TOC	UV	TOC	UV
01/10/2001							
Raw	3.39	0.063	1.86	---	---	---	---
Softened Water	3.51	0.049	1.40	-3.5%	22%	-3.5%	22%
Primary Conditioner	3.09	0.055	1.78	12%	-12%	8.8%	13%
Basin #6 Eff.	3.20	0.056	1.75	-3.6%	-1.8%	5.6%	11%
Filter Inf.	2.85	0.059	2.07	11%	-5.4%	16%	6.3%
Finished Water	2.80	0.056	2.00	1.8%	5.1%	17%	11%
04/09/2001							
Raw	4.96	0.137	2.76	---	---	---	---
Softened Water	3.58	0.076	2.12	28%	45%	28%	45%
Primary Conditioner	3.61	0.078	2.16	-0.8%	-2.6%	27%	43%
Basin #6 Eff.	4.05	0.089	2.20	-12%	-14%	18%	35%
Filter Inf.	3.51	0.078	2.22	13%	12%	29%	43%
Finished Water	3.49	0.076	2.18	0.6%	2.6%	30%	45%
08/27/2001							
Raw	4.22	0.093	2.20	---	---	---	---
Softened Water	3.40	0.068	2.00	19%	27%	19%	27%
Primary Conditioner	3.19	0.052	1.63	6.2%	24%	24%	44%
Basin #6 Eff.	2.97	0.058	1.95	6.9%	-12%	30%	38%
Filter Inf.	2.79	0.056	2.01	6.1%	3.4%	34%	40%
Finished Water	2.77	0.058	2.09	0.7%	-3.6%	34%	38%
11/26/2001							
Raw	3.61	0.082	2.27	---	---	---	---
Softened Water	2.69	0.047	1.75	25%	43%	25%	43%
Primary Conditioner	2.89	0.054	1.87	-7.4%	-15%	20%	34%
Basin #6 Eff.	2.43	0.050	2.06	16%	7%	33%	39%
Filter Inf.	2.29	0.051	2.23	5.8%	-2.0%	37%	38%
Finished Water	2.37	0.053	2.24	-3.5%	-3.9%	34%	35%
02/25/2002							
Raw	3.37	0.074	2.20	---	---	---	---
Softened Water	2.67	0.049	1.84	21%	34%	21%	34%
Primary Conditioner	3.34	0.050	1.50	-25%	-2.0%	1%	32%
Basin #6 Eff.	2.50	0.051	2.04	25%	-2.0%	26%	31%
Filter Inf.	2.55	0.054	2.12	-2.0%	-5.9%	24%	27%
Finished Water	2.48	0.055	2.22	2.7%	-1.9%	26%	26%

[a]UV = Ultraviolet absorbance reported in units of "inverse centimeters" (APHA, 1998)

[b]SUVA (L/mg-m) = Specific ultraviolet absorbance = 100*UV (cm^{-1})/DOC (mg/L) or UV (m^{-1})/DOC (mg/L), where DOC = dissolved organic carbon, which typically = 90-95% TOC (used TOC values in calculating SUVA) (e.g., UV = 0.063/cm = 0.063/(0.01 m) = 6.3/m, DOC = 3.39 mg/L, SUVA = (6.3 m^{-1})/(3.39 mg/L) = 1.86 L/mg-m)

On the January 2001, April 2001, September 2001, November 2001, and February 2002 samplings, the raw water at plant 10 contained up to 0.16 mg/L of ammonia (Table 8). Theoretically, it takes 7.6 mg/L of chlorine to breakpoint chlorinate 1.0 mg/L of ammonia-nitrogen. The theoretical inorganic chlorine demand (up to 1.2 mg/L) was significantly less than the initial chlorine dose applied at each of the trains when prechlorination was practiced (6-17 mg/L) (Table 2).

Table 8. Miscellaneous water quality parameters in raw water at plant 10

Location	Bromide (mg/L)	Alkalinity (mg/L)	Ammonia (mg/L as N)	Chlorine Demand[a] (mg/L)
01/10/2001				
Aldrich Train Raw	0.08	199	0.15	1.1
Conventional Train Raw	0.07	199	0.16	1.2
04/09/2001				
Aldrich Train Raw	0.05	176	ND[b]	0
Conventional Train Raw	0.05	173	0.08	0.6
09/05/2001				
Aldrich Train Raw	0.07	148	0.04	0.3
Conventional Train Raw	0.07	149	ND	0
11/26/2001				
Aldrich Train Raw	0.05	189	0.05	0.4
Conventional Train Raw	0.05	186	0.07	0.5
02/25/2002				
Aldrich Train Raw	0.05	175	0.06	0.5
Conventional Train Raw	0.05	188	0.14	1.1

[a]Chlorine demand from ammonia = 7.6 * ammonia (mg/L as N)

[b]ND = Not detected

Table 9. Miscellaneous water quality parameters in raw water at plant 9

Date	Bromide (mg/L)	Alkalinity (mg/L)	Ammonia (mg/L as N)	Chlorine Demand[a] (mg/L)
01/10/2001	0.19	221	0.37	2.8
04/09/2001	0.06	99	0.05	0.4
08/27/2001	0.1	175	ND	0
11/26/2001	0.2	182	0.07	0.5
02/25/2002	0.36	171	0.1	0.8

[a]Chlorine demand from ammonia = 7.6 * ammonia (mg/L as N)

In January 2001, the raw water at plant 9 contained 0.4 mg/L of ammonia, whereas in April 2001, August 2001, November 2001, and February 2002 it only had up to 0.1 mg/L of ammonia (Table 9). The theoretical inorganic chlorine demand in January 2001 (2.8 mg/L) was somewhat higher than the initial chlorine dose applied at the conditioning chamber (2.5 mg/L) (Table 3). Alternatively, the theoretical inorganic chlorine demand in February 2002 (0.8 mg/L) was lower than the initial chlorine dose applied at the conditioning chamber (2.0 mg/L).

DBPs

Tables 10 and 11 (1/10/01), Tables 13 and 14 (4/9/01), Tables 16 and 17 (8/27-9/5/01), Tables 18 and 19 (11/26/01), and Tables 22 and 23 (2/25/02) show results for the halogenated organic DBPs that were analyzed for at Metropolitan Water District of Southern California (MWDSC). Table 12 (1/10/01) and Table 20 (11/26/01) show results for additional target DBPs that were analyzed for at UNC. Table 20 (11/26/01) show results for halogenated furanones that were analyzed for at UNC. Table 15 (4/9/01 [plant 10], 8/27/01 [plant 9], and 2/25/02 [plant 10]) shows results from broadscreen analyses conducted at the U.S. Environmental Protection Agency (USEPA).

Summary of Tables for DBPs for Mississippi River WTPs

DBP Analyses (Laboratory)	1/10/01	4/9/01	8/27 or 9/5/01	11/26/01	2/25/02
Halogenated organic DBPs (MWDSC)	Tables 10-11	Tables 13-14	Tables 16-17	Tables 18-19	Tables 22-23
Additional target DBPs (UNC)	Table 12			Table 20	
Halogenated furanones (UNC)				Table 21	
Broadscreen analysis (USEPA)		Table 15[a]	Table 15[b]		Table 15[a]

[a]Plant 10
[b]Plant 9

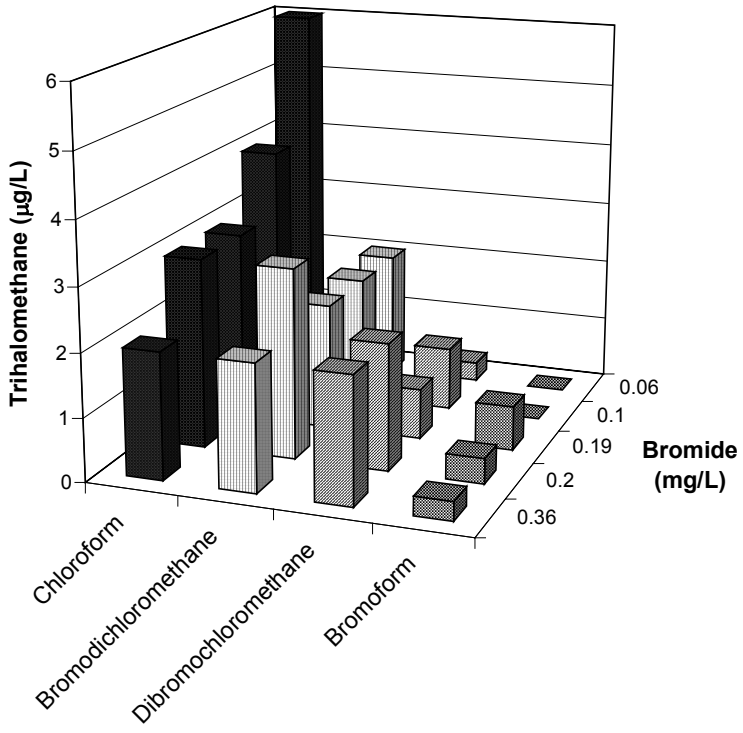
Halomethanes. Chlorine and/or chloramine disinfection at plant 10 in January and April 2001 resulted in the formation of 71-84 and 54 µg/L of the four regulated trihalomethanes (THM4) in the Aldrich purification units and in basins 4 and 5, respectively. THM formation was lower in the effluent of basins 1 and 2 in January (30 µg/L of chloroform) and April 2001 (31 µg/L of THM4) because free chlorine was only present in mixing tank number 2 before ammonia addition (upstream of basins 1 and 2). Chlorine only disinfection in September 2001 resulted in the formation of 144, 144, and 174 µg/L of THM4 in the Aldrich purification units, in basins 4 and 5, and in basins 1 and 2, respectively. Another major difference between the three seasons was temperature: 0.3-3ºC in January 2001, 13-15ºC in April 2001, and 26-30ºC in September 2001 (Table 4). Thus, THM formation was significantly higher in September 2001 due to the presence of only free chlorine (no chloramines) and the warmer water temperature. In contrast, the use of chloramines only at plant 10 in November 2001 and February 2002 resulted in the formation of 12-19 and 8-14 µg/L of THM4 in the Aldrich purification units and in basins 4 and 5, respectively.

Chlorine/chloramine disinfection at plant 9 in January 2001, April 2001, August 2001, November 2001, and February 2002 resulted in the formation of 6-8 µg/L of THM4. There was no seasonal variability in the concentration of THM4 at this plant during this time period. The very low concentration of THMs at plant 9 suggests that there was minimal free chlorine contact time prior to ammonia addition.

Although there were large differences in the total amounts of THMs formed, both WTPs produced a high percentage of the THMs as chloroform, followed by bromodichloromethane, when the raw-water bromide was less than or equal to 0.1 mg/L. Figure 3 shows the impact of

bromide on THM speciation at plant 9. As the concentration of bromide increased, the formation of chloroform decreased and the formation of dibromochloromethane increased.

Figure 3. Impact of bromide on THM speciation in finished water at plant 9



Dichloroiodomethane was detected at plant 10 in November 2001 and February 2002. Dichloroiodomethane, bromochloroiodomethane, and chlorodiiodomethane (February only) were detected at plant 9 in November 2001 and February 2002. Bromide was at its highest in the influent of plant 9 in the latter two months. In addition, two of the iodinated THMs were detected by the broadscreen gas chromatography/mass spectrometry (GC/MS) methods at both WTPs (dichloroiodomethane and bromochloroiodomethane; Table 15).

Dibromomethane, a volatile organic compound (VOC), was detected (0.13 µg/L)—slightly above the minimum reporting level (MRL) (0.11 µg/L)—in a SDS sample of plant 9 in January 2001. In other research, this dihalogenated methane had been detected in a high-bromide water that had been disinfected with chloramines (Krasner et al., 1996). In addition, bromomethane was detected at its MRL (0.2 µg/L) in a plant 9 distribution system sample in November 2001.

Table 10. DBP results at plant 10 (1/10/01)

01/10/2001	MRL[a]	Aldrich[b]			Conventional[b]					Combined Plant[b]				
Compound	µg/L	Raw	Filt Eff	Clearwell	Raw	Basins 4&5	Basins 1&2	Filt Eff	Clearwell	Finished	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes														
Chloromethane	0.15	ND[c]		ND	ND	ND		ND	ND	ND	ND		ND	
Bromomethane	0.20	ND		ND	ND	ND		ND	ND	ND	ND		ND	
Bromochloromethane	0.14	ND		ND	ND	ND		ND	ND	ND	ND		ND	
Dibromomethane	0.11	ND		ND	ND	ND		ND	ND	ND	ND		ND	
Chloroform[d]	0.1	0.1	60	60	0.1	40	30	45	40	45	50	60	45	60
Bromodichloromethane[d]	0.10	ND	NR[e]	20	0.1	12	NR	13	12	13	15	NR	14	NR
Dibromochloromethane[d]	0.07	ND	NR	4	ND	2	NR	2	2	2	2	NR	2	NR
Bromoform[d]	0.6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
THM4[f]		0.1	NR	84	0.2	54	NR	60	54	60	67	NR	61	NR
Dichloroiodomethane	0.25	ND	NR	ND	ND	ND	NR	ND	ND	ND	ND	NR	ND	NR
Bromochloroiodomethane	0.20	ND	NR	ND	ND	ND	NR	ND	ND	ND	ND	NR	ND	NR
Dibromoiodomethane	0.6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.14	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.06	ND		0.3	ND	ND		ND	ND	0.07	0.1		0.08	
Haloacetic acids														
Monochloroacetic acid[d]	2		10	10		8.8	1.3	7.8	6.5	6.0	6.9		7.2	
Monobromoacetic acid[d]	1		1.0	ND		ND	ND	ND	ND	ND	ND		ND	
Dichloroacetic acid[d]	1		29	29		24	19	21	23	24	24		24	
Bromochloroacetic acid[d]	1		6.1	6.0		4.6	3.7	4.4	4.9	5.1	5.1		4.8	
Dibromoacetic acid[d]	1		1.0	1.0		ND	ND	ND	ND	ND	ND		ND	
Trichloroacetic acid[d]	1		54	55		44	22	45	40	43	44		35	
Bromodichloroacetic acid	1		11	10		9.1	5.3	9.2	8.5	9.1	8.8		8.2	
Dibromochloroacetic acid	1		1.7	1.7		1.4	1.0	1.3	1.2	1.4	1.4		1.0	
Tribromoacetic acid	2		ND	ND		ND	ND	ND	ND	ND	ND		ND	
HAA5[g]			95	95		77	42	74	70	73	75		66	
HAA9[h]			114	113		92	52	89	84	89	90		80	
DXAA[i]			36	36		29	23	25	28	29	29		29	
TXAA[j]			67	67		55	28	56	50	54	54		44	
Haloacetonitriles														
Chloroacetonitrile	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromoacetonitrile	0.10	ND	ND	1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[d]	0.10	ND	4	4	ND	3	2	2	2	2	3	3	2	3
Bromochloroacetonitrile[d]	0.10	ND	2	2	ND	1	0.5	0.5	0.6	0.7	0.9	1	0.7	1
Dibromoacetonitrile[d]	0.10	ND	0.2	0.2	ND	0.1	ND	ND	ND	0.1	0.1	0.1	0.1	0.1
Trichloroacetonitrile[d]	0.10	ND	0.5	0.6	0.1	ND	0.2	0.4	0.3	0.4	0.4	ND	ND	ND
Haloketones														
Chloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	0.2	0.2	ND	ND	ND	ND
1,1-Dichloropropanone[d]	0.10	ND	1	1	ND	0.9	1	0.7	0.8	0.8	0.9	1	0.8	1
1,3-Dichloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	N/A			NR	NR	NR		NR	NR	NR	NR		NR	
1,1,1-Trichloropropanone[d]	0.10	ND	4	4	ND	3	2	3	3	3	3	3	3	3
1,1,3-Trichloropropanone	0.10	ND	0.1	0.1	ND	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.1	0.1
1-Bromo-1,1-dichloropropanone	N/A			NR	NR	NR		NR	NR	NR	NR		NR	
1,1,1-Tribromopropanone	N/A			NR	NR	NR		NR	NR	NR	NR		NR	
1,1,3-Tribromopropanone	N/A			NR	NR	NR		NR	NR	NR	NR		NR	
1,1,3,3-Tetrachloropropanone	0.10	ND	0.6	0.3	ND	0.4	0.3	0.2	0.2	0.2	0.2	0.3	0.4	0.3
1,1,3,3-Tetrabromopropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetaldehydes														
Dichloroacetaldehyde	0.16	ND	5	5	ND	4	2	4	4	4	4	4	4	5
Bromochloroacetaldehyde	0.10	ND	1	1	ND	1	1	0.9	1	1	1	2	1	2
Chloral hydrate[d]	0.10	ND	4	5	ND	3	1	2	3	3	4	4	3	4
Tribromoacetaldehyde	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes														
Bromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	N/A			NR	NR	NR		NR	NR	NR	NR		NR	
Dibromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloropicrin	0.10	ND	1	1	ND	0.8	0.9	0.8	0.8	0.8	0.9	1	0.8	1
Miscellaneous Compounds														
Methyl ethyl ketone	N/A	NR		NR	NR	NR		NR	NR	NR	NR		NR	
Methyl *tertiary* butyl ether	0.16	ND		ND	ND	ND		ND	ND	ND	ND		ND	
Benzyl chloride	N/A	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR

Table 11. DBP results at Plant 9 (1/10/01)

01/10/2001	MRL[a]	Plant 9[k]								
Compound	µg/L	Raw	1^{O} Cond	Basin #6	Filt Inf	Finished	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes										
Chloromethane	0.15	ND[c]	ND	ND		ND	ND		ND	
Bromomethane	0.20	ND	ND	ND		ND	ND		ND	
Bromochloromethane	0.14	ND	ND	ND		ND	ND		ND	
Dibromomethane	0.11	ND	ND	ND		ND	ND		0.13	
Chloroform[d]	0.1	ND	1	2	3	3	3	3	3	3
Bromodichloromethane[d]	0.10	0.1	0.5	0.7	NR[e]	2	2	NR	2	NR
Dibromochloromethane[d]	0.07	ND	0.2	0.3	NR	0.8	1	NR	1	NR
Bromoform[d]	0.6	ND	ND	ND	ND	0.7	1	1	0.7	0.8
THM4[f]		0.1	2	3	NR	7	7	NR	7	NR
Dichloroiodomethane	0.25	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromochloroiodomethane	0.20	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibromoiodomethane	0.6	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.6	ND	ND	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.14	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.06	ND	ND	ND		ND	ND		ND	
Haloacetic acids										
Monochloroacetic acid[d]	2		ND	ND		ND	ND		ND	
Monobromoacetic acid[d]	1		ND	ND		ND	ND		ND	
Dichloroacetic acid[d]	1		2.2	2.5		3.1	3.4		3.5	
Bromochloroacetic acid[d]	1		1.0	1.1		1.4	1.6		1.5	
Dibromoacetic acid[d]	1		1.0	1.2		1.3	1.7		1.5	
Trichloroacetic acid[d]	1		ND	ND		ND	ND		ND	
Bromodichloroacetic acid	1		ND	ND		ND	ND		ND	
Dibromochloroacetic acid	1		ND	ND		ND	ND		ND	
Tribromoacetic acid	2		ND	ND		ND	ND		ND	
HAA5[g]			3.2	3.7		4.4	5.1		5.0	
HAA9[h]			4.2	4.8		5.8	6.7		6.5	
DXAA[i]			4.2	4.8		5.8	6.7		6.5	
TXAA[j]			ND	ND		ND	ND		ND	
Haloacetonitriles										
Chloroacetonitrile	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromoacetonitrile	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[d]	0.10	ND	0.1	0.1	0.3	0.3	0.3	0.2	0.2	0.1
Bromochloroacetonitrile[d]	0.10	ND	ND	ND	0.1	0.1	0.2	0.1	0.1	0.1
Dibromoacetonitrile[d]	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trichloroacetonitrile[d]	0.10	ND	0.1	0.1	0.1	ND	ND	ND	ND	ND
Haloketones										
Chloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloropropanone[d]	0.10	ND	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.2
1,3-Dichloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	N/A	NR	NR	NR		NR	NR		NR	
1,1,1-Trichloropropanone[d]	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3-Trichloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	N/A	NR	NR	NR		NR	NR		NR	
1,1,1-Tribromopropanone	N/A	NR	NR	NR		NR	NR		NR	
1,1,3-Tribromopropanone	N/A	NR	NR	NR		NR	NR		NR	
1,1,3,3-Tetrachloropropanone	0.10	0.2	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetaldehydes										
Dichloroacetaldehyde	0.16	ND	ND	0.5	0.6	0.6	0.6	0.8	0.9	1
Bromochloroacetaldehyde	0.10	ND	0.3	0.1	0.1	ND	ND	ND	ND	ND
Chloral hydrate[d]	0.10	ND	0.2	0.2	0.5	0.5	0.5	0.3	0.2	0.1
Tribromoacetaldehyde	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes										
Bromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	N/A	NR	NR	NR		NR	NR		NR	
Dibromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[d]	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
Miscellaneous Compounds										
Methyl ethyl ketone	N/A	NR	NR	NR		NR	NR		NR	
Methyl *tertiary* butyl ether	0.16	0.3	ND	ND		ND	0.3		ND	
Benzyl chloride	N/A	NR	NR	NR	NR	NR	NR	NR	NR	NR

[k]Plant 9 sampled at (1) raw water, (2) primary conditioner, (3) basin #6 effluent, (4) filter influent, (5) finished water, distribution system (DS) at (6) average and at (7) maximum detention times, and SDS testing of finished water at (8) average and at (9) maximum detention times

[a]MRL = Minimum reporting level, which equals method detection limit (MDL)
or lowest calibration standard or concentration of blank
[b]Plant 10 sampled at train for Aldrich Purification units at (1) raw water, (2) filter influent, and (3) clearwell effluent;
at conventional treatment train at (4) raw water, (5) basins 4&5 effluent, (6) basins 1&2 effluent, (7) combined filter effluent, and (8) clearwell effluent;
and for combined treated waters at (9) finished water, distribution system (DS) at (10) average and at (11) maximum detention times,
and SDS testing of finished water at (12) average and at (13) maximum detention times
[c]ND = Not detected at or above MRL
[d]DBP in the Information Collection Rule (ICR) (note: some utilities collected data for all 9
haloacetic acids for the ICR, but monitoring for only 6 haloacetic acids was required)
[e]NR = Not reported, due to interference problem on gas chromatograph or to problem with quality assurance
[f]THM4 = Sum of 4 THMs (chloroform, bromodichloromethane, dibromochloromethane, bromoform)
[g]HAA5 = Sum of 5 haloacetic acids (monochloro-, monobromo-, dichloro-, dibromo-, trichloroacetic acid)
[h]HAA9 = Sum of 9 haloacetic acids
[i]DXAA = Sum of dihaloacetic acids (dichloro-, bromochloro-, dibromoacetic acid)
[j]TXAA = Sum of trihaloacetic acids (trichloro-, bromodichloro-, dibromochoro-, tribromoacetic acid)

Table 12. Additional target DBP results (µg/L) at Mississippi River WTPs (1/10/01)

1/10/01	Plant 9[a]					Plant 10[b]				
Compound	Raw	PC	PE	DS	SDS	Raw	B4&5	B1&2	FE	PE
Monochloroacetaldehyde	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.8	0.8	0.4
Dichloroacetaldehyde	0.0	0.0	0.9	0.9	0.9	0.0	4.6	3.9	3.7	3.6
Bromochloroacetaldehyde	0.0	0.0	0.0	0.0	0.0	0.0	0.8	2.0	0.7	1.3
3,3-Dichloropropenoic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.4	0.6	0.8
Bromochloromethylacetate	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2,2-Dichloroacetamide	0.0	0.0	0.0	0.0	0.0	0.0	2.1	1.5	1.9	1.7
TOX (µg/L as Cl^-)	7.4	58.7	64.4	55.7	61.5	13.7	222	252	203	237
Cyanoformaldehyde	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
5-Keto-1-hexanal	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6-Hydroxy-2-hexanone	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Dimethylglyoxal	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
trans-2-Hexenal	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

[a]Plant 9 sampled at (1) raw water, (2) primary conditioner (PC), (3) finished water at plant effluent (PE), (4) distribution system (DS) at average detention time, and (5) SDS at maximum detection time.
[b]Plant 10 sampled at (1) raw water, (2) effluent of basins 4 and 5 (B4&5), (3) effluent of basins 1 and 2 (B1&2), (4) filter effluent (FE), and (5) PE.

Table 13. DBP results at plant 10 (4/9/01)

04/9/2001	MRL[a]	Aldrich[l]		Conventional[l]				Combined Plant[l]			
Compound	µg/L	Raw	Clearwell	Raw	Basins 4&5	Basins 1&2	Filt Eff	Finished	DS/Ave	SDS/Ave	SDS/Max
Halomethanes											
Chloromethane	0.5	ND[c]	ND	ND	ND		ND	ND	ND	ND	
Bromomethane	0.20	ND	ND	ND	ND		ND	ND	ND	ND	
Bromochloromethane	0.14	ND	ND	ND	ND		ND	ND	ND	ND	
Dibromomethane	0.11	ND	ND	ND	ND		ND	ND	ND	ND	
Chloroform[d]	0.1	ND	54	ND	40	22	46	50	45	42	54
Bromodichloromethane[d]	0.1	ND	15	ND	12	8	14	10	14	13	16
Dibromochloromethane[d]	0.1	ND	2	ND	2	0.8	2	1	2	2	2
Bromoform[d]	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
THM4[f]		ND	71	ND	54	31	62	61	61	57	72
Dichloroiodomethane	0.2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromochloroiodomethane	0.20	ND	ND	ND	ND	NR	ND	ND	ND	ND	NR
Dibromoiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.06	ND	0.12	ND	ND		0.11	0.10	0.13	0.10	
Tribromochloromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids											
Monochloroacetic acid[d]	2		13		14	4.0	8.6	7.5	7.5	7.8	
Monobromoacetic acid[d]	1		ND		ND	ND	ND	ND	ND	ND	
Dichloroacetic acid[d]	1		33		36	23	21	27	25	28	
Bromochloroacetic acid[d]	1		5.6		6.5	3.7	3.0	5.3	4.8	5.0	
Dibromoacetic acid[d]	1		ND		ND	ND	ND	ND	ND	ND	
Trichloroacetic acid[d]	1		37		40	24	35	37	35	36	
Bromodichloroacetic acid	1		13		15	5.1	11	12	11	12	
Dibromochloroacetic acid	1		1.9		2.2	1.1	1.6	1.8	1.6	1.6	
Tribromoacetic acid	2		ND		ND	ND	ND	ND	ND	ND	
HAA5[g]			83		90	51	65	72	68	72	
HAA9[h]			104		114	61	80	91	85	90	
DXAA[i]			39		43	27	24	32	30	33	
TXAA[j]			52		57	30	48	51	48	50	
Haloacetonitriles											
Chloroacetonitrile	0.1	ND	0.5	ND	0.2	ND	0.2	0.1	0.3	0.2	0.3
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[d]	0.10	ND	8	ND	7	3	3	3	4	4	4
Bromochloroacetonitrile[d]	0.1	ND	1	ND	1	0.5	0.5	0.4	0.7	0.7	1
Dibromoacetonitrile[d]	0.2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trichloroacetonitrile[a]	0.1	ND	0.4	ND	0.2	0.2	0.3	0.2	0.3	0.3	0.1
Haloketones											
Chloropropanone	0.5	ND	0.8	ND	0.5	ND	0.7	0.5	0.9	0.7	0.6
1,1-Dichloropropanone[d]	0.10	ND	1	ND	0.9	1	0.6	0.5	1	1	2
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloropropanone[d]	0.1	ND	6	ND	8	2	6	3	4	5	3
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	0.3	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	0.1	ND	0.6	ND	0.8	0.4	0.5	0.3	0.4	0.4	ND
1,1,1-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3-Tribromopropanone	0.14	ND	ND	ND	ND	0.1	ND	ND	ND	ND	ND
1,1,3,3-Tetrachloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	0.10	ND	ND	ND	0.1	0.1	ND	ND	ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetaldehydes											
Dichloroacetaldehyde	0.22	0.2	2	ND	2	2	1	1	2	2	3
Bromochloroacetaldehyde	0.1	ND	ND	ND	ND	0.4	ND	ND	ND	ND	0.2
Chloral hydrate[d]	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Tribromoacetaldehyde	0.1	ND	ND	ND	ND	0.2	ND	ND	ND	ND	ND
Halonitromethanes											
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	0.5	ND	0.4	ND	0.4	0.2	0.3	ND	0.3	0.3	0.1
Bromochloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[d]	0.1	ND	2	ND	2	2	2	2	2	2	3
Miscellaneous Compounds											
Methyl ethyl ketone	1.9	ND	ND	ND	ND		ND	ND	ND	ND	
Methyl *tertiary* butyl ether	0.16	ND	ND	ND	ND		ND	ND	ND	ND	
Benzyl chloride	NA	ND	ND	ND	ND	NR[e]	ND	ND	ND	ND	NR

[l]Plant 10 sampled at train for Aldrich Purification units at (1) raw water and (2) clearwell effluent;
at conventional treatment train at (3) raw water, (4) basins 4&5 effluent, (5) basins 1&2 effluent, and (6) combined filter effluent;
and for combined treated waters at (7) finished water and (8) DS at average detention time,
and SDS testing of finished water at (9) average and at (10) maximum detention times

Table 14. DBP results at Plant 9 (4/9/01)

04/9/2001	MRL[a]	Plant 9[k]								
Compound	µg/L	Raw	1^{O} Cond	Basin #6	Filt Inf	Finished	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes										
Chloromethane	0.15	ND[c]	ND	ND		ND	ND		ND	
Bromomethane	0.20	ND	ND	ND		ND	ND		ND	
Bromochloromethane	0.14	ND	ND	ND		ND	ND		ND	
Dibromomethane	0.11	ND	ND	ND		ND	ND		ND	
Chloroform[d]	0.1	ND	6	5	6	6	5	6	7	7
Bromodichloromethane[d]	0.1	ND	1	1	2	2	3	3	3	2
Dibromochloromethane[d]	0.1	ND	0.1	ND	0.3	0.3	0.4	0.4	0.3	0.3
Bromoform[d]	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
THM4[f]		ND	7	6	8	8	8	9	10	9
Dichloroiodomethane	0.2	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromochloroiodomethane	0.20	ND	ND	ND	NR[e]	ND	ND	NR	ND	NR
Dibromoiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.06	ND	ND	ND		ND	ND		ND	
Tribromochloromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids										
Monochloroacetic acid[d]	2		ND	ND		ND	ND		ND	
Monobromoacetic acid[d]	1		ND	ND		ND	ND		ND	
Dichloroacetic acid[d]	1		11	12		15	14		18	
Bromochloroacetic acid[d]	1		1.4	1.3		2.9	2.6		2.4	
Dibromoacetic acid[d]	1		ND	ND		ND	ND		ND	
Trichloroacetic acid[d]	1		1.1	1.3		2.7	2.1		2.3	
Bromodichloroacetic acid	1		ND	ND		ND	ND		ND	
Dibromochloroacetic acid	1		ND	ND		ND	ND		ND	
Tribromoacetic acid	2		ND	ND		ND	ND		ND	
HAA5[g]			12	13		18	16		20	
HAA9[h]			14	15		21	19		23	
DXAA[i]			12	13		18	17		20	
TXAA[j]			1.1	1.3		2.7	2.1		2.3	
Haloacetonitriles										
Chloroacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[d]	0.10	ND	0.4	ND	0.3	0.3	0.1	0.1	0.1	0.1
Bromochloroacetonitrile[d]	0.1	ND	ND	ND	0.1	0.1	0.1	ND	ND	ND
Dibromoacetonitrile[d]	0.2	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trichloroacetonitrile[d]	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Haloketones										
Chloropropanone	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloropropanone[d]	0.10	ND	0.7	0.3	0.4	0.4	0.2	0.2	0.1	0.1
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloropropanone[d]	0.1	ND	0.1	0.1	ND	0.4	ND	ND	ND	ND
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	0.3	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	0.1	ND	ND	ND	ND	0.1	ND	ND	ND	ND
1,1,1-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3-Tribromopropanone	0.14	ND	ND	ND	ND	0.1	ND	ND	ND	ND
1,1,3,3-Tetrachloropropanone	0.1	ND	ND	0.1	ND	ND	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	0.10	ND	ND	0.1	ND	0.1	ND	ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.6	ND	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetaldehydes										
Dichloroacetaldehyde	0.22	ND	1	2	2	3	2	2	2	2
Bromochloroacetaldehyde	0.1	ND	ND	ND	ND	0.2	ND	ND	ND	ND
Chloral hydrate[d]	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Tribromoacetaldehyde	0.1	ND	ND	0.1	ND	0.4	ND	ND	ND	ND
Halonitromethanes										
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	0.5	ND	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.2
Bromochloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[d]	0.1	ND	0.1	ND	0.2	0.2	0.1	0.1	0.1	ND
Miscellaneous Compounds										
Methyl ethyl ketone	1.9	ND	ND	ND		ND	ND		ND	
Methyl *tertiary* butyl ether	0.16	ND	ND	ND		ND	ND		ND	
Benzyl chloride	NA	ND	ND	ND	NR	ND	ND	NR	ND	NR

Table 15. Occurrence of other DBPs[a] at Mississippi River WTPs: finished waters at plant effluents

Compound	Plant 10		Plant 9
	4/9/01	2/25/02	8/27/01
Halomethanes			
Bromodichloromethane[b]	x	x	x
Dibromochloromethane	x	x	x
Bromoform	x	-	x
Dichloroiodomethane	x	x	x
Bromochloroiodomethane	x	x	x
Haloacids			
Dichloroacetic acid	x	x	x
Bromochloroacetic acid	x	x	x
Dibromoacetic acid	-	-	x
Bromodichloroacetic acid	x	-	-
Trichloroacetic acid	x	x	-
3,4,4-Trichloro-3-butenoic acid	x	-	-
cis-2-Bromo-3-methylbutenedioic acid	x	-	-
Haloacetonitriles			
Dichloroacetonitrile	x	x	x
Bromochloroacetonitrile	x	x	x
Dibromoacetonitrile	x	x	x
Dibromochloroacetonitrile	x	-	-
Haloaldehydes			
2-Bromo-2-methylpropanal	x	x	x
Haloketones			
1,1-Dichloropropanone	x	x	-
1-Bromo-1-chloropropanone	x	x	-
1,1,1-Trichloropropanone	x	-	-
1-Bromo-1,1-dichloropropanone	x	-	-
1,1,3-Tribromo-3-chloropropanone	-	-	x
1,1,3,3-Tetrabromopropanone	-	-	x
Pentachloropropanone	x	-	x
Hexachloropropanone	x	-	-
Halonitromethanes			
Dichloronitromethane	x	x	-
Bromochloronitromethane	x	-	-
Bromodichloronitromethane	x	-	-
Halofuranones			
Ox-MX	x	-	-
Miscellaneous Halogenated DBPs			
1,2-Dichloroethylbenzene	x	-	-
Dichlorophenol	-	-	x
Tetrachlorocyclopentadiene	x	-	-
Hexachlorocyclopentadiene	x	-	-
Bromopentachlorocyclopentadiene	x	-	-
Non-halogenated DBPs			
Glyoxal	x	-	-
4-Methylpentanoic acid	-	-	x
Dodecanoic acid	x	-	-

[a]DBPs detected by broadscreen gas chromatography/mass spectrometry (GC/MS) technique.
[b]Compounds listed in italics were confirmed through the analysis of authentic standards; haloacids and non-halogenated carboxylic acids identified as their methyl esters.

Table 16. DBP results at plant 10 (9/5/01)

09/05/2001	MRL[a]	Aldrich[l]		Conventional[l]				Combined Plant[l]			
Compound	µg/L	Raw	Clearwell	Raw	Basins 4&5	Basins 1&2	Filt Eff	Finished	DS/Ave	SDS/Ave	SDS/Max
Halomethanes											
Chloromethane	0.2	ND[c]	ND	ND	ND		ND	ND	ND	ND	
Bromomethane	0.2	ND	ND	ND	ND		ND	ND	ND	ND	
Bromochloromethane	0.5	ND	ND	ND	ND		ND	ND	ND	ND	
Dibromomethane	0.5	ND	ND	ND	ND		ND	ND	ND	ND	
Chloroform[d]	0.1	ND	100	0.2	100	120	110	120	150	120	270
Bromodichloromethane[d]	0.1	ND	40	ND	40	50	40	40	50	30	60
Dibromochloromethane[d]	0.1	ND	4	ND	4	4	4	4	6	4	9
Bromoform[d]	0.1	ND	ND	ND	ND	ND	ND	ND	ND	0.2	0.2
THM4[f]	0	ND	144	ND	144	174	154	164	206	154	339
Dichloroiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromochloroiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibromoiodomethane	0.52	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.2	ND	0.3	ND	ND		ND	ND	ND	ND	
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids											
Monochloroacetic acid[d]	2		9.0		5.9	6.5	ND	2.4	5.2	ND	
Monobromoacetic acid[d]	1		1.2		1.1	1.2	ND	ND	1.0	ND	
Dichloroacetic acid[d]	1		64		51	53	13	24	41	26	
Bromochloroacetic acid[d]	1		9.4		9.0	9.0	2.4	4.4	6.1	5.4	
Dibromoacetic acid[d]	1		ND		1.0	1.0	ND	ND	ND	ND	
Trichloroacetic acid[d]	1		91		90	85	73	80	87	82	
Bromodichloroacetic acid	1		19		16	18	16	17	18	18	
Dibromochloroacetic acid	1		1.2		1.9	1.1	1.1	1.7	1.2	1.8	
Tribromoacetic acid	2		3.3		2.7	2.5	ND	ND	2.4	ND	
HAA5[g]			165		149	147	86	106	134	108	
HAA9[h]			198		179	177	106	130	162	133	
DXAA[i]			73		61	63	15	28	47	31	
TXAA[j]			115		111	107	90	99	109	102	
Haloacetonitriles											
Chloroacetonitrile	0.1	ND	1	ND	0.6	0.8	0.6	0.7	0.9	1	0.9
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND	0.2	0.3
Dichloroacetonitrile[d]	0.1	ND	22	ND	21	23	9	12	19	16	18
Bromochloroacetonitrile[d]	0.1	ND	1	ND	2	2	0.6	1	2	1	1
Dibromoacetonitrile[d]	0.1	ND	0.2	ND	0.4	ND	ND	ND	0.3	ND	0.2
Trichloroacetonitrile[d]	0.1	ND	ND	ND	0.2	0.2	0.1	0.1	ND	ND	ND
Bromodichloroacetonitrile	0.5			ND	0.8		ND	ND			
Dibromochloroacetonitrile	0.5			ND	ND		ND	ND			
Tribromoacetonitrile	0.91			ND	ND		ND	ND			
Haloketones											
Chloropropanone	0.1	ND	0.5	ND	0.7	0.7	0.8	0.8	1	0.7	0.8
1,1-Dichloropropanone[d]	0.10	ND	0.5	ND	0.6	1	0.9	0.8	0.4	0.5	0.2
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloropropanone[d]	0.1	ND	7	ND	9	8	6	7	7	7	0.8
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	0.1	ND	ND	ND	0.3	ND	ND	ND	ND	ND	ND
1,1,1-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	NR[e]	NR
1,1,3-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrachloropropanone	0.1	ND	0.2	ND	0.2	1	ND	ND	0.3	0.3	0.1
1,1,1,3-Tetrachloropropanone	0.10	ND	0.3	ND	0.3	0.8	0.5	0.4	0.3	0.4	0.2
1,1,3,3-Tetrabromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table 16 (continued)

09/05/2001	MRL[a]	Aldrich[l]		Conventional[l]				Combined Plant[l]			
Compound	µg/L	Raw	Clearwell	Raw	Basins 4&5	Basins 1&2	Filt Eff	Finished	DS/Ave	SDS/Ave	SDS/Max
Haloacetaldehydes											
Dichloroacetaldehyde	0.221	ND	4	ND	4	7	3	4	3	4	2
Bromochloroacetaldehyde	0.5	ND	2	ND	2	2	0.7	ND	ND	1	ND
Chloral hydrate[d]	0.1	ND	29	2	22	22	16	16	26	28	62
Tribromoacetaldehyde	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes											
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	0.1	ND	0.3	ND	0.4	0.2	ND	ND	0.2	0.2	0.3
Bromochloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[d]	0.1	ND	2	ND	1	0.8	0.8	0.7	1	0.7	1
Bromodichloronitromethane	0.5			ND	0.9		0.5	0.6			
Dibromochloronitromethane	0.505			ND	ND		ND	ND			
Bromopicrin	2.1			ND	ND		ND	ND			
Miscellaneous Compounds											
Methyl ethyl ketone	0.5	ND	ND	ND	0.6		0.6	0.6	0.6	0.7	
Methyl *tertiary* butyl ether	0.2	1.6	1.0	1.3	1.0		1.0	0.9	0.8	1.0	
Benzyl chloride	0.5	ND	ND	ND	ND	NR	ND	ND	ND	ND	NR
1,1,2,2-Tetrabromo-2-chloroethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table 17. DBP results at plant 9 (8/27/01)

08/27/2001	MRL[a]	Plant 9[k]								
Compound	µg/L	Raw	1^{O} Cond	Basin #6	Filt Inf	Finished	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes										
Chloromethane	0.2	ND[c]	ND	ND		ND	ND		ND	
Bromomethane	0.2	ND	ND	ND		ND	ND		ND	
Bromochloromethane	0.5	ND	ND	ND		ND	ND		ND	
Dibromomethane	0.5	ND	ND	ND		ND	ND		ND	
Chloroform[d]	0.1	ND	4	4	5	4	6	8	5	5
Bromodichloromethane[d]	0.1	ND	2	2	2	2	3	2	3	2
Dibromochloromethane[d]	0.1	ND	0.3	0.5	0.9	1	1	0.7	1	1
Bromoform[d]	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
THM4[f]		ND	6	7	8	7	10	11	9	8
Dichloroiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromochloroiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibromoiodomethane	0.52	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chlorodiiodomethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.2	ND	ND	ND		ND	ND		ND	
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids										
Monochloroacetic acid[d]	2		ND	ND		ND	ND		ND	
Monobromoacetic acid[d]	1		ND	ND		ND	ND		ND	
Dichloroacetic acid[d]	1		8.4	11		15	18		17	
Bromochloroacetic acid[d]	1		1.7	1.6		2.9	3.5		3.7	
Dibromoacetic acid[d]	1		ND	ND		1.1	1.3		ND	
Trichloroacetic acid[d]	1		1.3	1.1		1.3	1.6		1.2	
Bromodichloroacetic acid	1		ND	ND		1.0	1.0		ND	
Dibromochloroacetic acid	1		ND	ND		ND	ND		ND	
Tribromoacetic acid	2		ND	ND		ND	ND		ND	
HAA5[g]			9.7	12		17	21		18	
HAA9[h]			11	14		21	25		22	
DXAA[i]			10	13		19	23		21	
TXAA[j]			1.3	1.1		2.3	2.6		1.2	
Haloacetonitriles										
Chloroacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[d]	0.1	ND	0.5	ND	ND	ND	ND	ND	ND	ND
Bromochloroacetonitrile[d]	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibromoacetonitrile[d]	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trichloroacetonitrile[d]	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodichloroacetonitrile	0.5	ND	ND			ND				ND
Dibromochloroacetonitrile	0.5	ND	ND			ND				ND
Tribromoacetonitrile	0.91	ND	ND			ND				ND
Haloketones										
Chloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	0.1	ND
1,1-Dichloropropanone[d]	0.10	ND	0.7	ND	ND	ND	ND	ND	ND	ND
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloropropanone[d]	0.1	ND	0.3	ND	ND	ND	ND	ND	ND	ND
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrachloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	0.10	ND	ND	0.5	0.2	0.2	ND	ND	ND	0.4
1,1,3,3-Tetrabromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table 17 (continued)

08/27/2001	MRL[a]	Plant 9[k]								
Compound	µg/L	Raw	1[O] Cond	Basin #6	Filt Inf	Finished	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloacetaldehydes										
Dichloroacetaldehyde	0.221	ND	1	1	0.6	1	0.9	ND	0.2	0.9
Bromochloroacetaldehyde	0.5	ND	ND	ND	ND	ND	ND	ND	ND	0.8
Chloral hydrate[d]	0.1	ND	0.5	0.5	ND	0.3	0.2	ND	ND	0.6
Tribromoacetaldehyde	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Halonitromethanes										
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromochloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[d]	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodichloronitromethane	0.5	ND	ND			ND				0.6
Dibromochloronitromethane	0.51	ND	ND			0.6				ND
Bromopicrin	2.1	ND	ND			ND				ND
Miscellaneous Compounds										
Methyl ethyl ketone	0.5	ND	ND	ND		1	0.5		0.5	
Methyl *tertiary* butyl ether	0.2	0.2	ND	ND		ND	ND		ND	
Benzyl chloride	0.5	ND	ND	ND	NR[e]	ND	ND	NR	ND	NR
1,1,2,2-Tetrabromo-2-chloroethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table 18. DBP results at plant 10 (11/26/01)

11/26/2001	MRL[a]	Aldrich[l]		Conventional[l]				Combined Plant[l]			
Compound	µg/L	Raw	Clearwell	Raw	Basins 4&5	Basins 1&2	Filt Eff	Finished	DS/Ave	SDS/Ave	SDS/Max
Halomethanes											
Chloromethane	0.2	ND[c]	ND	ND	ND		ND	ND	ND	ND	
Bromomethane	0.2	ND	ND	ND	ND		ND	ND	ND	ND	
Bromochloromethane	0.5	ND	ND	ND	ND		ND	ND	ND	ND	
Dibromomethane	0.5	ND	ND	ND	ND		ND	ND	ND	ND	
Chloroform[d]	0.2	ND	13	ND	10	NS[m]	12	12	14	12	NA[n]
Bromodichloromethane[d]	0.1	ND	5	ND	4	NS	4	4	5	5	NA
Dibromochloromethane[d]	0.1	ND	0.6	ND	0.4	NS	0.4	0.5	0.6	0.6	NA
Bromoform[d]	0.11	ND	ND	ND	ND	NS	ND	ND	ND	ND	NA
THM4[f]	0	ND	19	ND	14	NS	16	17	20	18	NA
Dichloroiodomethane	0.5	ND	1	ND	1	NS	0.9	1	1	1	NA
Bromochloroiodomethane	0.5	ND	ND	ND	ND	NS	ND	ND	ND	ND	NA
Dibromoiodomethane	0.52	ND	ND	ND	ND	NS	ND	ND	ND	ND	NA
Chlorodiiodomethane	0.1	ND	ND	ND	ND	NS	ND	ND	ND	ND	NA
Bromodiiodomethane	0.5	ND	ND	ND	ND	NS	ND	ND	ND	ND	NA
Iodoform	2	ND	ND	ND	ND	NS	ND	ND	ND	ND	NA
Carbon tetrachloride	0.2	ND	0.3	ND	ND		ND	ND	ND	ND	
Tribromochloromethane	0.5	ND	ND	ND	ND	NS	ND	ND	ND	ND	NA
Haloacetic acids											
Monochloroacetic acid[d]	2		ND		2.8	NS	ND	ND	3.5	ND	
Monobromoacetic acid[d]	1		1.2		ND	NS	1.0	ND	1.3	1.2	
Dichloroacetic acid[d]	1		16		14	NS	6.2	11	13	11	
Bromochloroacetic acid[d]	1		2.3		2.0	NS	ND	2.4	2.2	2.4	
Dibromoacetic acid[d]	1		ND		ND	NS	ND	ND	ND	ND	
Trichloroacetic acid[d]	1		6.5		5.4	NS	4.4	6.1	6.0	6.1	
Bromodichloroacetic acid	1		1.1		ND	NS	ND	1.0	ND	1.0	
Dibromochloroacetic acid	1		ND		ND	NS	ND	ND	ND	ND	
Tribromoacetic acid	2		ND		ND	NS	ND	ND	ND	ND	
HAA5[g]			24		22	NS	12	17	24	18	
HAA9[h]			27		24	NS	12	21	26	22	
DXAA[i]			18		16	NS	6.2	13	15	13	
TXAA[j]			7.6		5.4	NS	4.4	7.1	6.0	7.1	
Haloacetonitriles											
Chloroacetonitrile	0.1	ND	ND	ND	ND	NS	ND	ND	ND	ND	NA
Bromoacetonitrile	0.1	ND	ND	ND	ND	NS	ND	ND	ND	ND	NA
Dichloroacetonitrile[d]	0.1	ND	2	ND	1	NS	0.7	1	2	1	NA
Bromochloroacetonitrile[d]	0.1	ND	ND	ND	ND	NS	ND	ND	0.3	0.2	NA
Dibromoacetonitrile[d]	0.14	ND	ND	ND	ND	NS	ND	ND	ND	ND	NA
Trichloroacetonitrile[d]	0.1	ND	ND	ND	ND	NS	ND	ND	ND	ND	NA
Bromodichloroacetonitrile	0.5			ND	ND		ND	ND			
Dibromochloroacetonitrile	0.5			ND	ND		ND	ND			
Tribromoacetonitrile	0.5			ND	ND		ND	ND			
Haloketones											
Chloropropanone	0.1	ND	ND	ND	ND	NS	ND	ND	ND	ND	NA
1,1-Dichloropropanone[d]	0.10	ND	1	ND	1	NS	0.6	0.8	1	0.8	NA
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	NS	ND	ND	ND	ND	NA
1,1-Dibromopropanone	0.1	ND	ND	ND	ND	NS	ND	ND	ND	ND	NA
1,1,1-Trichloropropanone[d]	0.1	ND	1	ND	1	NS	0.8	0.9	1	0.9	NA
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	NS	ND	ND	ND	ND	NA
1-Bromo-1,1-dichloropropanone	0.1	ND	ND	ND	ND	NS	ND	ND	ND	ND	NA
1,1,1-Tribromopropanone	2.5	NR	ND	ND	ND	NS	ND	ND	ND	ND	NA
1,1,3-Tribromopropanone	0.14	ND	ND	ND	ND	NS	ND	ND	ND	ND	NA
1,1,3,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	NS	ND	ND	ND	ND	NA
1,1,1,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	NS	ND	ND	ND	ND	NA
1,1,3,3-Tetrabromopropanone	0.5	ND	ND	ND	ND	NS	ND	ND	ND	ND	NA

Table 18 (continued)

11/26/2001	MRL[a]	Aldrich[l]		Conventional[l]				Combined Plant[l]			
Compound	µg/L	Raw	Clearwell	Raw	Basins 4&5	Basins 1&2	Filt Eff	Finished	DS/Ave	SDS/Ave	SDS/Max
Haloacetaldehydes											
Dichloroacetaldehyde	1.1	ND	4	ND	2	NS	2	2	3	2	NA
Bromochloroacetaldehyde	0.5	ND	0.9	ND	0.6	NS	ND	0.6	1	1	NA
Chloral hydrate[d]	0.1	ND	2	ND	1	NS	1	1	2	1	NA
Tribromoacetaldehyde	0.1	ND	ND	ND	ND	NS	ND	ND	ND	ND	NA
Halonitromethanes											
Bromonitromethane	0.1	ND	ND	ND	ND	NS	ND	ND	ND	ND	NA
Dichloronitromethane	0.1	ND	ND	ND	ND	NS	ND	ND	0.1	0.1	NA
Bromochloronitromethane	0.1	ND	ND	ND	ND	NS	ND	ND	ND	ND	NA
Dibromonitromethane	0.10	ND	ND	ND	ND	NS	ND	ND	ND	ND	NA
Chloropicrin[d]	0.1	ND	0.8	ND	0.4	NS	0.5	0.5	0.7	0.6	NA
Bromodichloronitromethane	0.5			ND	ND		ND	ND			
Dibromochloronitromethane	0.5			ND	ND		ND	ND			
Bromopicrin	0.90			ND	ND		ND	ND			
Miscellaneous Compounds											
Methyl ethyl ketone	0.5	ND	ND	ND	ND		ND	ND	ND	ND	
Methyl *tertiary* butyl ether	0.2	ND	ND	ND	ND		ND	ND	ND	ND	
Benzyl chloride	0.25	NR	ND	ND	ND	NS	ND	ND	ND	ND	NA
1,1,2,2-Tetrabromo-2-chloroethane	0.5	ND	ND	ND	ND	NS	ND	ND	ND	ND	NA

[m]NS = Not sampled

[n]NA = Not available

Table 19. DBP results at plant 9 (11/26/01)

11/26/2001	MRL[a]	Plant 9[k]								
Compound	µg/L	Raw	1[O] Cond	Basin #6	Filt Inf	Finished	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes										
Chloromethane	0.2	ND[c]	ND	ND		ND	ND		ND	
Bromomethane	0.2	ND	ND	ND		ND	0.2		ND	
Bromochloromethane	0.5	ND	ND	ND		ND	ND		ND	
Dibromomethane	0.5	ND	ND	ND		ND	ND		ND	
Chloroform[d]	0.2	ND	4	2	2	3	4	6	2	NA[n]
Bromodichloromethane[d]	0.1	ND	2	2	2	3	5	6	2	NA
Dibromochloromethane[d]	0.1	ND	0.9	0.9	2	2	4	4	2	NA
Bromoform[d]	0.11	ND	ND	0.1	0.4	0.4	1	1	0.5	NA
THM4[f]		ND	7	5	6	8	14	17	7	NA
Dichloroiodomethane	0.5	ND	<0.5[o]	<0.5	NR[e]	1	2	NR	1	NA
Bromochloroiodomethane	0.5	ND	ND	ND	ND	ND	<0.5	ND	ND	NA
Dibromoiodomethane	0.52	ND	ND	ND	ND	ND	ND	ND	ND	NA
Chlorodiiodomethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	NA
Bromodiiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	NA
Iodoform	2	ND	ND	ND	ND	ND	ND	ND	ND	NA
Carbon tetrachloride	0.2	ND	ND	ND		ND	ND		ND	
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	NA
Haloacetic acids										
Monochloroacetic acid[d]	2		ND	ND		ND	2.4		2.9	
Monobromoacetic acid[d]	1		1.2	1.3		1.2	1.2		ND	
Dichloroacetic acid[d]	1		5.1	5.0		6.2	7.9		6.2	
Bromochloroacetic acid[d]	1		1.8	2.2		2.5	4.2		3.4	
Dibromoacetic acid[d]	1		1.0	1.3		2.1	3.0		1.9	
Trichloroacetic acid[d]	1		ND	ND		ND	ND		ND	
Bromodichloroacetic acid	1		ND	ND		ND	ND		ND	
Dibromochloroacetic acid	1		ND	ND		ND	ND		ND	
Tribromoacetic acid	2		ND	ND		ND	ND		ND	
HAA5[g]			7.3	7.6		9.5	15		11	
HAA9[h]			9.1	9.8		12	19		14	
DXAA[i]			7.9	8.5		11	15		12	
TXAA[j]			ND	ND		ND	ND		ND	
Haloacetonitriles										
Chloroacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND	NA
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	NA	NA
Dichloroacetonitrile[d]	0.10	ND	ND	ND	ND	ND	ND	ND	NA	NA
Bromochloroacetonitrile[d]	0.1	ND	ND	ND	ND	ND	ND	ND	ND	NA
Dibromoacetonitrile[d]	0.14	ND	ND	ND	ND	ND	ND	ND	ND	NA
Trichloroacetonitrile[d]	0.1	ND	ND	ND	ND	ND	ND	ND	NA	NA
Bromodichloroacetonitrile	0.5	ND	ND			ND				ND
Dibromochloroacetonitrile	0.5	ND	ND			ND				ND
Tribromoacetonitrile	0.5	ND	ND			ND				ND
Haloketones										
Chloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	NA
1,1-Dichloropropanone[d]	0.10	ND	0.1	ND	ND	ND	ND	ND	ND	NA
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	NA	NA
1,1-Dibromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	NA	NA
1,1,1-Trichloropropanone[d]	0.1	ND	ND	ND	ND	ND	ND	ND	ND	NA
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	NA	NA
1-Bromo-1,1-dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	NA
1,1,1-Tribromopropanone	2.5	ND	ND	ND	NR	ND	ND	NR	ND	NA
1,1,3-Tribromopropanone	0.14	ND	ND	ND	ND	ND	ND	ND	NA	NA
1,1,3,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	NA	NA
1,1,1,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	NA	NA
1,1,3,3-Tetrabromopropanone	0.5	ND	ND	ND	ND	ND	ND	ND	NA	NA

Table 19 (continued)

11/26/2001	MRL[a]	Plant 9[k]								
Compound	µg/L	Raw	1[O] Cond	Basin #6	Filt Inf	Finished	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloacetaldehydes										
Dichloroacetaldehyde	1.1	ND	1	2	2	2	3	2	NA	NA
Bromochloroacetaldehyde	0.5	ND	ND	ND	ND	ND	ND	ND	NA	NA
Chloral hydrate[d]	0.1	ND	0.3	ND	0.1	ND	0.6	0.4	NA	NA
Tribromoacetaldehyde	0.1	ND	ND	ND	ND	ND	ND	ND	NA	NA
Halonitromethanes										
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	NA	NA
Dichloronitromethane	0.1	ND	ND	ND	ND	ND	0.2	0.1	ND	NA
Bromochloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	NA
Dibromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND	ND	NA
Chloropicrin[d]	0.1	ND	ND	ND	ND	ND	0.3	ND	NA	NA
Bromodichloronitromethane	0.5	ND	ND			0.7				0.7
Dibromochloronitromethane	0.5	ND	ND			1				ND
Bromopicrin	0.90	ND	ND			2				3
Miscellaneous Compounds										
Methyl ethyl ketone	0.5	1	ND	ND		ND	0.8		1	
Methyl *tertiary* butyl ether	0.2	ND	ND	ND		ND	ND		ND	
Benzyl chloride	0.25	ND	ND	ND	NR	ND	ND	NR	ND	NA
1,1,2,2-Tetrabromo-2-chloroethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	NA

[o]<0.5 = Less than MRL (0.5 µg/L)

Table 20. Additional target DBP results (µg/L) at Mississippi River WTPs (11/26/01)

11/26/01	Plant 9[c]					Plant 10[d]					
Compound	Soft.	PC	PE	DS	SDS	Raw	B4&5	B1&2	FE	PE	SDS
Monochloroacetaldehyde	0.0	0.4	0.0		0.0	0.0	0.0		0.0	0.0	
Dichloroacetaldehyde	0.0	4.6	5.0		1.1	0.0	4.6		2.5	2.3	
Bromochloroacetaldehyde	0.0	0.2	0.2		0.0	0.0	0.6		0.4	0.80	
3,3-Dichloropropenoic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.4		0.4	0.4	
Bromochloromethylacetate	0.0	0.0	0.0	0.0	0.0	0.0	0.0	NA	0.0	0.0	0.0
TOX (µg/L as Cl^-)	2.8	82.7	66.4	99.2		29.5	207		144	175	
Cyanoformaldehyde	<0.1	<0.1	<0.1	NA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
5-Keto-1-hexanal	<0.1	<0.1	<0.1	NA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6-Hydroxy-2-hexanone	<0.1	<0.1	<0.1	NA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Dimethylglyoxal	0.3	0.3	0.2	NA	0.4	<0.1	0.7	<0.1	0.1	0.3	<0.1
trans-2-Hexenal	<0.1	<0.1	<0.1	NA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

[c]Plant 9 sampled at softened water rather than at raw water.
[d]Plant 10 also sampled at SDS at maximum detection time.

Table 21. Halogenated furanone results (µg/L) at Mississippi River WTPs (11/26/01)

11/26/01	Plant 9[c]					Plant 10[e]			
Compound	Soft.	PC	PE	DS	SDS	Raw	B4&5	FE	PE
BMX-1	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.03	<0.02	<0.02
BEMX-1	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
BMX-2	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
BEMX-2	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
BMX-3	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.02	<0.02	<0.02
BEMX-3	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
MX	<0.02	<0.02	<0.02 (0.018)	<0.02 (0.013)	NA	<0.02	0.40	<0.02	0.06
EMX	<0.02	<0.02	<0.02	<0.02	NA	<0.02	<0.02	<0.02	<0.02
ZMX	<0.02 (0.01)	0.03	0.02	<0.02	NA	<0.02	<0.02	0.04	<0.02
Ox-MX	<0.02	<0.02	<0.02	<0.02	NA	<0.02	<0.02	<0.02	<0.02
Mucochloric acid (ring)	<0.02	0.03	0.08	0.07	NA	<0.02	<0.02	0.03	<0.02
Mucochloric acid (open)	<0.02 (0.01)	0.03	0.08	0.10	NA	<0.02	<0.02	0.03	<0.02

[e]Plant 10 sampled at (1) raw water, (2) B4&5, (3) FE, and (4) PE.

Table 22. DBP results at plant 10 (2/25/02)

02/25/2002	MRL[a]	Aldrich[l]		Conventional[l]				Combined Plant[l]			
Compound	µg/L	Raw	Clearwell	Raw	Basins 4&5	Basins 1&2	Filt Eff	Finished	DS/Ave	SDS/Ave	SDS/Max
Halomethanes											
Chloromethane	0.2	ND[c]	ND	ND	ND		ND	ND	ND	ND	
Bromomethane	0.2	ND	ND	ND	ND		ND	ND	ND	ND	
Bromochloromethane	0.5	ND	ND	ND	ND		ND	ND	ND	ND	
Dibromomethane	0.5	ND	ND	ND	ND		ND	ND	ND	ND	
Chloroform[d]	0.2	ND	8	ND	5	NR[e]	8	10	11	11	NR
Bromodichloromethane[d]	0.2	ND	3	ND	2	NR	3	4	5	5	4
Dibromochloromethane[d]	0.2	ND	0.5	ND	0.4	NR	0.4	0.6	0.7	0.7	0.7
Bromoform[d]	0.2	ND	<0.2[p]	ND	<0.2	ND	<0.2	<0.2	<0.2	<0.2	ND
THM4[f]		ND	12	ND	8	NR	12	15	17	17	NR
Dichloroiodomethane	0.5	ND	<0.5	ND	ND	NR	<0.5	<0.5	<0.5	<0.5	NR
Bromochloroiodomethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibromoiodomethane	0.5	ND	ND	ND	ND	NR	ND	ND	ND	ND	NR
Chlorodiiodomethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodiiodomethane	0.52	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.2	ND	ND	ND	ND		ND	ND	ND	ND	
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids											
Monochloroacetic acid[d]	2		2.5		2.9	NR	ND	ND	ND	ND	
Monobromoacetic acid[d]	1		ND		ND	NR	ND	ND	ND	ND	
Dichloroacetic acid[d]	1		12		13	NR	14	14	14	12	
Bromochloroacetic acid[d]	1		2.2		2.2	NR	2.7	2.7	2.7	2.0	
Dibromoacetic acid[d]	1		ND		ND	NR	ND	ND	ND	ND	
Trichloroacetic acid[d]	1		6.2		6.9	NR	11	11	11	6.9	
Bromodichloroacetic acid	1		1.3		1.4	NR	2.6	2.6	2.5	1.4	
Dibromochloroacetic acid	1		3.0		4.0	NR	2.9	2.5	2.7	1.4	
Tribromoacetic acid	2		ND		ND	NR	ND	ND	ND	ND	
HAA5[g]			21		23	NR	25	25	25	19	
HAA9[h]			27		30	NR	33	33	33	24	
DXAA[i]			14		15	NR	17	17	17	14	
TXAA[j]			11		12	NR	17	16	16	9.7	
Haloacetonitriles											
Chloroacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[d]	0.2	ND	0.4	ND	0.5	NR	0.4	0.5	0.4	0.4	NR
Bromochloroacetonitrile[d]	0.2	NR	ND	ND	ND	NR	ND	ND	ND	ND	NR
Dibromoacetonitrile[d]	1.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trichloroacetonitrile[d]	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodichloroacetonitrile	0.5			ND	ND		ND	ND			
Dibromochloroacetonitrile	0.5			ND	ND		ND	ND			
Tribromoacetonitrile	0.955			ND	ND		ND	ND			
Haloketones											
Chloropropanone	0.5	ND	ND	ND	ND	NR	ND	ND	ND	ND	NR
1,1-Dichloropropanone[d]	1.0	ND	<1[q]	ND	<1	NR	ND	<1	<1	<1	NR
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloropropanone[d]	0.5	NR	0.9	ND	0.6	NR	0.5	0.9	1	0.7	NR
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	0.1	ND	ND	ND	ND	0.1	ND	ND	ND	<1	ND
1,1,1-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table 22 (continued)

02/25/2002	MRL[a]	Aldrich[l]		Conventional[l]				Combined Plant[l]			
Compound	µg/L	Raw	Clearwell	Raw	Basins 4&5	Basins 1&2	Filt Eff	Finished	DS/Ave	SDS/Ave	SDS/Max
Haloacetaldehydes											
Dichloroacetaldehyde	0.98	ND	2	ND	2	3	2	2	2	4	3
Bromochloroacetaldehyde	0.5	ND	0.5	ND	ND	0.6	ND	ND	0.7	1	0.9
Chloral hydrate[d]	0.1	ND	0.8	0.2	0.7	2	0.9	1	1	2	2
Tribromoacetaldehyde	0.1	ND	ND	ND	ND	ND	ND	ND	ND	<1	ND
Halonitromethanes											
Chloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	0.10	ND	ND	ND	ND	0.1	ND	ND	ND	ND	0.1
Bromochloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[d]	0.25	ND	0.5	ND	0.3	ND	0.5	0.6	0.7	0.6	NR
Bromodichloronitromethane	0.5			ND	0.5		ND	ND			
Dibromochloronitromethane	0.5			ND	ND		ND	ND			
Bromopicrin	0.5			ND	ND		ND	ND			
Miscellaneous Compounds											
Methyl ethyl ketone	0.5	2	ND	ND	ND		ND	ND	ND	ND	
Methyl *tertiary* butyl ether	0.2	ND	ND	ND	ND		ND	ND	0.7	1	
Benzyl chloride	0.5	ND	ND	ND	ND	NR	ND	ND	ND	ND	NR
1,1,2,2-Tetrabromo-2-chloroethane	0.11	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

[p]<0.2 = Less than MRL (0.2 µg/L)

[q]<1 = Less than MRL (e.g., 1 µg/L)

Table 23. DBP results at plant 9 (2/25/02)

02/25/2002	MRL[a]	Plant 9[k]								
Compound	µg/L	Raw	1^{O} Cond	Basin #6	Filt Inf	Finished	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Halomethanes										
Chloromethane	0.2	ND[c]	ND	ND		ND	ND		ND	
Bromomethane	0.2	ND	ND	ND		ND	ND		ND	
Bromochloromethane	0.5	ND	ND	ND		ND	ND		ND	
Dibromomethane	0.5	ND	ND	ND		ND	ND		ND	
Chloroform[d]	0.2	ND	3	1	NR[e]	2	4	NR	2	1
Bromodichloromethane[d]	0.2	ND	4	2	NR	2	3	NR	3	2
Dibromochloromethane[d]	0.2	ND	2	1	NR	2	1	NR	2	1
Bromoform[d]	0.2	ND	0.4	<0.2[p]	NR	0.3	0.3	NR	0.4	0.2
THM4[f]		ND	9	4	NR	6	8	NR	7	4
Dichloroiodomethane	0.5	ND	<0.5[o]	<0.5	NR	<0.5	0.5	NR	<0.5	ND
Bromochloroiodomethane	0.5	ND	<0.5	<0.5	ND	<0.5	<0.5	ND	<0.5	ND
Dibromoiodomethane	0.5	ND	ND	ND	NR	ND	ND	NR	ND	ND
Chlorodiiodomethane	0.1	ND	ND	ND	ND	ND	ND	0.6	ND	ND
Bromodiiodomethane	0.52	ND	ND	ND	ND	ND	ND	ND	ND	ND
Iodoform	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	0.2	ND	ND	ND		ND	ND		ND	
Tribromochloromethane	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Haloacetic acids										
Monochloroacetic acid[d]	2		ND	ND		ND	ND		ND	
Monobromoacetic acid[d]	1		ND	ND		ND	ND		ND	
Dichloroacetic acid[d]	1		6.2	4.0		4.9	7.6		4.5	
Bromochloroacetic acid[d]	1		3.7	2.4		3.0	2.6		3.4	
Dibromoacetic acid[d]	1		3.0	2.2		2.7	2.2		1.8	
Trichloroacetic acid[d]	1		1.1	ND		ND	1.3		ND	
Bromodichloroacetic acid	1		1.2	ND		ND	ND		ND	
Dibromochloroacetic acid	1		ND	ND		ND	ND		ND	
Tribromoacetic acid	2		ND	ND		ND	ND		ND	
HAA5[g]			10	6.2		7.6	11		6.3	
HAA9[h]			15	8.6		11	14		10	
DXAA[i]			13	8.6		11	12		10	
TXAA[j]			2.3	ND		ND	1.3		ND	
Haloacetonitriles										
Chloroacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromoacetonitrile	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloroacetonitrile[d]	0.2	ND	0.4	ND	NR	0.2	ND	NR	ND	0.2
Bromochloroacetonitrile[d]	0.2	ND	0.8	ND	NR	0.2	ND	NR	ND	0.4
Dibromoacetonitrile[d]	1.0	ND	<1[q]	<1	<1	<1	ND	<1	<1	<1
Trichloroacetonitrile[d]	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodichloroacetonitrile	0.5	ND	ND			ND				ND
Dibromochloroacetonitrile	0.5	ND	ND			ND				ND
Tribromoacetonitrile	0.96	ND	ND			ND				ND
Haloketones										
Chloropropanone	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloropropanone[d]	1.0	ND	<1	ND	NR	ND	ND	NR	ND	ND
1,3-Dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dibromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloropropanone[d]	0.5	ND	0.5	ND	NR	ND	ND	NR	ND	ND
1,1,3-Trichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1-Bromo-1,1-dichloropropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3-Tribromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1,3-Tetrachloropropanone	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,3,3-Tetrabromopropanone	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table 23 (continued)

02/25/2002	MRL[a]	Plant 9[k]								
Compound	µg/L	Raw	1[O] Cond	Basin #6	Filt Inf	Finished	DS/Ave	DS/Max	SDS/Ave	SDS/Max
Haloacetaldehydes										
Dichloroacetaldehyde	0.98	ND	1	2	2	2	2	2	2	3
Bromochloroacetaldehyde	0.5	ND	ND	ND	ND	ND	<0.5	ND	ND	0.5
Chloral hydrate[d]	0.1	0.5	0.4	0.2	0.3	0.1	0.5	0.1	0.2	0.7
Tribromoacetaldehyde	0.1	<1	ND	ND	ND	ND	<1	ND	ND	<1
Halonitromethanes										
Chloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromonitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloronitromethane	0.10	ND	ND	ND	ND	ND	0.1	ND	ND	ND
Bromochloronitromethane	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibromonitromethane	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloropicrin[d]	0.25	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodichloronitromethane	0.5	ND	0.6			0.6				0.9
Dibromochloronitromethane	0.5	ND	0.6			0.6				0.9
Bromopicrin	0.5	ND	ND			ND				ND
Miscellaneous Compounds										
Methyl ethyl ketone	0.5	ND	ND	ND		ND	ND		ND	
Methyl *tertiary* butyl ether	0.2	ND	ND	ND		ND	ND		ND	
Benzyl chloride	0.5	ND	ND	ND	NR	ND	ND	NR	ND	ND
1,1,2,2-Tetrabromo-2-chloroethane	0.11	ND	ND	ND	ND	ND	ND	ND	ND	ND

Haloacids. At plant 10 in January and April 2001, chlorine and/or chloramine disinfection resulted in the formation of 83-95, 77-90, and 42-51 µg/L of the five regulated haloacetic acids (HAA5) in the Aldrich purification units, in basins 4 and 5, and in basins 1 and 2, respectively. As with the THM results, less HAAs were produced in basins 1 and 2 in January and April 2001 because of the earlier addition of ammonia to form chloramines. Chlorine only disinfection in September 2001 resulted in the formation of 165, 149, and 147 µg/L of HAA5 in the Aldrich purification units, in basins 4 and 5, and in basins 1 and 2, respectively. In contrast, the use of chloramines only at plant 10 in November 2001 and February 2002 resulted in the formation of 21-24 µg/L of HAA5 in the Aldrich purification units and in basins 4 and 5.

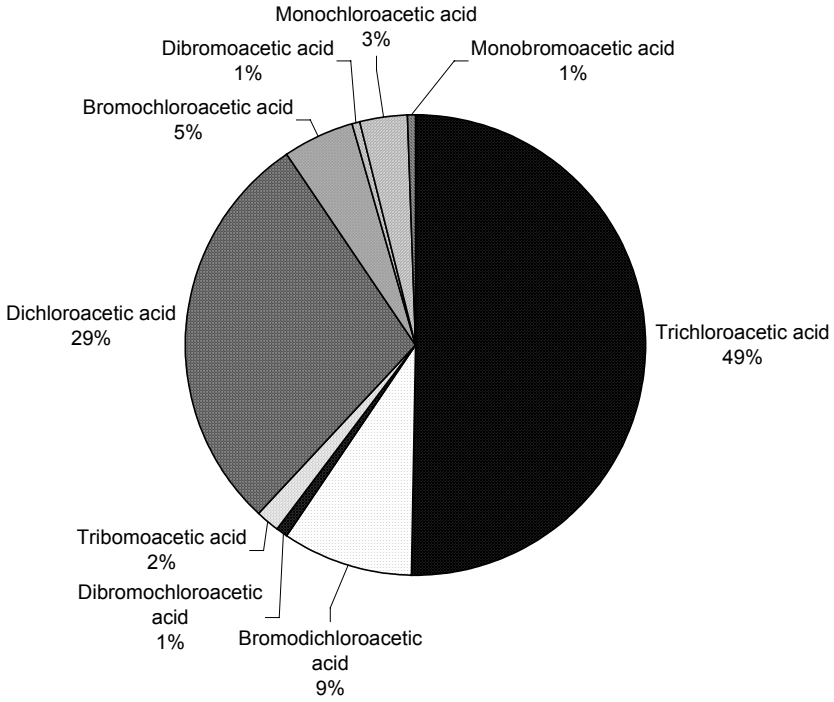
At plant 9 in January 2001, April 2001, August 2001, November 2001, and February 2002, chlorine/chloramine disinfection resulted in the formation of 4-18 µg/L of HAA5. Higher formation of HAAs was observed in April and August as compared to in January 2001, with intermediate HAA formation in November 2001 and February 2002.

In addition, all nine HAAs (HAA9) were measured, which included all of the brominated HAA species. At plant 10, the level of HAA9 in the Aldrich purification units, in basins 4 and 5, and in basins 1 and 2, was 104-114, 92-114, and 52-61 µg/L, respectively, in January and April 2001 and was 177-198 µg/L in September 2001. In contrast, with chloramines only, HAA9 was 24-30 µg/L in November 2001 and February 2002 in the Aldrich Purification units and in basins 4 and 5. At plant 10, HAA formation was higher than THM formation. At plant 9, the level of HAA9 in the finished water was 6-21 µg/L.

When pre-chlorination was used at plant 10 (January, April, and September 2001), trihalogenated HAAs (TXAAs) were in higher proportion than the dihalogenated species (DXAAs) (e.g., 111 versus 61 µg/L in basins 4&5 in September 2001). In other research, TXAAs were found to constitute the greatest mole fraction of HAA9 in chlorinated waters at pH 8 (Cowman and Singer, 1996). (The plant 10 waters were chlorinated at pH levels in the range of 7 to 8.) When pre-chloramination was used at plant 10 (November 2001 and February 2002), DXAAs were in higher proportion than the TXAAs (e.g., 16 versus 5 µg/L in basins 4&5 in November 2001). In other research, chloramines have been shown to produce little or no THMs and TXAAs, whereas DXAAs formed (Krasner et al., 1996). With either pre-chlorination or pre-chloramination at plant 10, in each HAA subgroup (monohalogenated HAAs [MXAAs], DXAAs, TXAAs), the fully chlorinated species (monochloro-, dichloro-, and trichloroacetic acid) predominated, followed by the bromochloro species (bromochloro- and bromodichloroacetic acid) (Figure 4).

At plant 9, most of the HAAs that were formed were DXAAs; very low amounts of TXAAs were detected (Figure 5). In other research, pH (in the range of 5 to 9.4) had no significant effect on dichloroacetic acid formation, whereas trichloroacetic acid formation was lower at pH 9.4 than at the lower pH levels (and THM formation was higher with increasing pH) (Stevens et al., 1989). The THM and HAA (DXAA versus TXAA) data (Figure 5) suggest the following: (1) minimal free chlorine contact time and the very high pH of chlorination (typically ~10) initially impacted the DBP formation and speciation; and (2) the presence of chloramines in

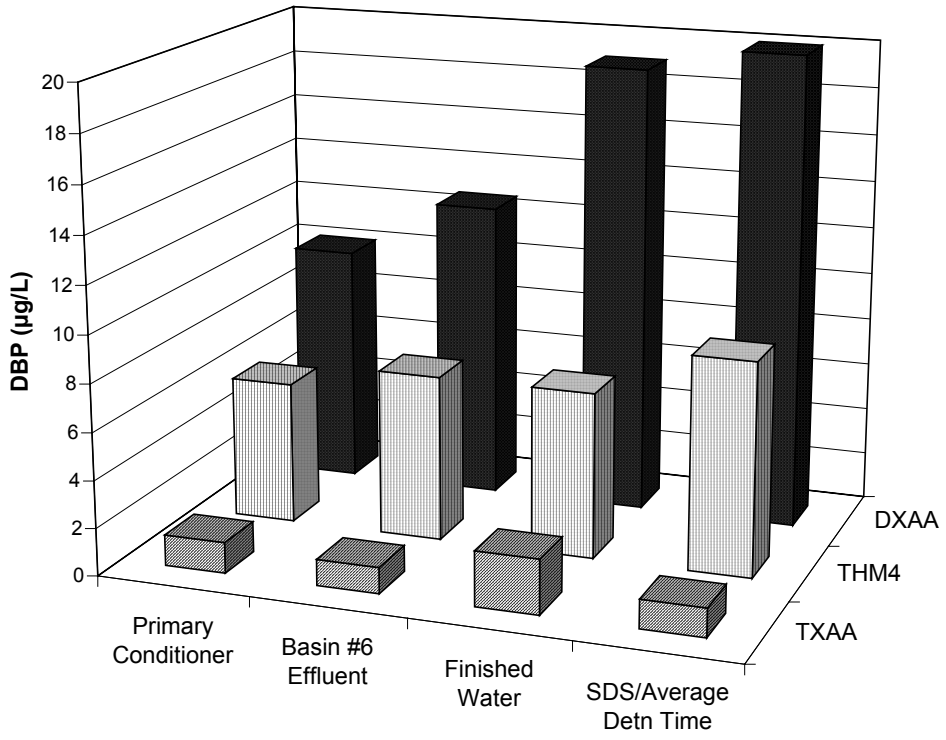
Figure 4. HAA speciation in Basins 4&5 at plant 10 in September 2001



the downstream basins minimized further THM and TXAA formation but allowed DXAAs to continue to form.

In other research, it was demonstrated that HAAs can be removed by GAC filtration, presumably by biodegradation processes within the filter bed (Singer et al., 1999). The extent of removal depended upon water temperature and the residual chlorine concentration. Because the combined filter effluent at the conventional plant was a combination of water from basins 4&5 and basins 1&2, the filter effluent was compared to a flow-weighted filter influent. For example, in April 2001, basins 4&5 had a flow of 20.6 mgd and 43 µg/L of DXAAs, and basins 1&2 had a flow of 11 mgd and 27 µg/L of DXAAs. So the flow-weighted filter influent had 37 µg/L of DXAAs: $(20.6 \times 43 + 11 \times 27)/(20.6 + 11)$. Figure 6 shows the seasonal variations in HAA removal through the GAC filters. In January 2001, HAAs were not removed when the water temperature was 0.3-3.5ºC. In April 2001, when the water temperature was 14-15ºC, the DXAAs were reduced in concentration by 35 %, whereas the levels of the other two subclasses of HAAs were relatively constant. In September 2001, when the water temperature was 27-29ºC, the DXAAs were reduced in concentration by 75 % and the MXAAs were not detected (ND) in the filter effluent, whereas the level of TXAAs was marginally reduced. In November 2001, when the water temperature was 13-16ºC, the DXAAs and MXAAs were reduced in concentration by 61 and 64 %, respectively, whereas the level of TXAAs was marginally reduced. In February 2002, HAA data were not available for basins 1&2. Because most of the

Figure 5. Impact of chloramines and pH of chlorination (~10) on THM and HAA formation and speciation at plant 9: August 27, 2001



flow in the conventional treatment train was from basins 4&5, the data for the former basins were used to estimate the combined filter influent concentrations. In the latter month, when the water temperature was 6ºC, the DXAAs and TXAAs were not removed, and the MXAAs were not detected (ND) in the filter effluent. These results are consistent with other research in which DXAAs were found to be biodegradable, whereas TXAAs were not, and the phenomenon was temperature dependent (Baribeau et al., 2000).

Figure 6. Seasonal variations in removal of HAAs through GAC filters at plant 10: water temperature at filters provided by each sample date (ND = not detected in filter effluent)

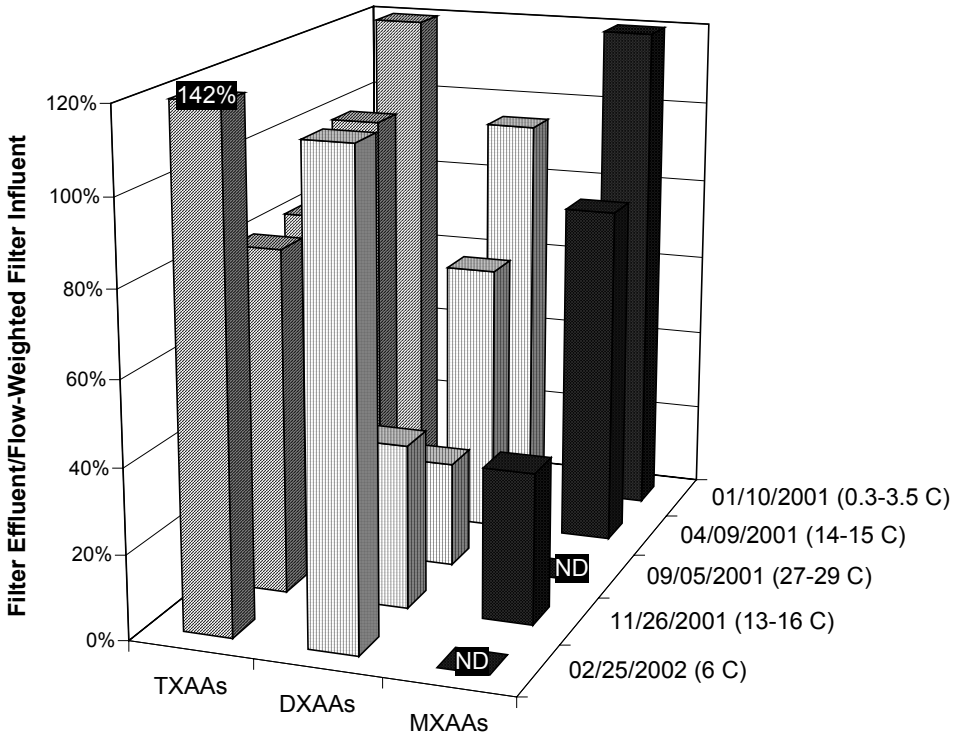
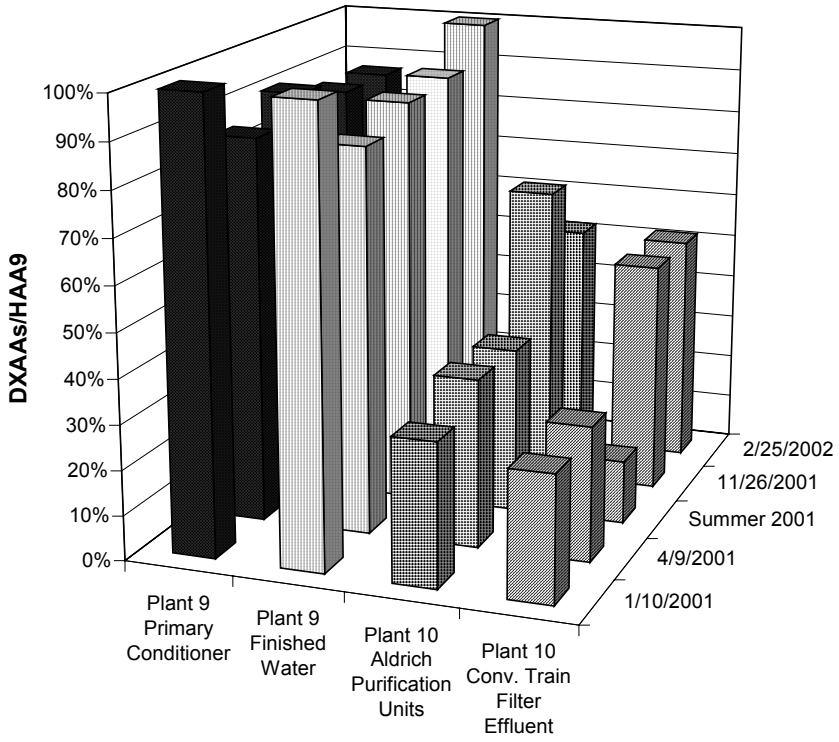


Figure 7 shows a comparison of DXAA and TXAA speciation at the two Mississippi River WTPs. The use of either chloramines or disinfection at pH levels of $\geq$9 favored DXAA formation over TXAA formation at plant 9, whereas pre-chlorination at pH 7-8 at plant 10 (January, April, and summer 2001) resulted in somewhat more TXAA formation than DXAA formation. Alternatively, pre-chloramination at pH 7-8 at plant 10 (November 2001 and February 2002) resulted in somewhat more DXAA formation than TXAA formation. Also, GAC filtration (in the conventional treatment trains) at plant 10 was more effective at removing DXAAs than TXAAs (especially in summer 2001). Thus, the difference in HAA speciation at these two utilities reflected the different effects of chlorine and chloramines, as well as pH and GAC filtration, on HAA formation and control.

Figure 7. Impact of chloramines and chlorine, pH and GAC filtration on HAA speciation at plant 9 and plant 10



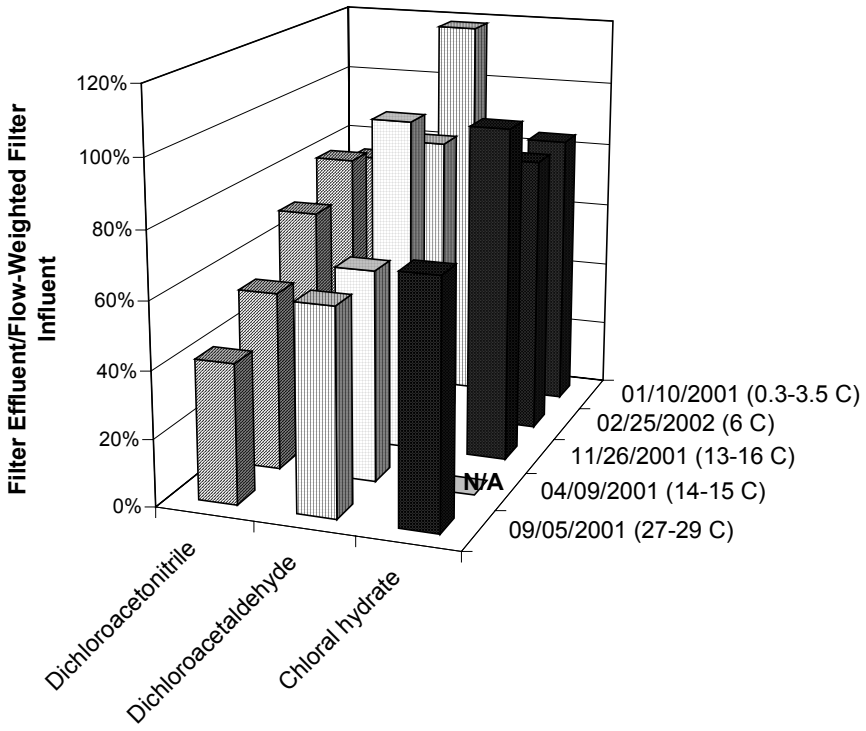
In addition to the target HAAs, two other haloacids were detected at plant 10 in April 2001 by the broadscreen GC/MS methods: 3,4,4-trichloro-3-butenoic acid and *cis*-2-bromo-3-methylbutenedioic acid (Table 15). November 2001 results from UNC also show the presence of another target halo-acid, 3,3-dichloropropenoic acid, at a level of 0.4 µg/L in finished waters from plant 10 (Table 20).

Haloacetonitriles. In other research, haloacetonitriles (HANs) have been found to be produced at approximately one-tenth the level of the THMs (Oliver, 1983). In the plant 10 samples, a comparison was made between the four HANs in the Information Collection Rule (ICR) (HAN4) (dichloro- [DCAN], bromochloro-, dibromo-, and trichloroacetonitrile [TCAN]) and THM4. The ratio of HAN4 to THM4 (on a weight basis) for the January, April, and September 2001 samplings was 8, 15, and 16 %, respectively.

A similar relationship was also observed (in part) in the plant 9 samples. Because the THM concentrations were at low µg/L levels at plant 9, the ICR HANs were detected at sub-µg/L levels. The major HAN formed, DCAN, typically went down in concentration in the plant, distribution system, and/or SDS samples. DCAN undergoes base-catalyzed hydrolysis (Croué and Reckhow, 1989), so it is not surprising that it would not be stable at the pH of treatment and distribution at plant 9 (i.e., pH = 9-10).

Similar to the HAAs (Figure 6), seasonal variations in the removal of DCAN through GAC filters was evaluated (Figure 8). In January 2001 and February 2002, the concentration of DCAN was 74-80 % of the level in the flow-weighted filter influent. In April and November 2001, when the water temperature was warmer, DCAN was reduced in concentration by 30-47 %. In September 2001, when the water temperature was the warmest, DCAN was reduced in concentration by 58 %. These results are similar to the seasonal removal of DXAAs (Figure 6).

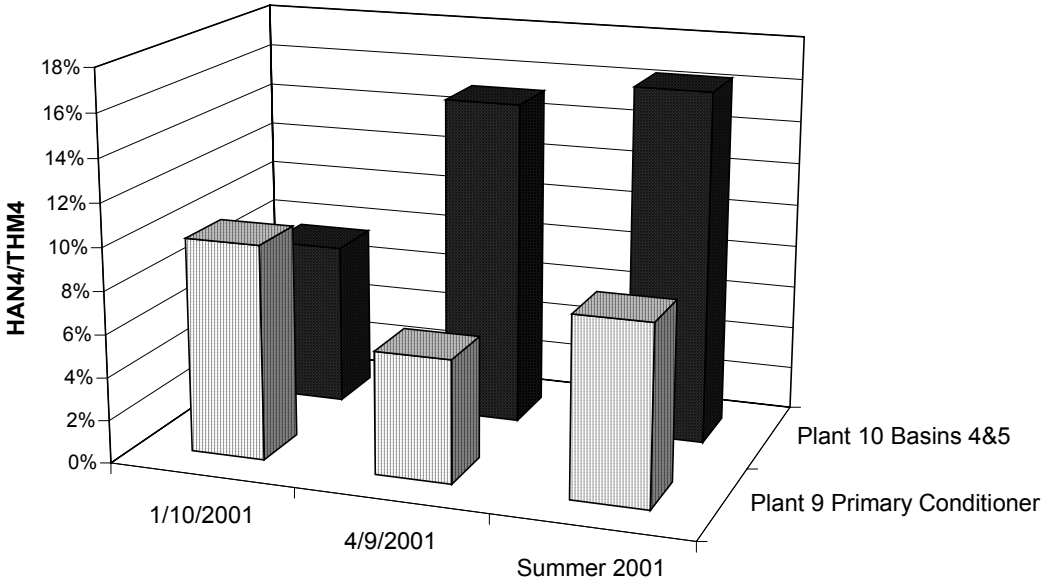
Figure 8. Seasonal variations in removal of other DBPs through GAC filters at plant 10: water temperature at filters provided by each sample date (results arranged in order of decreasing water temperature); N/A = not available



A comparison of HAN formation was made between the primary conditioner at plant 9 (at the beginning of the treatment process, prior to downstream base-catalyzed hydrolysis) and the effluent of basins 4&5 at plant 10 (before GAC filtration) for January, April, and November 2001 (Figure 9). The ratio of HAN4 and THM4 (on a weight basis) was 6-10 % at plant 9 and 8-16 % at plant 10. The ratio was somewhat higher at plant 10, probably because of the lower pH of chlorination, which minimized base-catalyzed hydrolyis of the HANs.

In addition to the ICR HANs, other target HANs (chloro-, bromo-, bromodichloro-, and dibromochloroacetonitrile) were detected in selected samples at plant 10. (The latter HAN was detected during the broadscreen GC/MS analyses [Table 15]). None of the other target HANs were detected at plant 9.

Figure 9. Relative formation of HANs to THMs at the Mississippi River WTPs



Haloketones. In addition to the formation of low levels of haloketone (HK) compounds from the ICR (1,1-dichloro- and 1,1,1-trichloropropanone), low levels of some of the target HKs were detected in some of the samples at plant 9 and plant 10 (Figure 10). At plant 10, the formation of 1,1,1-trichloropropanone was much higher, especially when pre-chlorination was utilized (e.g., April 2001). In other research, 1,1,1-trichloropropanone was detected at acidic and neutral pH levels, but was not detected at a pH of 9.4 (Stevens et al., 1989). Thus, the presence of chlorine for longer contact times at a lower pH level resulted in more formation of this HK at plant 10. Alternatively, 1,1-dichloropropanone levels were comparable at both plants in April 2001, suggesting that pH did not impact this HK to the same extent. When pre-chlorination was used at plant 10, the level of 1,1,1-trichloropropanone was much higher than that of 1,1-dichloropropanone, whereas when pre-chloramination was used the levels of the two HKs were similar (Figure 10).

Figure 11 shows the impact of distribution-system disinfectant on the formation and stability of THMs and HKs at plant 10, comparing the SDS samples set up for a maximum detention time (five days) to the original finished water. In April 2001, when chloramines were used, the concentrations of the THMs and many of the HKs were relatively constant. However, there was a significant increase in the formation of 1,1-dichloropropanone. In other research, chloramines were found to control the formation of THMs and TXAAs better than they control the formation of DXAAs (Krasner et al., 1996). Thus, 1,1-dichloropropanone may continue to form in chloraminated water. In September 2001, when chlorine was used, the concentration of

Figure 10. Haloketone formation in finished waters at plant 9 (4/9/01) and plant 10 (4/9/01 and 11/26/01) (haloketones not detected in finished water at plant 9 on 11/26/01)

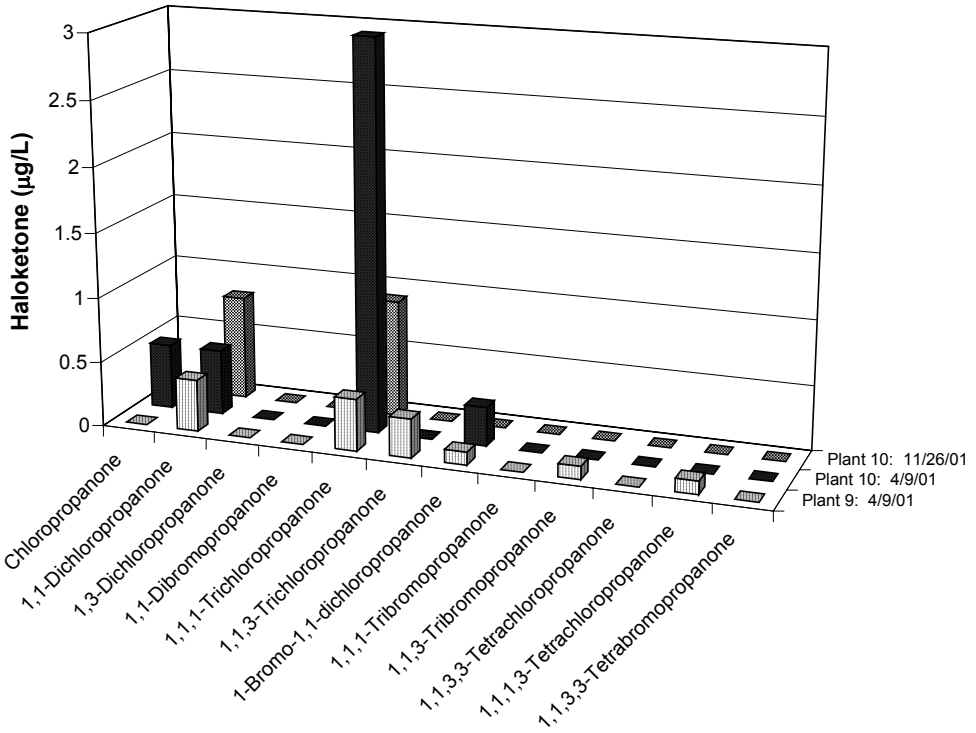
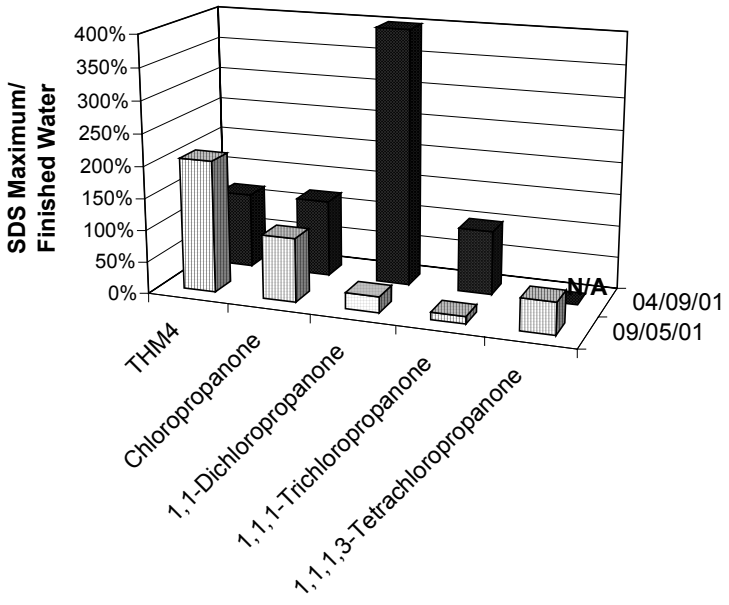


Figure 11. Plant 10 (N/A = not available):

Impact of Distribution-System Disinfectant on the Formation and Stability of THMs and Haloketones in SDS/Maximum Detention Time Samples: Chloramines on 4/9/01, Chlorine on 9/5/01



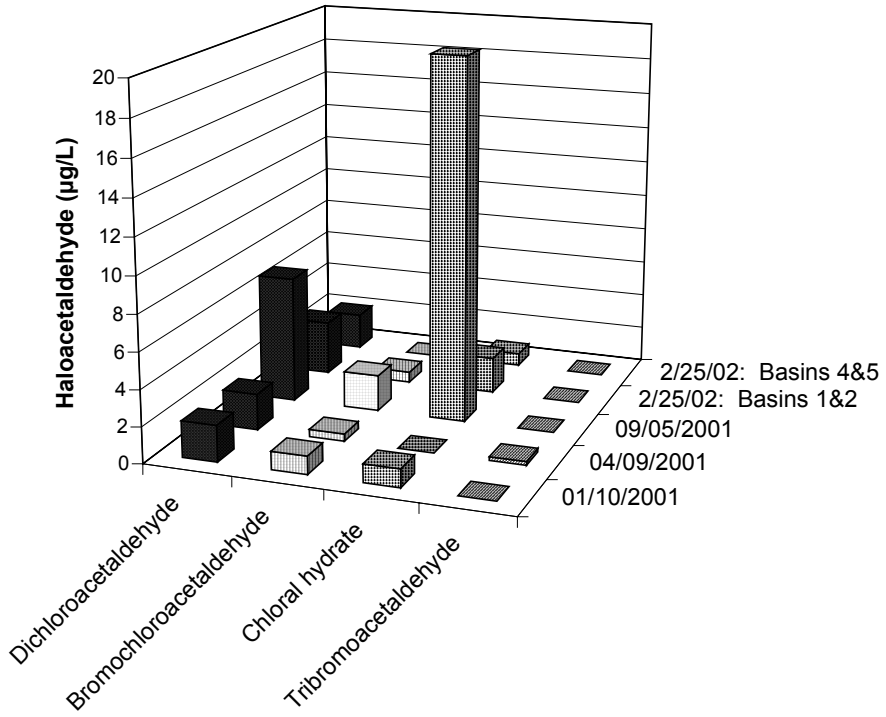
the THMs significantly increased, the concentration of chloropropanone was unchanged, and the concentrations of some of the other HKs decreased to varying degrees, especially that of 1,1,1-trichloropropanone (from 7 to 0.8 µg/L). In other research, 1,1,1-trichloropropanone was shown to decrease in the presence of chlorine, perhaps as a result of the direct reaction of chlorine with this HK (Reckhow and Singer, 1985).

In addition to the target HKs, other HKs were detected in selected samples by the broadscreen GC/MS methods (Table 15). Two of these HKs were analogous to the di- and tetrahalogenated HKs monitored for by MWDSC, except that these were mixed bromochloro species. Another two HKs that were detected at these WTPs by the broadscreen GC/MS methods was pentachloro- (PCP) and hexachloropropanone (HCP). MWDSC had attempted to include PCP and HCP in its target compound list, but they both degraded immediately and completely in water under all conditions evaluated (Gonzalez et al., 2000).

Haloaldehydes. In addition to the formation of chloral hydrate (trichloroacetaldehyde) (an ICR DBP), low levels of the target haloacetaldehydes (e.g., dichloroacetaldehyde) were detected at plant 10 (Figure 12). In January 2001, April 2001, and February 2002, chloraminated water was in settling basins 1&2 (with upstream pre-chlorination in mixing tank number 2) (Figure 1), whereas in September 2001, chlorine only was in settling basins 1&2. The sum of the concentration of the two dihalogenated acetaldehydes (2.4-3.6 µg/L) was greater than the sum of the concentration of the two trihalogenated acetaldehydes (0.2-2 µg/L) when the water was chloraminated. When the water was chlorinated, chloral hydrate formation (22 µg/L) was much greater than the formation of the sum of the two dihalogenated acetaldehydes (9 µg/L). In addition, the warmer water temperature in September 2001 contributed to more haloacetaldehyde formation overall.

In February 2002, pre-chloramination in basins 4&5 versus chlorine/chloramines in basins 1&2 resulted in much more control of chloral hydrate (0.7 versus 2 µg/L) than for dichloroacetaldehyde (2 versus 3 µg/L). In other research, chloramines were found to minimize the formation of chloral hydrate, whereas certain dihalogenated DBPs were formed to greater extents (Young et al., 1995). Consistent with that research, the formation of dihalogenated acetaldehydes was favored over trihalogenated species at plant 10 when chloramines were used, especially with pre-chloramination.

Figure 12. Haloacetaldehyde formation and speciation in Basins 1&2 at plant 10: chlorine/chloramines in January 2001, April 2001, and February 2002; chlorine only in September 2001 (Basins 4&5 with pre-chloramination in February 2002 provided for comparison)



At plant 9, dichloroacetaldehyde formation was typically greater than that of chloral hydrate (Figure 13). This was due, in part, because chloral hydrate undergoes base-catalyzed hydrolysis at high pH (e.g., ~9) (Stevens et al., 1989). With the measurement of dihalogenated and/or brominated analogues of chloral hydrate, the haloacetaldehydes represented the third largest class of DBPs formed at plant 9 (on a weight basis).

Figure 13. Seasonal variations in the formation and speciation of the haloacetaldehydes in the finished water of plant 9

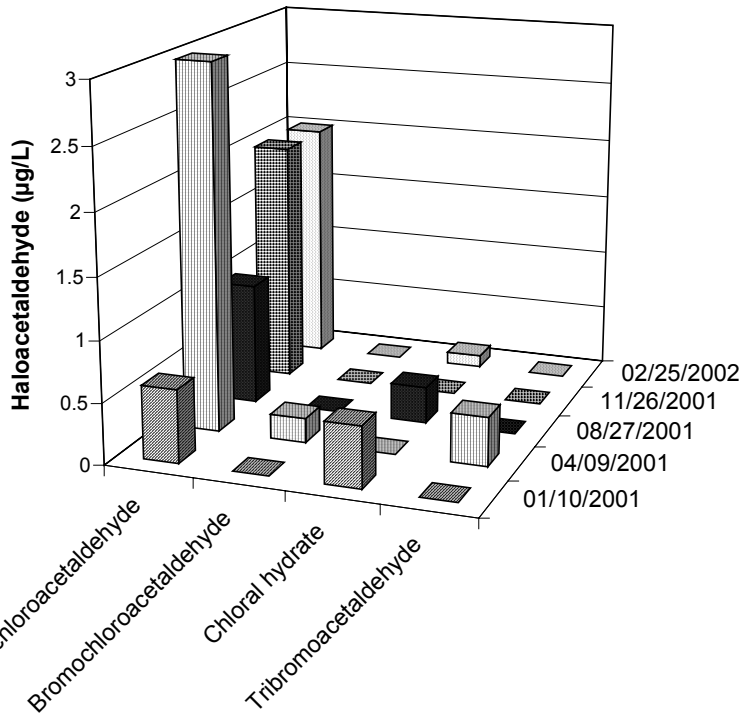
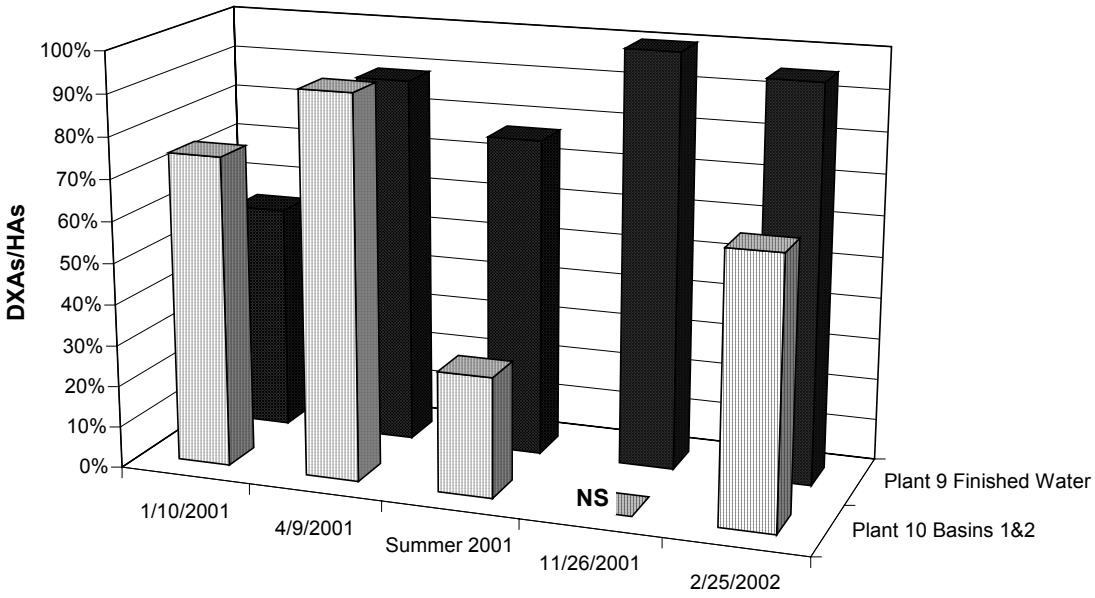


Figure 14 shows the relative speciation of the sum of the two measured dihalo-acetaldehydes (DXAs) to the sum of the four measured species. At plant 9, DXAs represented 55 to 100 % (median = 89 %) of the measured haloacetaldehydes (HAs). At plant 10, the DXAs represented 64 to 92 % of the haloacetaldehydes in basins 1&2 when chloramines were used and 29 % of this class of DBPs when chlorine only was used. In February 2002, when pre-chloramination was used in basins 4&5, the DXAs represented 74 % of the haloacetaldehydes (Figure 12).

As with the other classes of DBPs, the formation of the chlorinated species at plant 10 was highest for each subclass of haloacetaldehyde, and the bromochloro species was next highest in concentration (Figure 12).

Figure 14. Impact of chloramines and chlorine, and pH on haloacetaldehyde (HA) speciation (e.g., dihaloacetaldehydes [DXAs]) at the Mississippi River WTPs (NS = not sampled)

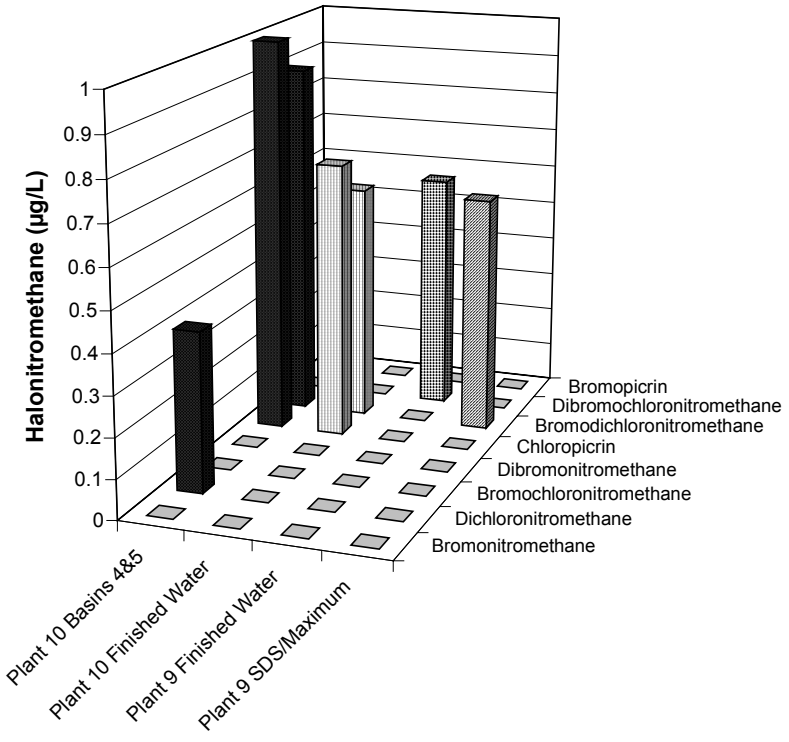


Similar to the HAAs (Figure 6) and DCAN (Figure 8), seasonal variations in the removal of dichloro- and trichloroacetaldehyde [chloral hydrate]) were examined (Figure 8). In January 2001 and February 2002, the concentrations of these two haloacetaldehydes were 84-119 % of the levels in the flow-weighted filter influents. In April 2001, when the water temperature was warmer, dichloroacetaldehyde was reduced in concentration by 37 % (data were not available (N/A) for chloral hydrate). However, in November 2001, when the water temperature was similar to that in April 2001, there was no reduction in the concentration of the haloacetaldehydes though the GAC filters. In September 2001, when the water temperature was the warmest, dichloroacetaldehyde and chloral hydrate were reduced in concentration by 39 and 27 %, respectively. These results are similar, in part, to the relative seasonal removal of DXAAs and TXAAs (Figure 6) and DCAN (Figure 8).

In addition to the target haloaldehydes, one other haloaldehyde was detected at both WTPs by the broadscreen GC/MS methods: 2-bromo-2-methylpropanal (Table 15).

Halonitromethanes. Low levels of chloropicrin (trichloronitromethane) (an ICR DBP) were detected at plant 10. This DBP was only detected in the April and November 2001 samples at plant 9. Other halonitromethanes (HNMs) were detected in selected samples from both WTPs

Figure 15. Halonitromethane formation at the Mississippi River WTPs in August/September 2001

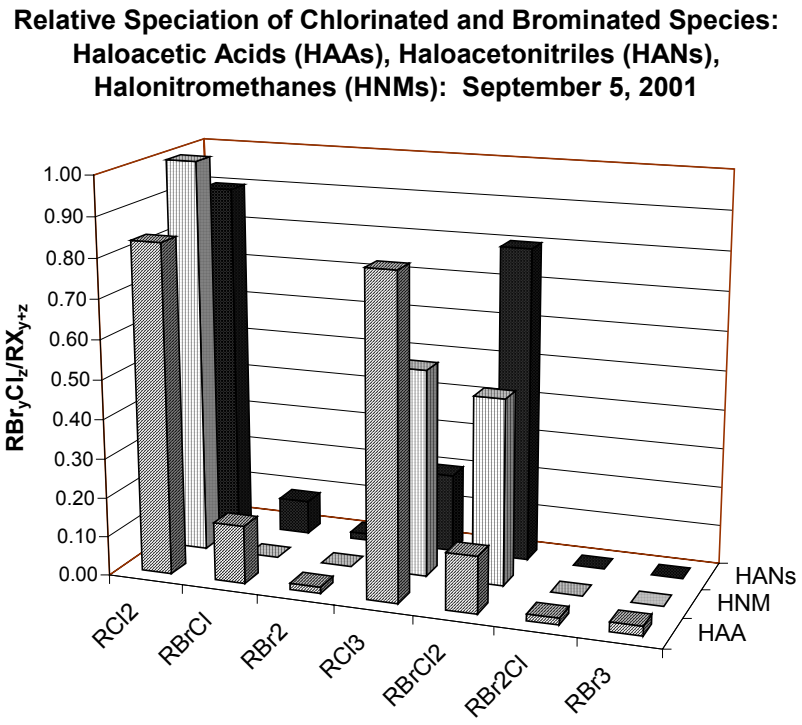


(e.g., Figure 15). Although there was a large difference in THM and HAA formation between the two utilities, the difference in HNM formation was not as high.

As with the HAAs, there are nine HAN species and nine NHMs (two monohalogenated species, three dihalogenated species, and four trihalogenated species). The relative speciation of brominated and chlorinated HANs and HNMs (for the di- and trihalogenated species) was compared to the HAAs for the effluent of basins 4&5 from the September 2001 sampling. Each DBP can be abbreviated based on the number of halogens and the speciation of the halogens as follows: RBr_yCl_z, where the number of bromine and chlorine atoms are y and z, respectively, and R corresponds to the remainder of the DBP molecule (i.e., carbon, hydrogen, oxygen, and nitrogen atoms). The concentration of each DBP was "normalized" by dividing its concentration by the sum of the concentrations of all of the DBPs for that "subclass" of DBPs (RX_{y+z}) (Figure 16). For example, the concentration of dichloroacetic acid was divided by the sum of all the DXAAs.

For the dihalogenated DBPs (RX_2), the dichlorinated species represented 84 to 100 % of the sum of the dihalogenated DBPs in each class of DBPs examined. The bromochloro species represented 0 to 15 % of the class sums, and the dibromo species represented 0 to 2 % of the class sums. For the HAAs, HANs, and HNMs, there was a similar relative speciation of brominated and chlorinated DBPs for the dihalogenated subclass. For the trihalogenated DBPs (RX_3), the trichlorinated, bromodichlorinated, dibromochlorinated, and tribrominated species

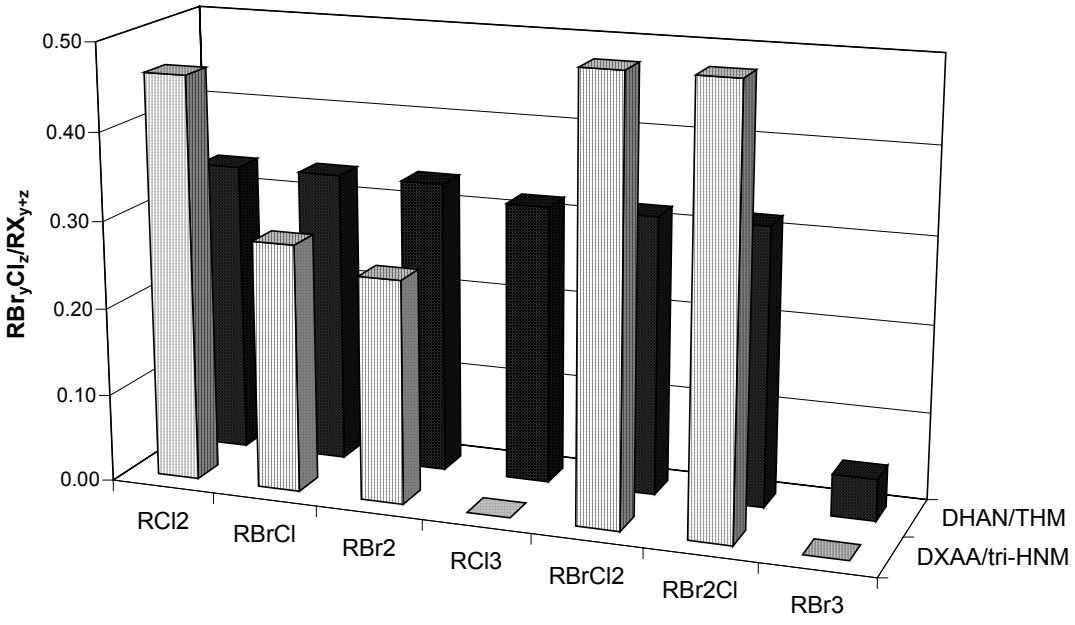
Figure 16. Effluent of Basins 4&5 at plant 10:



represented 20 to 81 %, 14 to 80 %, 0 to 2 %, and 0 to 2 % of the subclass sums, respectively. Although not shown in this figure, for THM4, chloroform, bromodichloromethane, dibromochloromethane, and bromoform represented 69, 28, 3, and 0 % of that class sum, respectively. The relative speciation of the THMs was in between that of the speciation for the HAAs and the HNMs. The reason the relative speciation for the trihalogenated HANs may have been different is probably due to the relative instability of TCAN. In other research, TCAN has been shown to undergo base-catalyzed hydrolysis in the pH range of 7 to 8, whereas it is stable at pH 6 (Croué and Reckhow, 1989). The pH of basins 4&5 was 7.2, so it is likely that TCAN simultaneously formed and degraded in these basins.

For plant 9, the relative speciation of brominated and chlorinated HNMs (for the trihalogenated species) was compared to the THMs, the dihaloacetonitriles (DHANs), and the DXAAs for the February 2002 finished water (Figure 17). (TXAAs and dihalogenated HNMs were not detected in this sample.) For the RX_2, the dichlorinated species represented 33 to 46 % of the sum of the dihalogenated DBPs in that subclass of DBPs (on a weight basis). The bromochloro species represented 28 to 33 % of the subclass sum, and the dibromo species represented 25 to 33 % of the subclass sum. For the RX_3, the trichlorinated, bromodichlorinated, dibromochlorinated, and tribrominated species for the HNMs and THMs represented 0 to 32 %, 32 to 50 %, 32 to 50 %, and 0 to 5 % of the class sum, respectively. In February 2002, the raw-water bromide level was the highest for the plant 9 samples. For the THMs, HAAs, DHANs, and HNMs, there was a similar relative speciation of brominated and chlorinated DBPs at plant 9, with a shift to more of the brominated species.

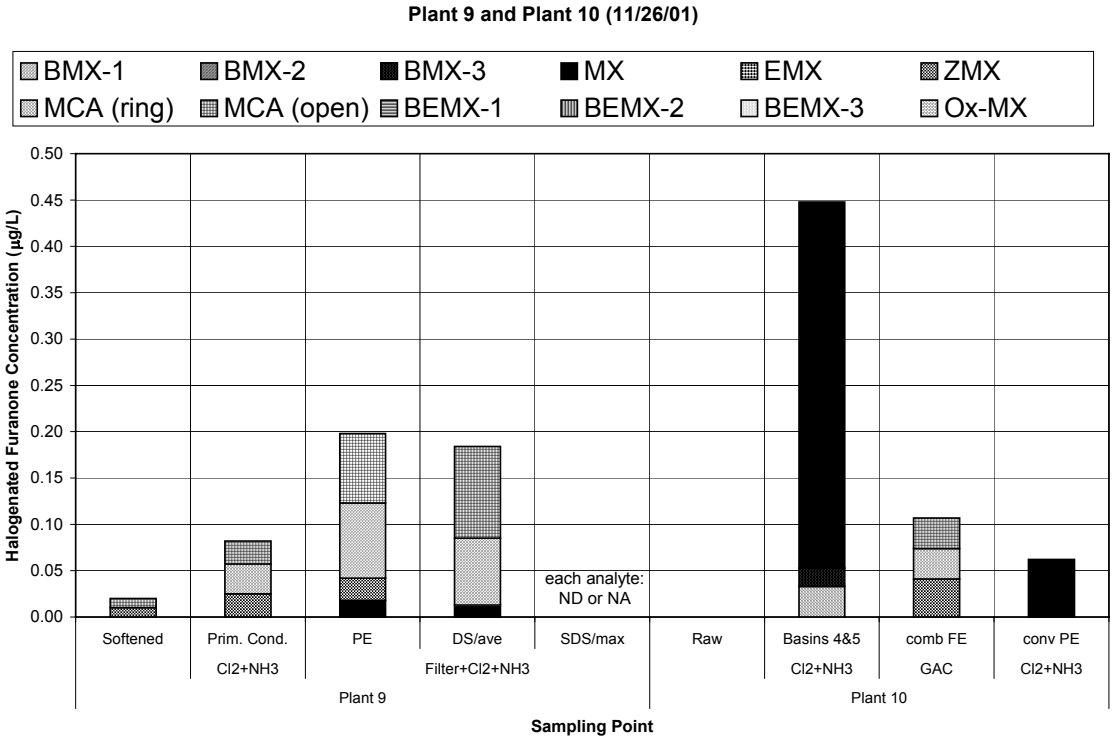
Figure 17. Relative speciation of chlorinated and brominated species in finished water at plant 9 (2/25/02): dihaloacetic acids (DXAAs), dihaloacetonitriles (DHANs), trihalomethanes (THMs), trihalogenated halonitromethanes (tri-HNMs)



Halogenated furanones. Table 21 shows the results for halogenated furanones in the November 2001 sampling for plant 9 and plant 10. Data are included for 3-chloro-4-(dichloromethyl)-5-hydroxy-2[5H]-furanone, otherwise known as MX; (E)-2-chloro-3-(dichloromethyl)-4-oxobutenoic acid, otherwise known as EMX; (Z)-2-chloro-3-(dichloromethyl)-4-oxobutenoic acid (ZMX); the oxidized form of MX (Ox-MX); brominated forms of MX and EMX (BMXs and BEMXs); and mucochloric acid (MCA), which can be found as a closed *ring* or in an *open* form. Results are displayed graphically in Figure 17.

There was an increase in the concentrations of MCA-*ring* and MCA-*open* in the presence of chloramines at plant 9 (11/26/01) (Table 21). Brominated analogues of MX were not detected at plant 9. Plant 10 showed a significant formation of MX, with a levels of 400 ng/L observed after treatment with chloramines (in a sample collected from settling basins 4 & 5) (Figure 18). However, subsequent GAC filtration removed the MX, with no MX measured in the filter effluent. This is consistent with the removal of other DBPs in this study during the filtration process, which was probably due to biodegradation and not adsorption. Following the addition of chloramines after GAC filtration, MX was reformed at a significantly lower level in the plant effluent (60 ng/L). Two brominated analogues of MX (BMX-1 and BMX-3) were also formed at

Figure 18. Halogenated furanones.



plant 10 (30 and 20 ng/L, respectively), but GAC filtration was effective in removing them completely, and they were not reformed in the plant effluent samples (Table 21). In samples collected in April 2001 from plant 10, ox-MX was qualitatively identified in the plant effluent using broadscreen GC/MS analysis (Table 15).

Volatile Organic Compounds (VOCs). Carbon tetrachloride, which is a VOC and a possible DBP, was detected (0.07-0.3 µg/L) in several samples at plant 10, but was not found in the raw water (MRL = 0.06 or 0.2 µg/L). As mentioned in a previous chapter, carbon tetrachloride has been detected by some utilities in gaseous chlorine cylinders (EE&T, 2000), due to imperfections in the manufacturing process or improper cleaning procedures.

Methyl *tertiary* butyl ether (MtBE) was detected in the raw water of plant 10 on September 5, 2001 at a concentration of 1.6 µg/L. The level of MtBE decreased somewhat through plant 10. MtBE was detected (0.7-1 µg/L) in the distribution system and in SDS testing for plant 10 on February 25, 2002, but was not detected (with an MRL of 0.2 µg/L) in the raw water. MtBE was detected (0.2-0.3 µg/L) in the raw water samples for plant 9 in January and August 2001, but was not detected in the WTP samples (with an MRL of 0.2 µg/L). MtBE is a gasoline additive.

Methyl ethyl ketone (MEK) was detected in plant 9 on August 27, 2001 at 0.5-1 µg/L, but was not detected at or above the MRL of 0.5 µg/L in the raw water. MEK was detected (1 µg/L) in the raw water for plant 9 on November 26, 2001, and was detected in some downstream samples at 0.8-1 µg/L. MEK was detected in the plant 10 conventional treatment train at 0.6

µg/L on September 5, 2001, but was not detected at or above the MRL of 0.5 µg/L in the raw water. MEK was detected (2 µg/L) in the raw water for the Aldrich purification units at plant 10 on February 25, 2002, but was not detected in the treated water. MEK is an industrial solvent and it may also be a DBP. Because the level in the two WTPs in the summer 2001 samples was barely above the MRL, it can not be determined for sure if its presence was due to low-level raw-water contamination (as was observed in November 2001 at plant 9 and in February 2002 at plant 10) or if it was produced during the disinfection process.

Other Halogenated DBPs. A few additional, miscellaneous halogenated DBPs were also detected. UNC methods detected dichloroacetamide at 1.7 µg/L in finished water from plant 10 (1/10/01) (Table 12). In addition, broadscreen GC/MS analyses revealed the presence of 1,2-dichloroethylbenzene, tetrachlorocyclopentadiene, hexachlorocyclopentadiene, and bromopentachlorocyclopentadiene in finished water collected from plant 10 in April 2001 (Table 15). Dichlorophenol was identifed in finished water from plant 9 (Table 15). These compounds were not observed in the corresponding raw, untreated water.

Non-Halogenated DBPs. Very few non-halogenated DBPs were detected in finished waters from plant 10 or plant 9. Dimethylglyoxal was identified at 0.2 and 0.3 µg/L in finished waters from plant 9 and plant 10, respectively, in November 2001 (Table 20). Broadscreen GC/MS analysis revealed the presence of glyoxal and dodecanoic acid in finished water from plant 10 (April 2001), and 4-methylpentanoic acid was found in finished waters from plant 9 (August 2001) (Table 15).

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CONCLUSIONS

This Nationwide DBP Occurrence Study revealed that many of the high priority DBPs can occur in finished drinking water at levels similar to those of the commonly measured DBPs. For example, iodo-THM levels ranged from 0.2 to 15 µg/L and brominated nitromethane levels were as high as 3 µg/L. In addition, MX levels measured in this study were significantly higher than previously reported. Specifically, MX levels were often above 100 ng/L, with a maximum concentration of 310 ng/L; brominated forms of MX (BMX-1 and BEMX-3) reached 170 and 200 ng/L, respectively. These results suggest that some of the high priority DBPs should be the focus of new health effects research, particularly for the bromonitromethanes that are being shown to be significantly more genotoxic in mammalian cells than MX and most currently regulated DBPs. It has also been hypothesized that the iodinated species may be more carcinogenic than the brominated species. Given the levels of iodo-THMs that can be formed in waters high in bromide/iodide, it is recommended that the iodo-THMs also be targeted for expanded/accelerated health effects studies.

Several haloamides were quantified for the first time in this study and found to be present at levels similar to other commonly measured DBPs (low µg/L levels). This is a new class of DBP that has not been previously measured in treated, potable waters, and may be important due to the levels found.

With respect to treatment processes, we found that the use of ozone removed MX-analogue precursors, and that GAC filters removed MX-analogues via adsorption and/or biodegradation. However, it was also shown that post-chlorination or chloramination following GAC filtration can contribute to MX-analogue re-formation. Chlorine and ClO_2-chlorine were confirmed as the major producers of MX-analogues, as previously observed by Kronberg (1999). MX did not form from ClO_2 disinfection *per se*, rather ClO_2 oxidation did not destroy MX precursors (as ozone, another alternative disinfectant, does). The high concentrations of MX-analogues (>100 ng/L) observed in these water treatment plants were greater than that previously reported. Either previous methods for the detection of MX-analogues (all published concentrations <90 ng/L) may have systematically underestimated the true concentrations, due to degradation of the MX-analogues during lengthy sample storage and processing, or higher concentrations were detected in this study because utilities that treat waters high in TOC and/or bromide were included.

This study has also revealed that some of our previous understanding of the formation and control of DBPs with alternative disinfectants was not complete. For example, it has been assumed from past THM data that alternative disinfectants are a good means of controlling other potentially hazardous, halogenated DBPs. However, the results show here that some DBPs—particularly iodo-THMs and dihaloacetaldehydes—can occur at higher concentrations in treatment plants using alternative disinfectants. Thus, while alternative disinfectants can control the formation of the four currently regulated THMs, they do not necessarily control all halogenated DBPs of concern. Consider that MX was found at its highest level at a treatment plant that disinfected a

high-TOC water with chlorine dioxide, chlorine, and chloramines. Alternatively, at another plant that treated the same water with ozone, biodegradation (on GAC filter), and chlorine, halogenated furanone formation was significantly lower. As discussed above, this probably reflects differences in the ability of ClO_2 and ozone—as well as biodegradation and GAC filtration—to destroy MX precursors, which were probably quite high in this high-TOC water.

Many new DBPs were identified through the course of this study. In particular, iodinated acids were identified for the first time, along with a DBP tentatively identified as iodobutanal. Therefore, iodo-THMs are not the only possible iodinated DBPs that can form. Several new brominated acids were also identified, with carbon chain lengths of three and four being common, as well as the presence of diacids and double bonds in their structures. One of the high priority DBPs that was quantified in this study—3,3-dichloropropenoic acid—is an example of a chlorinated, three-carbon acid; it was frequently found in treated waters at levels ranging from 0.4 to 1.5 µg/L in finished waters. Therefore, the presence of haloacids other than the regulated, two-carbon haloacetic acids must be realized.

The stability of DBPs in potable water distribution systems and in simulated distribution system (SDS) tests varied. In most cases where chloramination was used for disinfection, the DBPs were relatively stable. However, when free chlorine was used, THMs and other DBPs, including haloacetic acids, increased in concentration in the distribution system and in SDS testing. Haloacetonitriles generally were stable (at the distribution-system pH levels encountered in this study) or increased in concentration in the distribution system, but many of the haloketones were found to degrade. Halonitromethanes and dihaloacetaldehydes were also generally found to be stable in distribution systems. MX analogues were sometimes stable and sometimes degraded somewhat in the distribution system and during SDS testing. When MX analogues showed some degradation in the distribution system, they were generally still present at detectable levels, indicating that they do not completely degrade. Many times, the brominated analogues of MX (BMXs) were stable in the distribution system.

APPENDIX

EXPERIMENTAL METHODS

CHEMICAL STANDARDS (for Methods Developed at MWDSC)

When commercial standards were not available, standards were synthesized for the project. The initial phase of the project required a survey of chemical companies to obtain as many of the target compounds as possible. The remaining compounds were then synthesized. This led to a step-wise approach to incorporating compounds as they became available for analysis. When synthesized materials were prepared in less than 10-mg allotments, additional standards were sometimes needed later in the project.

At Metropolitan Water District of Southern California (MWDSC), multiple methods were used to test for DBPs. It was necessary to make up two independent sets of stock solutions, in methyl *tertiary* butyl ether (MtBE) and methanol, depending on the solvent requirements of each technique. Each "pure" standard from the MtBE set was characterized individually to determine whether there were any impurities, to note what the impurities were and at what level (percentage). Many of the discovered impurities were, in fact, other DBPs. When all the standards were combined into spiking solutions, any additionally added DBPs (impurities) had to be accounted for through the use of correction factors, either to the final results or to the standards being used to generate calibration curves. When correction factors were applied, reported concentrations were more accurate because they reflected the true composition of the combined set of calibration standards.

Stock Solutions

Several commercially available certified standards and mixes were purchased (Table 1). These mixes were spiked directly or used to create additional compound class mixtures for calibration purposes and spikes of unknown samples.

Typically, at the beginning of each quarter, new stock solutions were prepared in MtBE and methanol. In September 2000, the first set was created that would last through the Fall 2000 quarter's sampling. The next set of stock solutions covered all of the Winter 2001 quarter and the samples from early Spring 2001. Another set was created in May 2001 and was used through the end of the year, covering both Summer and Fall 2001 quarter's samplings. The last set of stock solutions was made in January 2002, and was used with the final phase of sampling in the Winter 2002 quarter and an early Spring 2002 sampling.

The MtBE-diluted compounds were tested in full-scan mode to verify the electron impact (EI) mass spectrum of the pure compound and also to check for impurities or degradation products present (Figures 1-7). As part of an on-going check of the standards, the individual stock solutions would be periodically checked to note any changes in the calculated purity or the impurities present. Initially, the solutions were checked every 4-6 weeks. Subsequently, after approximately 3 month's usage, new stock solutions would be created, and the previous set stored for future reference.

Table 1. Certified commercial standards used at MWDSC

		Standards Used in Method[a]		
Certified Mixes	**Compound**	**LLE-GC/ECD**	**P&T-GC/MS**	**SPE-GC/MS**
Bromochloromethane				
Supelco 4-8067	Bromochloromethane		X	
2000 μg/mL in methanol				
Carbon Tetrachloride				
Supelco 40360-U	Carbon tetrachloride		X	
5000 μg/mL in methanol				
Chloral Hydrate				
Supelco 4-7335-U	Chloral hydrate	X		
1000 μg/mL in acetonitrile				
Dibromomethane				
Supelco 4-8339	Dibromomethane		X	
2000 μg/mL in methanol				
EPA 524.2 Fortification Solution	4-Bromofluorobenzene		X	
Supelco 47358-U	1,2-Dichlorobenzene-d4		X	
2000 μg/mL in methanol	Fluorobenzene		X	
EPA 551B Halogenated Volatiles	Bromochloroacetonitrile	X		X
Supelco 4-8046	Chloropicrin	X		X
2000 μg/mL in acetone	Dibromoacetonitrile	X		X
or	Dichloroacetonitrile	X	X	X
HCM-551B (Ultra Scientific)	1,1-Dichloropropanone	X	X	X
5000 μg/mL in methanol	Trichloroacetonitrile	X		X
	1,1,1-Trichloropropanone	X	X	X
EPA 624 Calibration Mix B	Bromomethane		X	
Supelco 46967-U	Chloroethane			
2000 μg/mL in methanol	Chloromethane		X	
	Trichlorofluoromethane			
	Vinyl chloride			
Methyl Tert-Butyl Ether				
Supelco 4-8483	Methyl *tert*-butyl ether		X	
2000 μg/mL in methanol				
Trihalomethane Calibration Mix	Bromodichloromethane	X	X	X
Supelco 4-8140-U, 2000 μg/mL in MeOH	Bromoform	X	X	X
or	Chloroform	X	X	X
THM-521 (Ultra Scientific)	Dibromochloromethane	X	X	X
5000 μg/mL in methanol				
2-Butanone				
Supelco 4-8877	Methyl ethyl ketone		X	
2000 μg/mL in MeOH/H_2O 90:10				

[a]LLE-GC/ECD: Liquid/liquid extraction-gas chromatography/electron capture detection
P&T-GC/MS: Purge-and-trap - GC/mass spectrometry
SPE-GC/MS: Solid-phase extraction - GC/MS

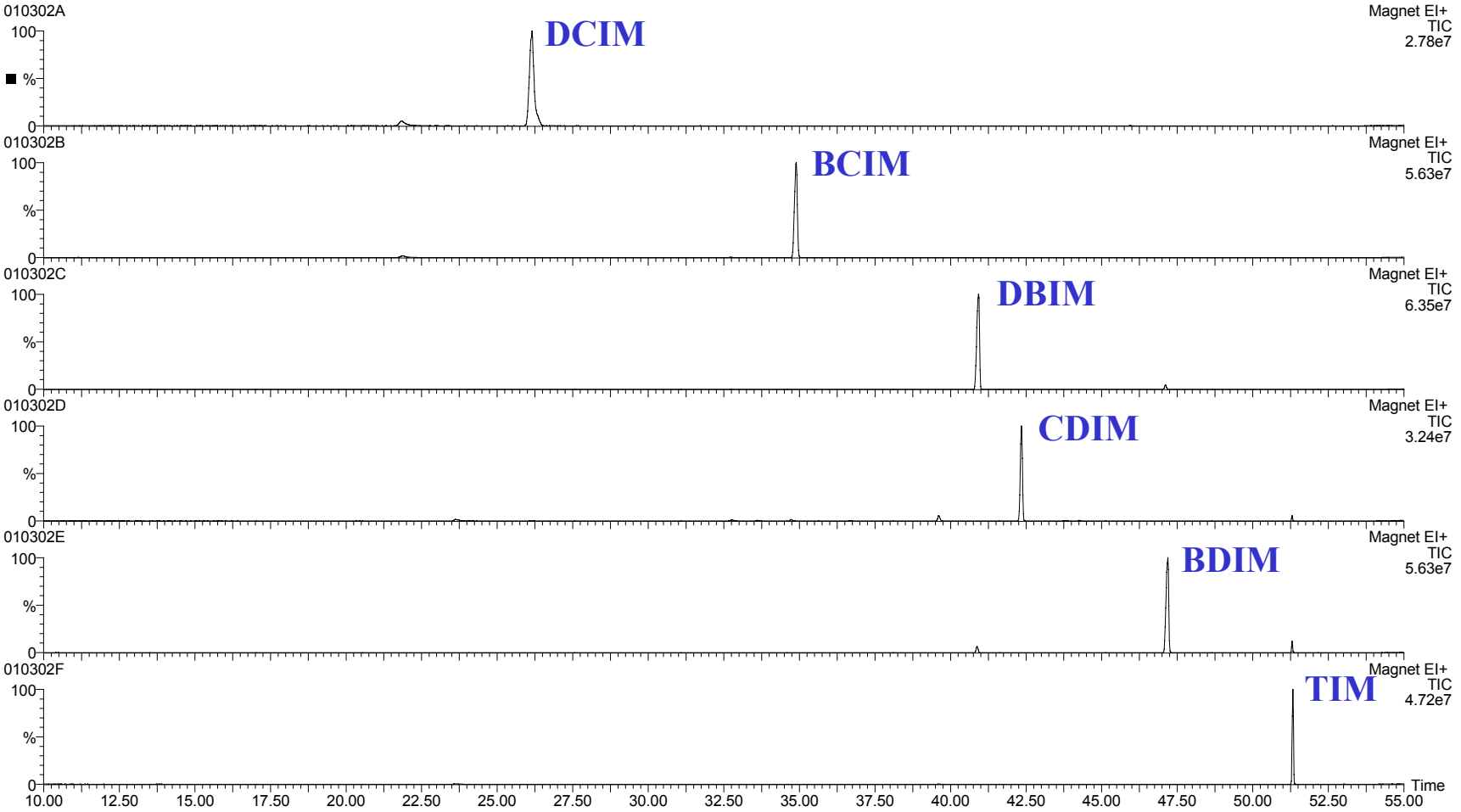

Figure 1. Full-scan total ion chromatograms of iodomethanes from January 2002 stock solution. DBP abbreviations provided in Table 2.

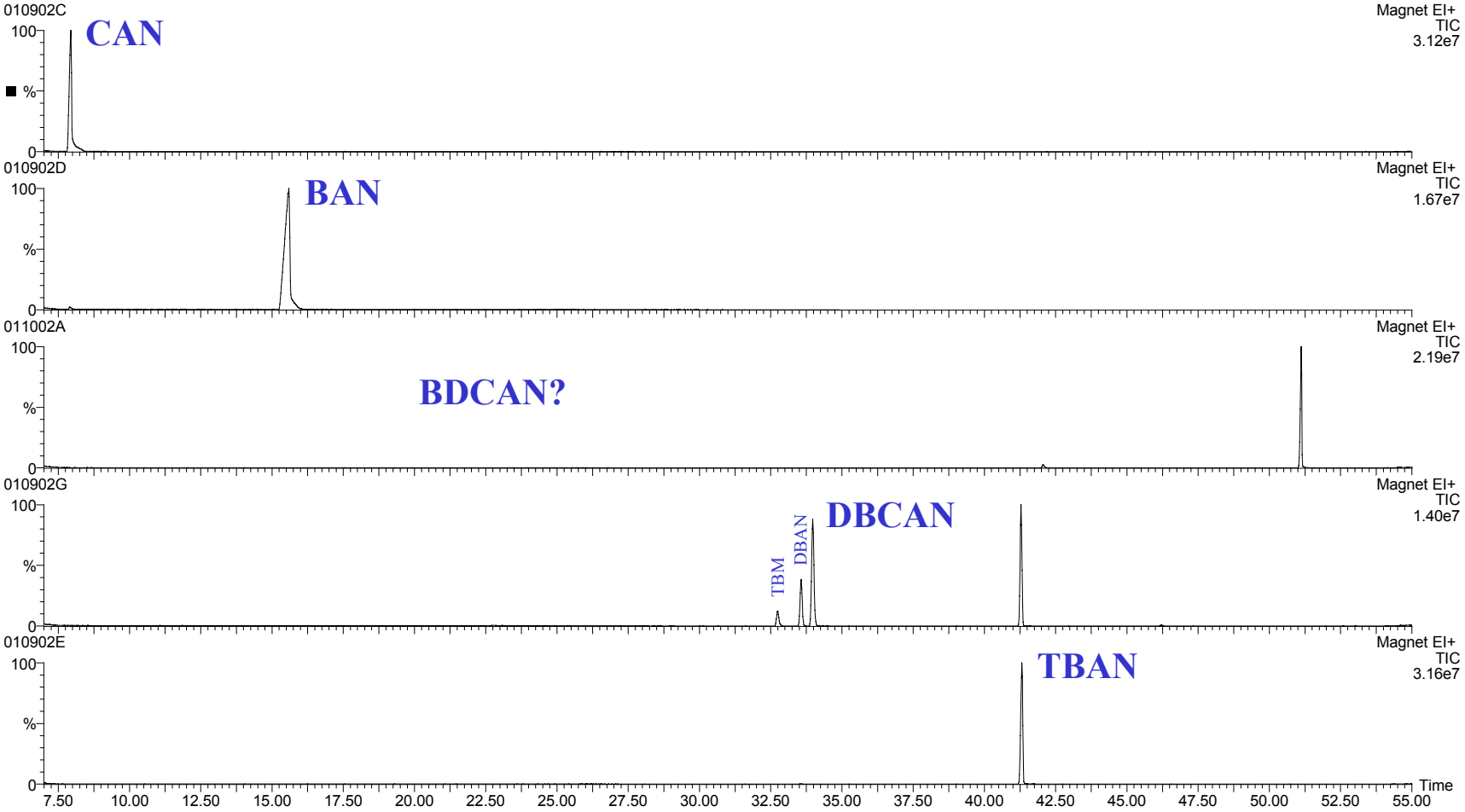

Figure 2. Full-scan total ion chromatograms for haloacetonitriles from January 2002 stock solution; a poor result for bromodichloroacetonitrile required the use of the May 2001 stock solution. DBP abbreviations provided in Table 2.

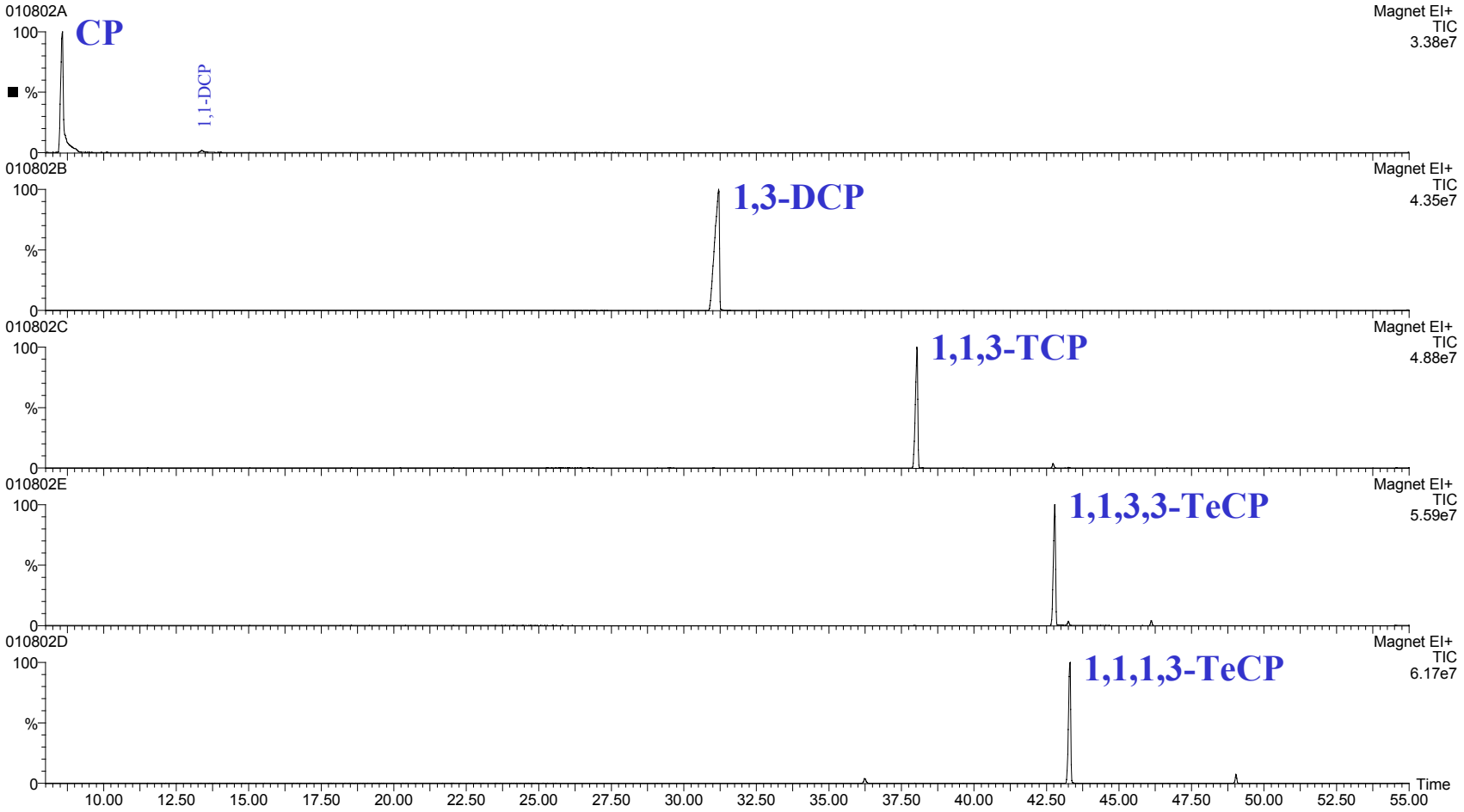

Figure 3. Full-scan total ion chromatograms of chloropropanones from January 2002 stock solution. DBP abbreviations provided in Table 2.

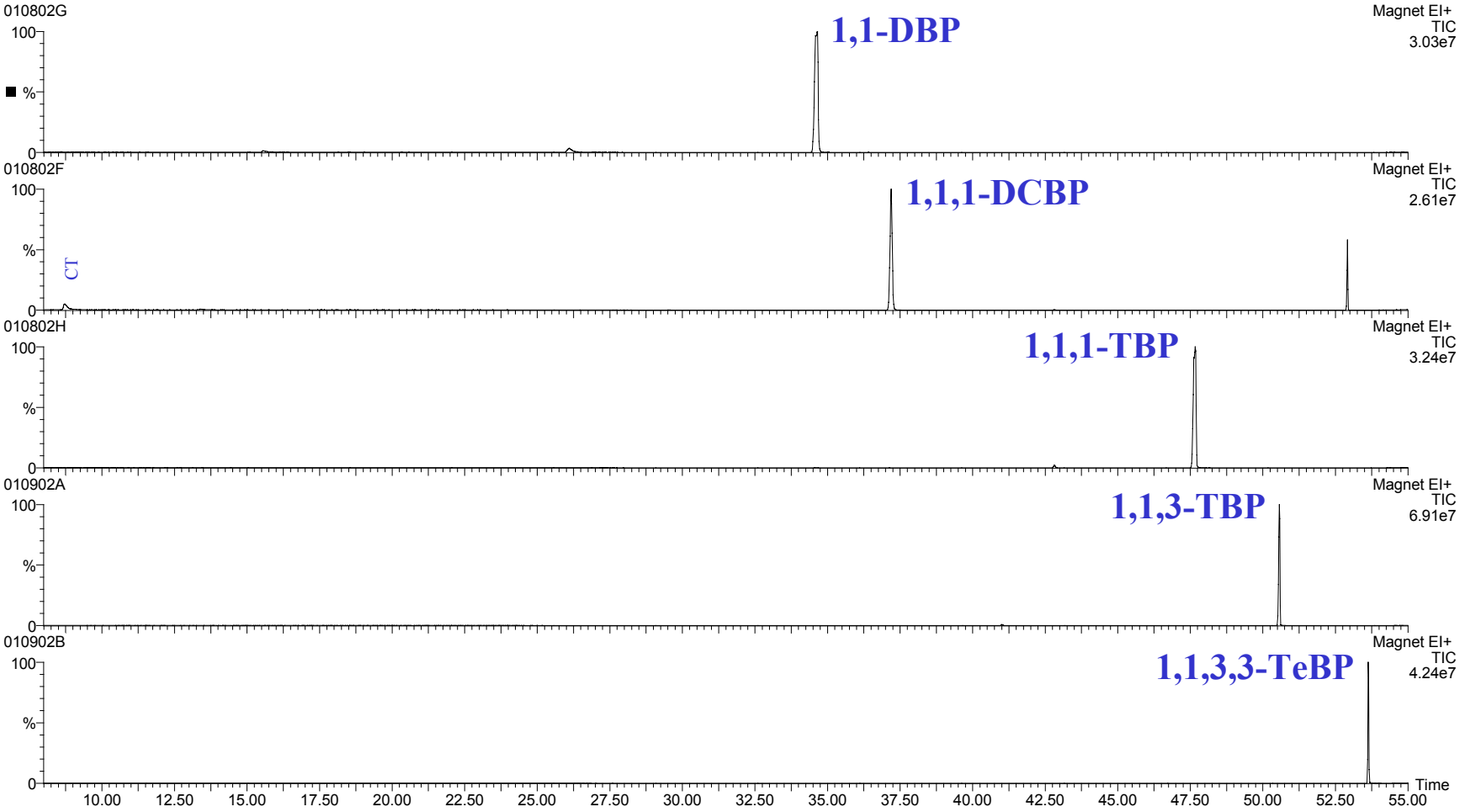

Figure 4. Full-scan total ion chromatograms of bromopropanones from January 2002 stock solution. DBP abbreviations provided in Table 2.

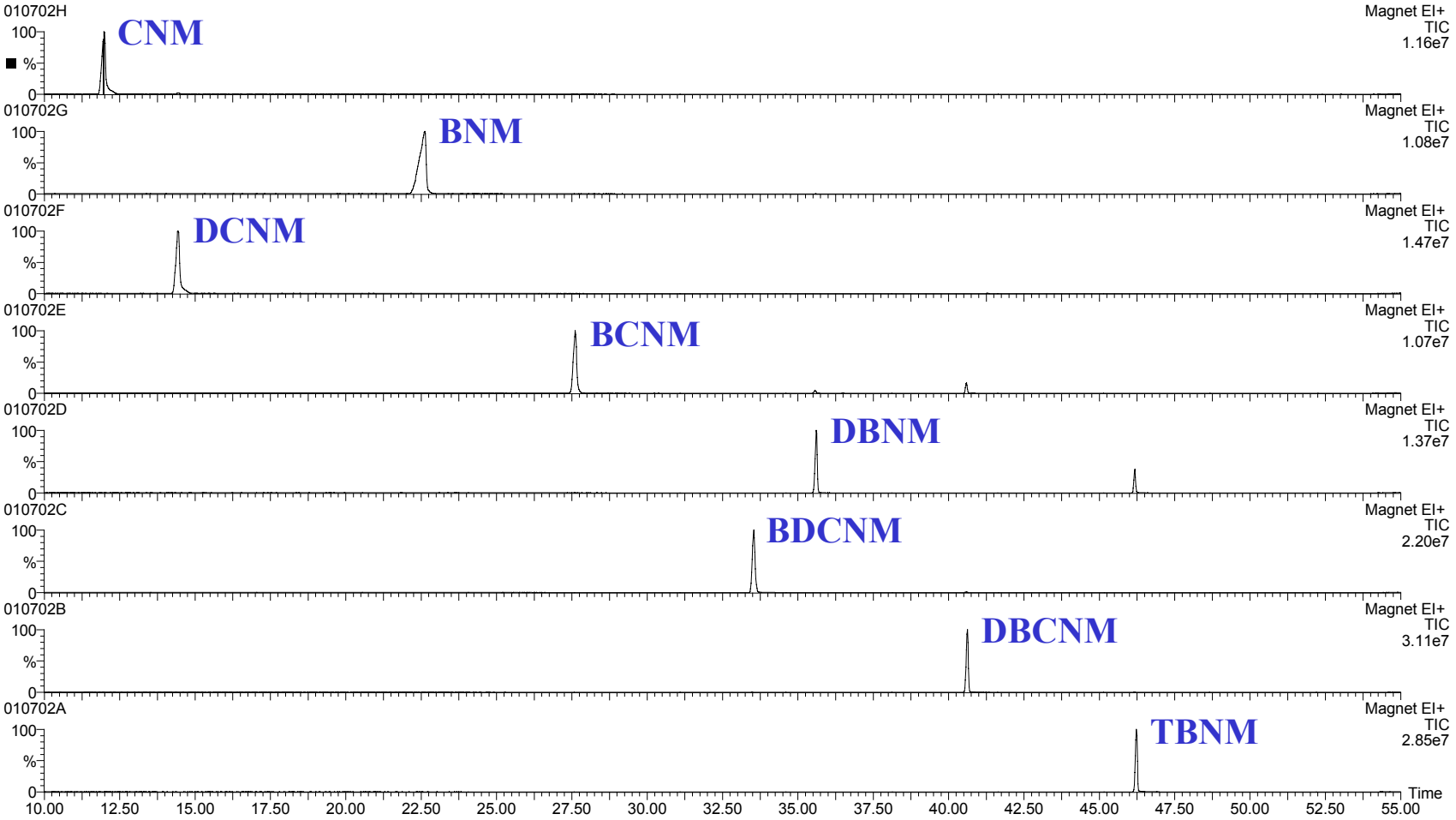

Figure 5. Full-scan total ion chromatograms of halonitromethanes from January 2002 stock solution. DBP abbreviations provided in Table 2.

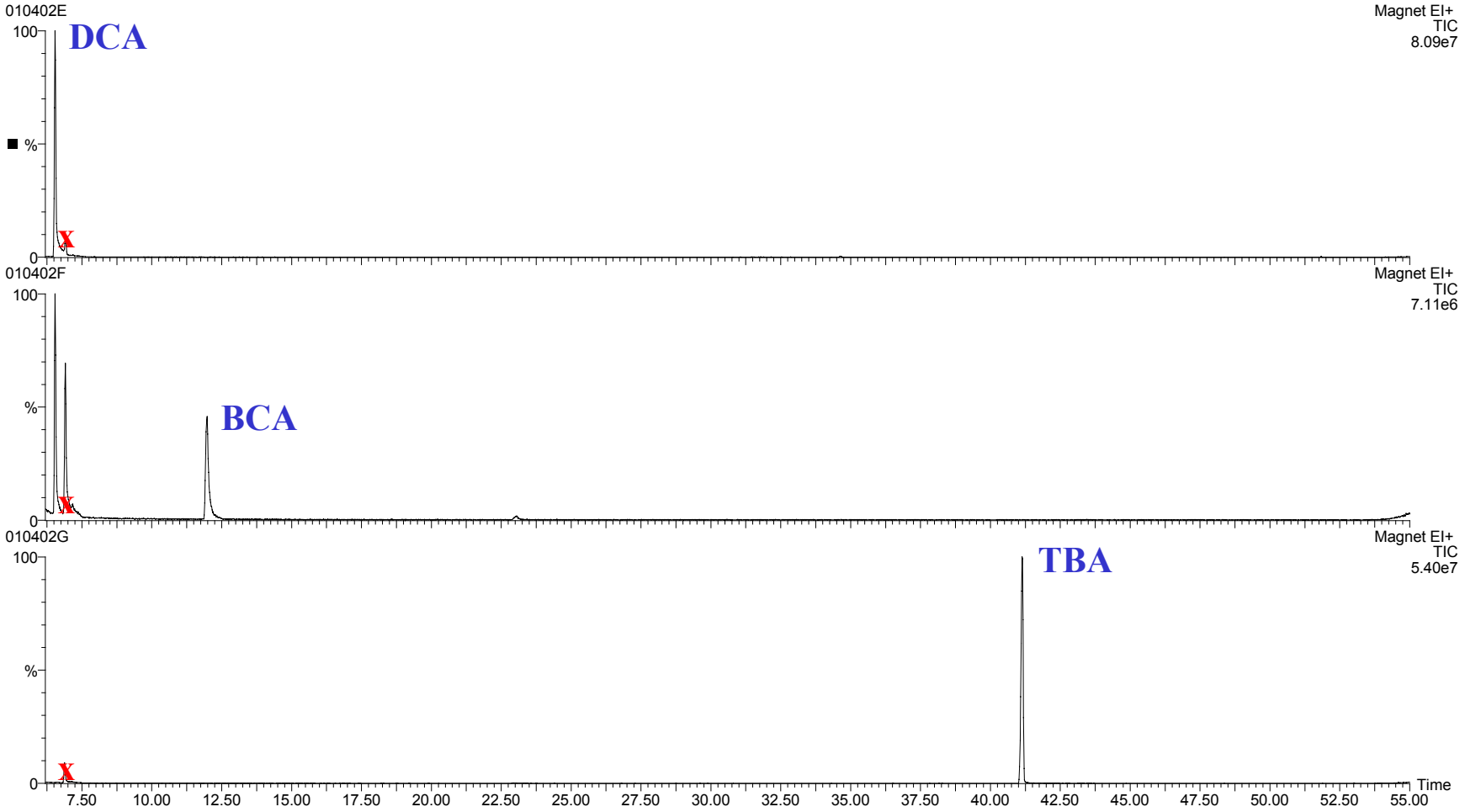

Figure 6. Full-scan total ion chromatograms of haloacetaldehydes from January 2002 stock solution; peaks marked with an "x" are solvent impurities. DBP abbreviations provided in Table 2.

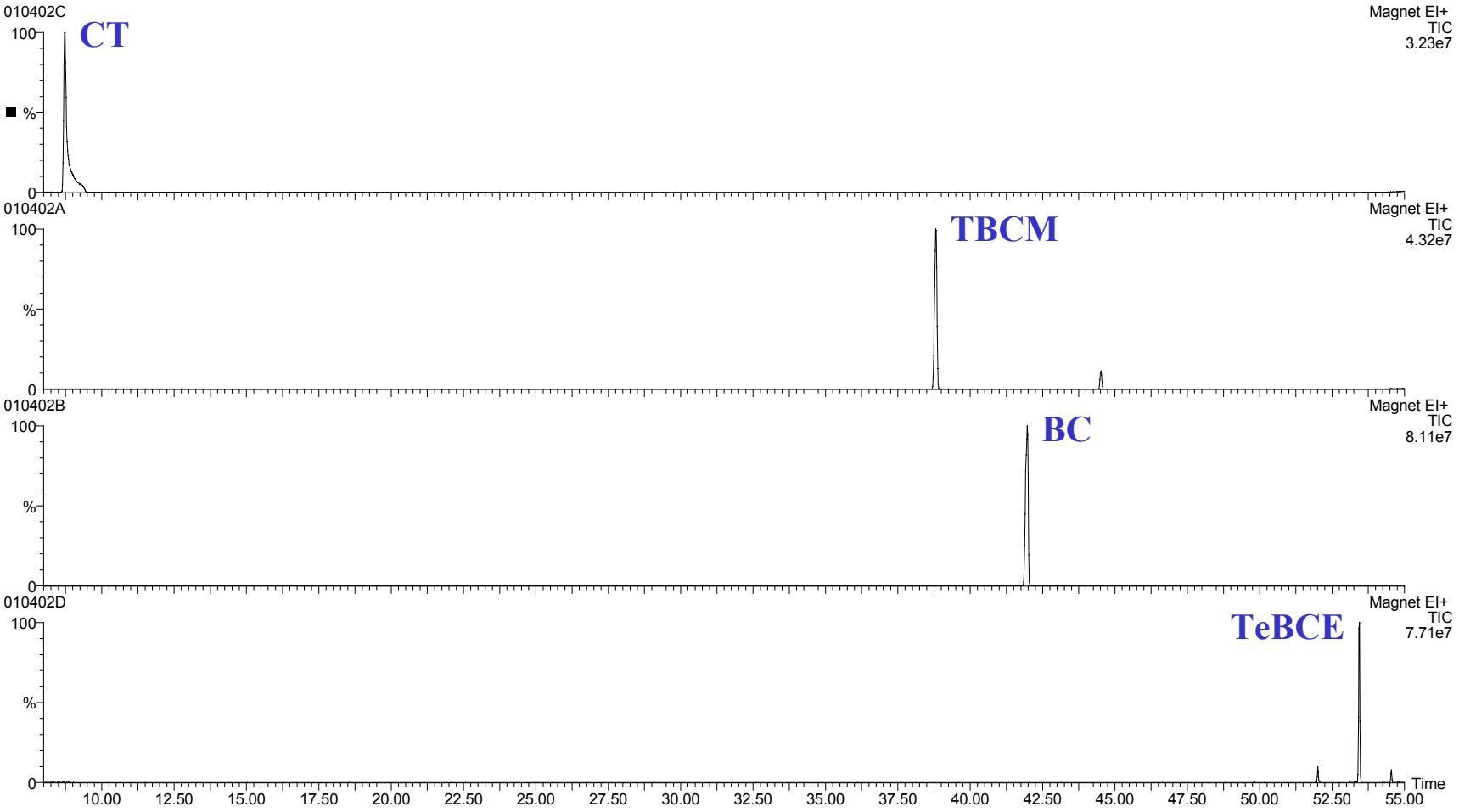

Figure 7. Full-scan total ion chromatograms of miscellaneous compounds from January 2002 stock solution. DBP abbreviations provided in Table 2.

Many of the additional peaks present in the pure compounds resulted from the synthesis procedure, where yields were less than 100 percent. Alternatively, some of the initially pure compounds may have been unstable and degraded over time, forming degradation products, some of which were other DBPs. In addition, some "impurities" were attributed to radical reactions or thermal lability of some compounds in the hot injection port and/or oven of the gas chromatograph (GC) (see section on GC Conditions below).

To obtain the highest accuracy in quantitation, the compound purities were taken into account to determine proper concentration values for standards. Thus, a 1.0 mg sample quantity weighed and diluted to 1.0 mL with solvent produced a 1000 mg/L stock solution. In the case that the compound was 90 % pure, the effective concentration of the stock solution was 900 mg/L.

Tables 2-4 detail DBP purities presented by chemical class. The identification for the impurities for the Winter 2002 quarter stock solutions is presented in Table 2. From the information in Table 2, combined chemical class mixtures were prepared at lower levels, such as 50 mg/L for solid-phase extraction (SPE). These individual master solutions were the spiking solutions used for standards preparation and also for the spiking of samples. The entire 47-compound set for SPE method development was achieved by combining six sets of mixtures that generally contained a particular chemical class. This approach was superior to quantitating individual compounds for every analysis. In addition, compound classes like the halonitromethanes, which had a propensity to degrade faster than other compound classes, could be made up more often as needed. Also, calibration curves could be prepared, which just included specific chemical classes, when more in-depth probing of sample concentrations was necessary.

Correction Factors

There are several ways to correct for concentration anomalies with the standards: (1) Calculate the actual concentration of each standard and apply it to the data analysis software. (2) Calculate the actual concentration of each standard and generate accurate calibration curves by hand for each compound of interest. (3) Determine the adjustment necessary to correct a standard and apply a correction factor to the final results. The first solution is by far the best because it applies the correction to standards early on in the data analysis process, and all subsequent samples are referenced against the correct curves. This was eventually applied to data generated using the Varian Star Workstation software for results of purge-and-trap (P&T) gas chromatography/mass spectrometry (GC/MS) and SPE-GC/MS. The second solution is extremely time-consuming because all raw areas need to be transported to an alternative software package for graphing purposes. This approach is necessary if the analysis software does not allow customization of individual concentration levels. The third solution is the quickest and easiest to implement because it looks at the overall adjustment for each of the standards and corrects the sample values after the fact.

Table 2. Making of stock solutions in MtBE for Winter 2002 Quarter

Compound	Abbreviation	Stock Date	Weight mg	Conc. (mg/L)	Checked Date	Purity	Adjusted Conc. (mg/L)	Impurities
THM/551B Mix								
Chloroform (trichloromethane)	TCM	-----		5000	-----	99+%	5000	
Bromodichloromethane	BDCM	-----		5000	-----	99+%	5000	
Dibromochloromethane	DBCM	-----		5000	-----	99+%	5000	
Bromoform (tribromomethane)	TBM	-----		5000	-----	99+%	5000	
Dichloroacetonitrile	DCAN	-----		5000	-----	99+%	5000	
Bromochloroacetonitrile	BCAN	-----		5000	-----	99+%	5000	
Dibromoacetonitrile	DBAN	-----		5000	-----	99+%	5000	
Trichloroacetonitrile	TCAN	-----		5000	-----	99+%	5000	
1,1-Dichloropropanone	1,1-DCP	-----		5000	-----	99+%	5000	
1,1,1-Trichloropropanone	1,1,1-TCP	-----		5000	-----	99+%	5000	
Chloropicrin (trichloronitromethane)	TCNM	-----		5000	-----	99+%	5000	
Iodomethane Mix								
Dichloroiodomethane	DCIM	12/27/01	6.7	6700	1/3/02	93.3%	6250	
Bromochloroiodomethane	BCIM	12/27/01	7.1	7100	1/3/02	96.7%	6850	
Dibromoiodomethane	DBIM	12/27/01	8.0	8000	1/3/02	97.2%	7800	BDIM (2.8%)
Chlorodiiodomethane	CDIM	12/27/01	5.3	5300	1/3/02	86.3%	4550	TIM (2.2%)
Bromodiiodomethane	BDIM	12/27/01	7.1	7100	1/3/02	91.5%	6500	DBIM (4.3%), TIM (4.1%)
Iodoform (triiodomethane)	TIM	12/27/01	4.3	4300	1/3/02	99+%	4300	
Haloacetonitrile Mix								
Chloroacetonitrile	CAN	12/27/01	2.8	2800	1/9/02	99+%	2800	
Bromoacetonitrile	BAN	12/27/01	5.3	5300	1/9/02	99+%	5300	
Tribromoacetonitrile	TBAN	12/27/01	6.6	6600	1/9/02	99+%	6600	
Bromodichloroacetonitrile	BDCAN	4/6/01	2.4	2400	1/16/02	91.0%	2200	CT (4.0%), DCAN (2.5%)
Dibromochloroacetonitrile	DBCAN	12/27/01	6.8	6800	1/9/02	41.1%	2800	TBAN (36.3%), DBAN (16.7%), TBM (6.0%)
Haloketone Mix								
Chloropropanone	CP	12/28/01	4.1	4100	1/8/02	98.1%	4000	1,1-DCP (1.9%)
1,3-Dichloropropanone	1,3-DCP	12/28/01	6.2	6200	1/8/02	99+%	6200	
1,1,3-Trichloropropanone	1,1,3-TCP	12/28/01	4.2	4200	1/8/02	97.7%	4100	1,1,3,3-TeCP (2.3%)
1,1,3,3-Tetrachloropropanone	1,1,3,3-TeCP	12/28/01	6.0	6000	1/8/02	94.9%	5700	1,1,1,3-TeCP (2.2%)
1,1,1,3-Tetrachloropropanone	1,1,1,3-TeCP	12/28/01	6.0	6000	1/8/02	91.7%	5500	
1-Bromo-1,1-dichloropropanone	1,1,1-BDCP	12/28/01	4.5	4500	1/8/02	76.2%	3450	CT (7.2%)
1,1-Dibromopropanone	1,1-DBP	12/28/01	5.5	5500	1/8/02	94.1%	5200	
1,1,1-Tribromopropanone	1,1,1-TBP	12/28/01	6.2	6200	1/8/02	98.6%	6100	
1,1,3-Tribromopropanone	1,1,3-TBP	12/28/01	6.6	6600	1/9/02	99.2%	6550	
1,1,3,3-Tetrabromopropanone	1,1,3,3-TeBP	12/28/01	4.0	4000	1/9/02	99+%	4000	
Halonitromethane Mix								
Chloronitromethane	CNM	12/27/01	4.3	4300	1/7/02	98.8%	4250	DCNM (1.2%)
Bromonitromethane	BNM	12/27/01	7.3	7300	1/7/02	99+%	7300	
Dichloronitromethane	DCNM	12/27/01	4.1	4100	1/7/02	99+%	4100	
Bromochloronitromethane	BCNM	12/27/01	5.2	5200	1/7/02	89.5%	4650	DBCNM (8.1%), DBNM (2.4%)
Dibromonitromethane	DBNM	12/27/01	5.9	5900	1/7/02	76.9%	4550	TBNM (23.1%)
Bromodichloronitromethane	BDCNM	12/27/01	5.5	5500	1/7/02	99+%	5500	
Dibromochloronitromethane	DBCNM	12/27/01	6.2	6200	1/7/02	99+%	6200	
Bromopicrin (tribromonitromethane)	TBNM	12/27/01	7.4	7400	1/7/02	99+%	7400	
Haloacetaldehyde Mix + Misc.								
Dichloroacetaldehyde	DCA	12/28/01	5.3	5300	1/4/02	99+%	5300	
Bromochloroacetaldehyde	BCA	12/28/01	1.4	1400	1/4/02	50.1%	700	DCA (47.7%)
Tribromoacetaldehyde	TBA	12/28/01	7.5	7500	1/4/02	99+%	7500	
Tribromochloromethane	TBCM	12/28/01	6.1	6100	1/4/02	92.4%	5650	
Carbon tetrachloride	CT	12/28/01	4.7	4700	1/4/02	99+%	4700	
1,1,2,2-Tetrabromo-2-chloroethane	1,1,2,2-TeB-2-CE	12/28/01	6.0	6000	1/4/02	92.1%	5550	
Benzyl chloride	BC	12/28/01	3.3	3300	1/4/02	99+%	3300	

Table 3. Correction factors for Winter 2002 Quarter when all standards were used

Compound	Purity	Impurities	Contributions for a 10 µg/L Standard	Corrected "10 Std"	Correction Factor
THM/551B Mix					
Chloroform	99+%				
Bromodichloromethane	99+%				
Dibromochloromethane	99+%				
Bromoform	99+%		1.46 ppb from DBCAN	11.46	1.15
Dichloroacetonitrile	99+%		0.27 ppb from BDCAN	10.27	1.03
Bromochloroacetonitrile	99+%				
Dibromoacetonitrile	99+%		4.06 ppb from DBCAN	14.06	1.41
Trichloroacetonitrile	99+%				
1,1-Dichloropropanone	99+%		0.19 ppb from CP	10.19	1.02
1,1,1-Trichloropropanone	99+%				
Chloropicrin	99+%				
Iodomethane Mix					
Dichloroiodomethane	93.3%				
Bromochloroiodomethane	96.7%				
Dibromoiodomethane	97.2%	BDIM (2.8%)	0.47 ppb from BDIM	10.47	1.05
Chlorodiiodomethane	86.3%	TIM (2.2%)			
Bromodiiodomethane	91.5%	DBIM (4.3%), TIM (4.1%)	0.29 ppb from DBIM	10.29	1.03
Iodoform	99+%		0.25 ppb from CDIM; 0.45 ppb from BDIM	10.70	1.07
Haloacetonitrile Mix					
Chloroacetonitrile	99+%				
Bromoacetonitrile	99+%				
Tribromoacetonitrile	99+%		8.83 ppb from DBCAN	18.83	1.88
Bromodichloroacetonitrile	91.0%	CT (4.0%), DCAN (2.5%)			
Dibromochloroacetonitrile	41.1%	TBAN (36.3%), DBAN (16.7%), TBM (6.0%)			
Haloketone Mix					
Chloropropanone	98.1%	1,1-DCP (1.9%)			
1,3-Dichloropropanone	99+%				
1,1,3-Trichloropropanone	97.7%	1,1,3,3-TeCP (2.3%)			
1,1,3,3-Tetrachloropropanone	94.9%	1,1,1,3-TeCP (2.2%)	0.24 ppb from 1,1,3-TCP	10.24	1.02
1,1,1,3-Tetrachloropropanone	91.7%		0.23 ppb from 1,1,3,3-TeCP	10.23	1.02
1-Bromo-1,1-dichloropropanone	76.2%	CT (7.2%)			
1,1-Dibromopropanone	94.1%				
1,1,1-Tribromopropanone	98.6%				
1,1,3-Tribromopropanone	99.2%				
1,1,3,3-Tetrabromopropanone	99+%				
Halonitromethane Mix					
Chloronitromethane	98.8%	DCNM (1.2%)			
Bromonitromethane	99+%				
Dichloronitromethane	99+%		0.12 ppb from CNM	10.12	1.01
Bromochloronitromethane	89.5%	DBCNM (8.1%), DBNM (2.4%)			
Dibromonitromethane	76.9%	TBNM (23.1%)	0.27 ppb from BCNM	10.27	1.03
Bromodichloronitromethane	99+%				
Dibromochloronitromethane	99+%		0.90 ppb from BCNM	10.90	1.09
Bromopicrin	99+%		3.00 ppb from DBNM	13.00	1.30
Haloacetaldehyde Mix + Misc.					
Dichloroacetaldehyde	99+%		9.52 ppb from BCA	19.52	1.95
Bromochloroacetaldehyde	50.1%	DCA (47.7%)			
Tribromoacetaldehyde	99+%				
Tribromochloromethane	92.4%				
Carbon tetrachloride	99+%		0.94 ppb from 1,1,1-BDCP; 0.44 ppb from BDCAN	11.38	1.14
1,1,2,2-TeB-2-CE	92.1%				
Benzyl chloride	99+%				

Adjustments were necessary when all compounds were added together into a single combined solution (Table 3). The column labeled “Corrected 10 Std" represents the concentration of the entire mass of material in a standard that was a sum of all the compounds and impurities. The values for each pure standard were corrected in the process of making intermediate solutions, such as the 50-mg/L compound class mixture discussed above. For example, if the stock solution concentration for chlorodiiodomethane (Table 2) was 5300 mg/L and the compound’s purity was 86.3 %, then the actual, rounded concentration of 4550 mg/L was used to calculate what was required to produce an exact 50 mg/L intermediate standard. Further dilutions were prepared to produce a “10 µg/L” standard. Because of the added impurities, the effective concentrations for some compounds were above 10 µg/L.

When a compound had a 91.0 % purity, 11.0 µg/L of that material was required to achieve a concentration of 10 µg/L for the analyte of interest (e.g., bromodichloroacetonitrile [BDCAN]); whereas, when a compound had a 41.1 % purity, 24.3 µg/L of that material was required to achieve a concentration of 10 µg/L for the analyte of interest (e.g., dibromo-chloroacetonitrile [DBCAN]) (Table 3). In terms of the contribution of impurities, for example, in Winter 2002, 2.5 % of the BDCAN standard was dichloroacetonitrile (DCAN) and 16.7 % of the DBCAN was dibromoacetonitrile (DBAN) (Table 3). Because 11.0 µg/L of the BDCAN and 24.3 µg/L of the DBCAN materials were required to prepare 10 µg/L standards, the contributions of the impurities were in actuality 2.5 % × 11.0 µg/L = 0.27 µg/L DCAN and 16.7 % × 24.3 µg/L = 4.06 µg/L DBAN. Even though the purity of the standards for DCAN and DBAN were each 99+ %, the contributions from the impurities in the BDCAN and DBCAN standards, respectively, resulted in the 10 µg/L calibration standard having 10 + 0.27 = 10.27 µg/L DCAN and 10 + 4.06 = 14.06 µg/L DBAN. Moreover, in some cases, such as for carbon tetrachloride—which was obtained as a high-purity standard—it was also found as an impurity in two of the synthesized standards (BDCAN and 1,1,1-bromodichloropropanone [1,1,1-BDCP]). Thus, the correction factor for carbon tetrachloride reflected the contributions from the two sources of impurity (Table 3).

The correction factors were applied to samples to correct values obtained with the standard calibration curves (Method #3). Alternatively, the factors were applied to the standards to graph accurate calibration curves, and the sample values were read directly from the chart (Method #1).

Finally, only those compounds that were measured with an analytical technique were counted in the correction factor calculations. For example, several DBPs (e.g., DBCAN) were ultimately dropped from the SPE-GC/MS method due to stability issues with the dechlorination agent ascorbic acid. Thus, the impurity contributions of DBCAN—tribromoacetonitrile (TBAN) (36.3 %), DBAN (16.7 %), and bromoform (tribromomethane, TBM) (6.0 %)—were no longer present in the SPE-GC/MS standards. TBAN was also removed from the SPE method, so its correction factor did not make any difference. DBAN’s and TBM’s correction factors of 1.41 and 1.15 were no longer needed with the elimination of DBCAN from the SPE method. Thus, each of the analytical methods required a modification of Table 3 to reflect the compounds that were being included in each method’s combined standard.

GC Conditions

For checking the purity of the standards, the original GC temperature program followed the U.S. Environmental Protection Agency (USEPA) Method 551.1 procedure (Munch and Hautman, 1995), using a DB-1 capillary column (J&W Scientific/Agilent, Folsom, CA; 1.0 μm film thickness, 0.25 mm ID x 30 m). Initially, the following program was used: hold at 35°C for 22 min; increase to 145°C at 10°C/min and hold at 145°C for 2 min; increase to 225°C at 20°C/min and hold at 225°C for 15 min. The GC injector temperature was 200°C, and the detector temperature was 290°C.

An additional temperature ramp to 260°C was eliminated because all of the compounds eluted during the third step of the temperature program. In addition, an injector temperature of 200°C caused significant degradation of some compounds. The injector temperature was set at 117°C based on an earlier GC method, which prevented the degradation of the thermally labile compound bromopicrin (Krasner et al., 1991). Furthermore, it was possible that some of the "impurities" found were actually radical reaction products formed in a hot injection port. Chen et al. (2002) saw similar behavior to bromopicrin with other trihalocompounds (e.g., the trihaloacetonitriles and other trihlonitromethanes).

The initial purity checks for the study—September 2000 and January 2001—used an injector temperature of approximately 115°C, while work continued to refine the GC temperature conditions. An updated GC program was adopted for the stock solutions starting with the May 2001 set. This new method improved chromatography and helped to eliminate some of the impurities by further dropping the injection temperature—from 115 to 89°C——as well as lowering the oven temperature at which many of the DBPs eluted. The new temperature program was as follows: hold at 35°C for 23 min; increase to 139°C at 4°C/min; increase to 301°C at 27°C/min and hold at 301°C for 5 min. The injector temperature was 89°C.

Table 4 summarizes the purity checks performed during the study. For tribromoacetonitrile, bromodichloroacetonitrile, dbromochloroacetonitrile, and bromopicrin, there was no significant change in purity with the switch from EPA Method 551.1's GC temperature program to the updated GC program in May 2001. For other compounds, such as the iodomethanes, there was a significant change (improvement) in purity with the updated GC temperature program: up to 25 % for iodoform and 37 % for bromodiiodomethane. Most compounds improved or stayed the same. Only two compounds appeared to diminish in purity after the GC temperature program change: 1,1,3-tribromo-propanone (1,1,3-TBP) and bromochloroacetaldehyde (BCA). Some compounds, such as 1,1,3-TBP, have stability issues, in general. A fresh standard of 1,1,3-TBP from Helix Biotech provided more pure material to complete the last set of Winter 2002 quarter stock solutions. BCA was always problematic because synthesized standards always contained a large contribution from dichloroacetaldehyde (DCA). The small loss in purity for BCA in May 2001 could have resulted from difficulty in quantitation of DCA.

Table 4. Purity checks of synthesized standards

Compound	Source	Purity Sep-00	Purity Jan-01	Purity[a] May-01	Status Summer-01	Purity[a] Jan-02
Iodomethanes						
Dichloroiodomethane	Agbar[b]	94.7%				
"	Agbar		**New 85.4%**	90.2%		93.3%
Bromochloroiodomethane	Agbar	75.3%				
"	Agbar		**New 89.7%**	96.4%		96.7%
Dibromoiodomethane	Agbar	13.4%				
"	Agbar		**New 86.5%**	99+%		97.2%
Chlorodiiodomethane	Agbar	65.0%				
"	Agbar		**New 52.7%**	68.3%		86.3%
Bromodiiodomethane	Agbar	Gone				
"	Agbar		**New 56.0%**	93.8%		91.5%
Iodoform	Mallinckrodt,[c] 99%	74.4%	73.3%	99+%		99+%
Haloacetonitriles						
Chloroacetonitrile	Aldrich,[d] 99%	99+%	99+%	99+%		99+%
Bromoacetonitrile	Aldrich, 97%	99+%	99+%	99+%		99+%
Tribromoacetonitrile	UNC[e]	97.2%	95.2%	99+%		99+%
Bromodichloroacetonitrile	UNC, 93%, < 10 mg	92.6%	92.4%	94.8%	Running low	91.0%[f]
Dibromochloroacetonitrile	UNC, 60%, < 10 mg	41.6%	36.4%	42.1%	Gone	
"	UNC, < 10 mg					**New 41.1%**
Haloketones						
Chloropropanone	Aldrich, 95%	96.4%	88.9%	98.0%		98.1%
1,3-Dichloropropanone	Aldrich, 95%	99+%	98.4%	99+%		99+%
1,1,3-Trichloropropanone	Fluka,[g] 85%	92.0%	78.1%	99.6%		97.7%
1,1,3,3-Tetrachloropropanone	UNC	90.4%	71.5%	99.0%	Running low	
"	Helix Biotech,[h] 93.5%				**New 96.5%**	94.9%
1,1,1,3-Tetrachloropropanone	UNC	**Not available**	66.3%	92.4%	Running low	
"	Helix Biotech, 86.0%				**New 82.7%**	91.7%
1-Bromo-1,1-dichloropropanone	UNC, 95%	75.0%	63.1%	77.6%		76.2%
1,1-Dibromopropanone	UNC	36.0%	17.0%	38.4%	Running low	
"	Helix Biotech, 92.5%				**New 94.0%**	94.1%
1,1,1-Tribromopropanone	Can Syn Corp[i]	89.0%	48.4%	97.0%	Running low	
"	Helix Biotech, 97.5%				**New 98.1%**	98.6%
1,1,3-Tribromopropanone	Can Syn Corp	89.0%	84.2%	55.8%	Gone	
"	Helix Biotech, 96.1%				**New 97.6%**	99.2%
1,1,3,3-Tetrabromopropanone	TCI America,[j] 98%	99+%	99.0%	99+%		99+%

Table 4 (continued)

Compound	Source	Purity Sep-00	Purity Jan-01	Purity[a] May-01	Status Summer-01	Purity[a] Jan-02
Halonitromethanes						
Chloronitromethane	Can Syn Corp	**Not available**	**Not available**	99+%	Gone	
"	Helix Biotech, 97.2%				**New 98.5%**	98.8%
Bromonitromethane	Aldrich, 90%	99.8%	98.7%	99+%		99+%
Dichloronitromethane	Can Syn Corp	99+%	96.5%	99+%		
"	Helix Biotech, 98.6%				**New 99+%**	99+%
Bromochloronitromethane	Can Syn Corp	**Not available**	82.8%	97.4%	Running low	
"	Helix Biotech, 87.1%				**New 85.3%**	89.5%
Dibromonitromethane	Majestic Research[k]	21.3%	77.4%	97.1%		76.9%
Bromodichloronitromethane	Can Syn Corp, < 10 mg	55.8%	**Not available**			
"	Can Syn Corp, 98.3%			**New 99+%**		
"	Helix Biotech, 95.8%				**New 99+%**	99+%
Dibromochloronitromethane	Can Syn Corp, < 10 mg	**Not available**	**Not available**			
"	Can Syn Corp, 95.2%			**New 99+%**		
"	Helix Biotech, 97.1%				**New 99+%**	99+%
Bromopicrin	Columbia Org Chem Co,[l] 95%	97.9%	95.9%	99+%		99+%
Haloacetaldehydes						
Dichloroacetaldehyde	TCI America, 95%	99+%	92.2%	99+%		99+%
Bromochloroacetaldehyde	UNC, < 10 mg	57.2%	52.0%	45.3%	Gone	
"	UNC, < 10 mg					**New 50.1%**
Tribromoacetaldehyde	Aldrich, 97%	99+%	91.4%	99+%		99+%
Miscellaneous						
Carbon tetrachloride	Supelco,[m] 99.97%	99+%	99+%	99+%		99+%
Tribromochloromethane	UNC, 90%	73.4%	76.4%	94.9%	Running low	
"	Helix Biotech, 90.3%				**New 84.3%**	92.4%
1,1,2,2-TeB-2-CE	Can Syn Corp	**Not available**	**Not available**	**Not available**	78.7%	92.1%
Benzyl chloride	Fluka, 99.5%	99+%	99+%	99+%		99+%

[a]Updated GC Program

[b]Agbar: Aigues of Barcelona (Spain)

[c]Mallinckrodt (Phillipsburg, N.J.)

[d]Aldrich Chemical Company (St. Louis, Mo.)

[e]UNC: Synthesized by University of North Carolina at Chapel Hill

[f]Stock solution from May 2001

[g]Fluka Chemical Co. (St. Louis, Mo.)

[h]Helix Biotech (New Westminster, B.C., Canada)

[i]Can Syn: Synthesized by Can Syn Chem Corp (Toronto, Ont., Canada)

[j]TCI America (Portland, Ore.)

[k]Majestic Research: Synthesized by George Majetich, University of Georgia (Athens, Ga.)

[l]Columbia: Synthesized by Columbia Organic Chemical Co., Inc. (Camden, S.C.)

[m]Supelco (Bellefonte, Pa.)

Problematic Compounds

Hexachloropropanone (HCP) and Pentachloropropanone (PCP). Hexachloropropanone (HCP) may undergo a haloform-type reaction in the presence of nucleophiles; consequently, it can degrade in acetone or methanol. Thus, HCP stock solutions were prepared in MtBE to check retention times. HCP and pentachloropropanone (PCP), however, degraded immediately by 100 % in water under all conditions. Trihalomethyl-ketones may react with hydroxide ions under basic conditions, forming a haloform and a carboxylate anion. Thus, HCP should form trichloroacetic acid (TCAA) and chloroform. This hydrolysis was investigated by spiking distilled water with 30 μg/L of HCP. An aliquot of the 30 μg/L HCP spiked water was acidified, extracted, and methylated with a solution of sulfuric acid/methanol. GC analysis showed the presence of 29.6 μg/L of TCAA, which was also confirmed by GC/MS. A liquid/liquid extraction-GC analysis of another aliquot of the spiked sample showed the presence of 28.6 μg/L of chloroform. Thus, the hydrolysis of HCP, forming TCAA and chloroform, was confirmed. A similar experiment was not performed with PCP-spiked water. However, the expected degradation by-products for this haloketone are dichloroacetic acid and chloroform.

1,1,2,2-Tetrabromo-2-chloroethane (1,1,2,2-TeB-2CE) and 1,1,1,2-Tetrabromo-2-chloroethane (1,1,1,2-TeB-2CE). These compounds presented great difficulty in terms of synthesis. A standard of 1,1,2,2-TeB-2CE was ultimately available in relatively high purity from Can Syn Corp., whereas the 1,1,1,2-TeB-2-CE was available at 28 % purity from Can Syn Corp., and as a small sample from the University of North Carolina (UNC) (Figure 8). The impurities of the first tetrabromochloroethane (TeBCE) sample (Figure 8a) are tribromodichloroethane (TBDCE) and pentabromoethane (PBE), based on the elution order of the compounds and also on the theoretical isotopic patterns for subsequent losses of bromine from each impurity.

A second standard from Can Syn Corp contained both TeBCE isomers together. There is very little difference between Br_2CHCBr_2Cl and $Br_3CCHBrCl$. Both have the same mass, which leads to similar retention times, and the two peaks co-eluted, even using the updated GC program (Figure 9b). Furthermore, the mass spectra are nearly the same, with the exception that the $Br_3CCHBrCl$ has a small contribution from CBr_3^+ (at only about 8 % of the most abundant peak). Thus, the "3+1" TeBCE (1,1,1,2-tetrabromo-2-chloroethane) cannot be easily distinguished from the "2+2" TeBCE (1,1,2,2-tetrabromo-2-chloroethane).

A decision was made to test for the 1,1,2,2-TeB-2-CE species, in part, because a standard of sufficient purity was available. In addition, it was not clear if the compound in the original study in which it was identified was the "3+1" or the "2+2" species. Any TeBCE compounds that were present would co-elute and be reported as a combined TeBCE result.

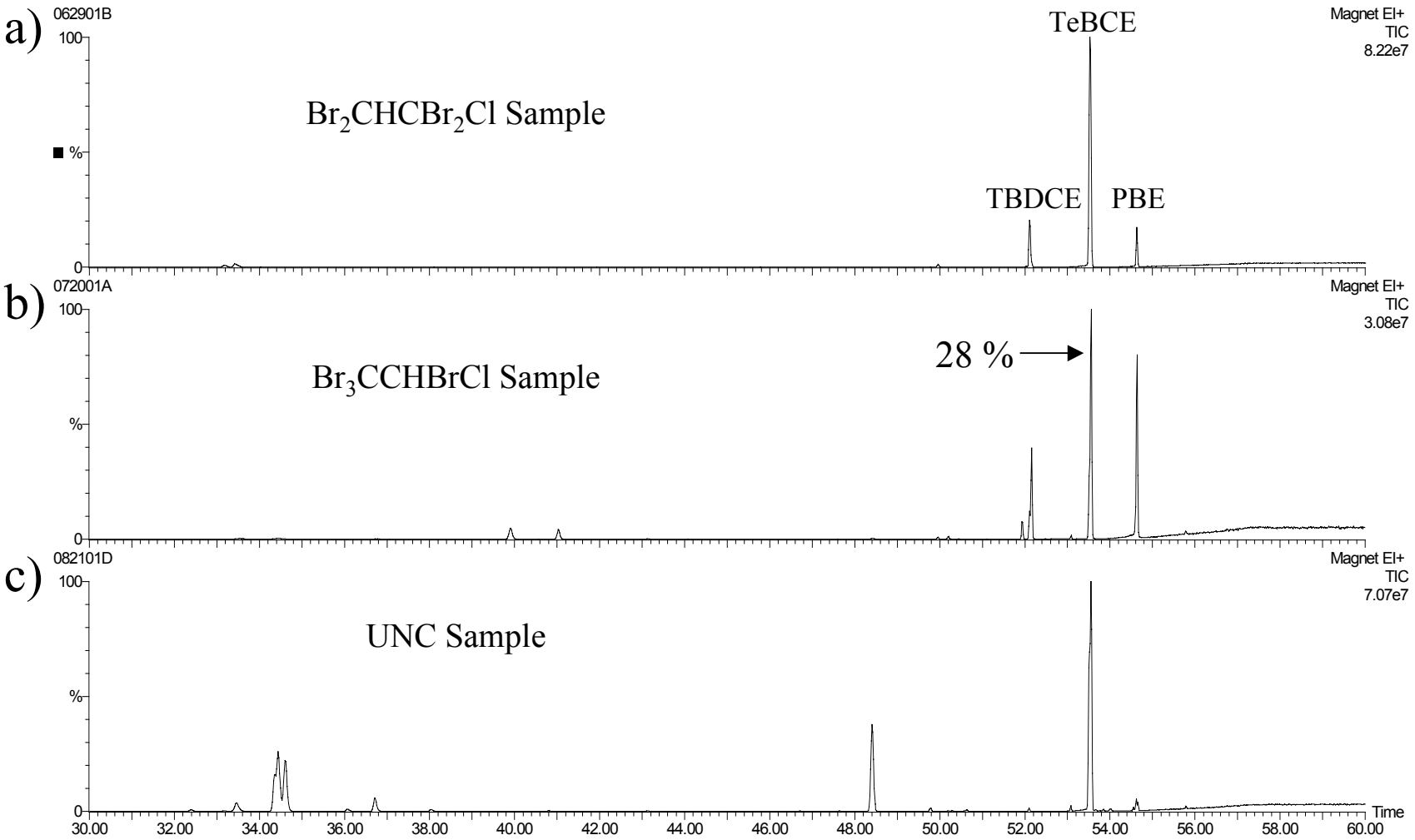

Figure 8. Total ion chromatograms for TeBCE samples: (a) Original shipment of 1,1,2,2-tetrabromo-2-chloroethane; (b) Target compound 1,1,1,2-tetrabromo-2-chloroethane at reported 28 % purity; (c) UNC sample.

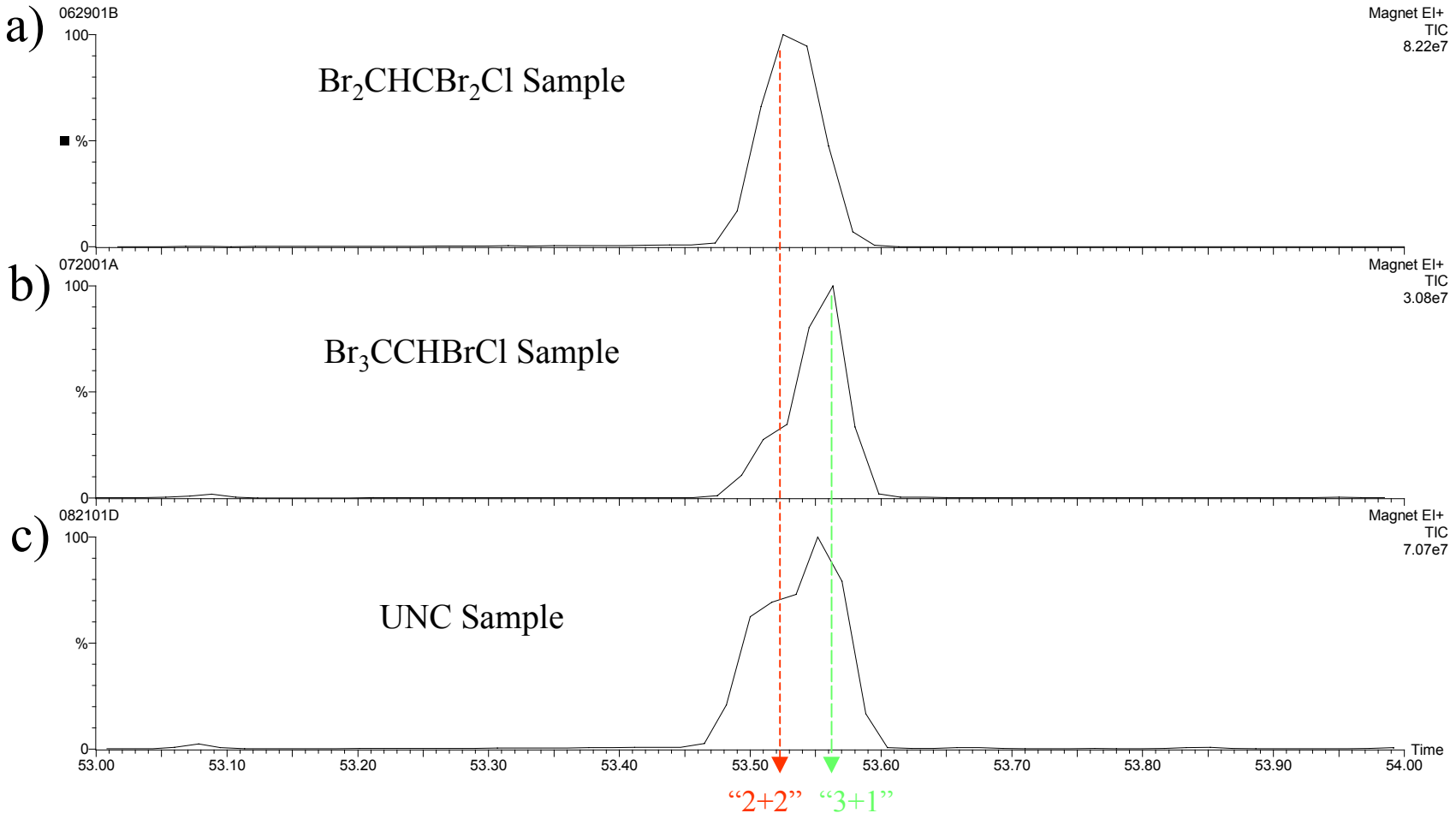

Figure 9. Expanded view of TeBCE samples: (a) Original shipment of 1,1,2,2-tetrabromo-2-chloroethane; (b) Target compound 1,1,1,2-Tetrabromo-2-chloroethane at reported 28 % purity;
(c) UNC sample.

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SOLID PHASE EXTRACTION-GAS CHROMATOGRAPHY/ MASS SPECTROMETRY METHOD

A solid phase extraction (SPE)-gas chromatography/mass spectrometry (GC/MS) method was developed for quantifying several of the targeted DBPs for this study (Figure 1). SPE offers an alternative extraction means to conventional liquid-liquid extraction, and the use of a mass spectrometric detector provides specificity that is not possible with electron capture detection (ECD) included in EPA Method 551.1. With the method developed here, concentration of 100 mL of drinking water by SPE provided a sufficient concentration factor to achieve low µg/L detection.

EXPERIMENTAL

Instrumentation

A Varian Saturn 2000 ion trap mass spectrometer (Varian Analytical Associates Inc., Walnut Creek, CA) equipped with a 3800 GC and a CTC A200s autosampler (CTC Analytics, Switzerland) was used. Early methods development was performed on a VG TS-250 medium-resolution mass spectrometer (VG Tritech – now Micromass, Inc., Manchester, England). A Hewlett-Packard/Agilent Model 5890 GC (Palo Alto, CA) was used for separations and was partially controlled by an Optic 2 injector (AI Cambridge Ltd., Cambridge, England). Both full-scan and selected ion monitoring (SIM) analyses were conducted.

Sample Preparation

Varian Bond Elut PPL (Varian Associates, Inc., Harbor City, CA) SPE cartridges were used for extraction of drinking water. Certified standard mixtures were obtained from Ultra Scientific (North Kingstown, RI). HCM-551B contains the following compounds at a level of 5000 µg/mL in acetone: bromochloroacetonitrile, chloropicrin, dibromoacetonitrile, dichloroacetonitrile, 1,1-dichloropropanone, trichloroacetonitrile, and 1,1,1-trichloropropanone. THM-521 mix contains chloroform, bromodichloromethane, dibromochloromethane, and bromoform at a level of 5000 µg/mL in methanol.

For the DBPs investigated in this study, stock solutions were prepared by accurately measuring 1.0 mL of methanol (Burdick & Jackson, purge and trap grade, Muskegon, MI) into a capped 1.4 mL autosampler vial and weighing it. Approximately 2-3 µL of pure standard were pulled into a clean syringe and spiked under the solvent after piercing the septum. The additional weight by difference, between 2-5 mg, was used to calculate an approximate concentration value. Alternatively, solid compounds were weighed by difference and deposited directly into an empty autosampler vial before solvent was added. The septum caps were changed before storage of the samples. Using diluted versions of these stock solutions, the purity of the stock solutions could be obtained, and adjustments made to the initial calculations (see separate section on Standards).

SPE was performed using a commercially available 12-port Visiprep vacuum manifold and 1/8-inch Teflon tubing with weighted stainless steel ends (Supelco Chromatography, Bellafonte, PA). Samples (100 mL) were placed in clean and dry 125-mL Erlenmeyer flasks that had been rinsed several times in pure water and baked for 1 hour at 130 ºC. The Teflon tubing was heated for 10 min at 130 ºC.

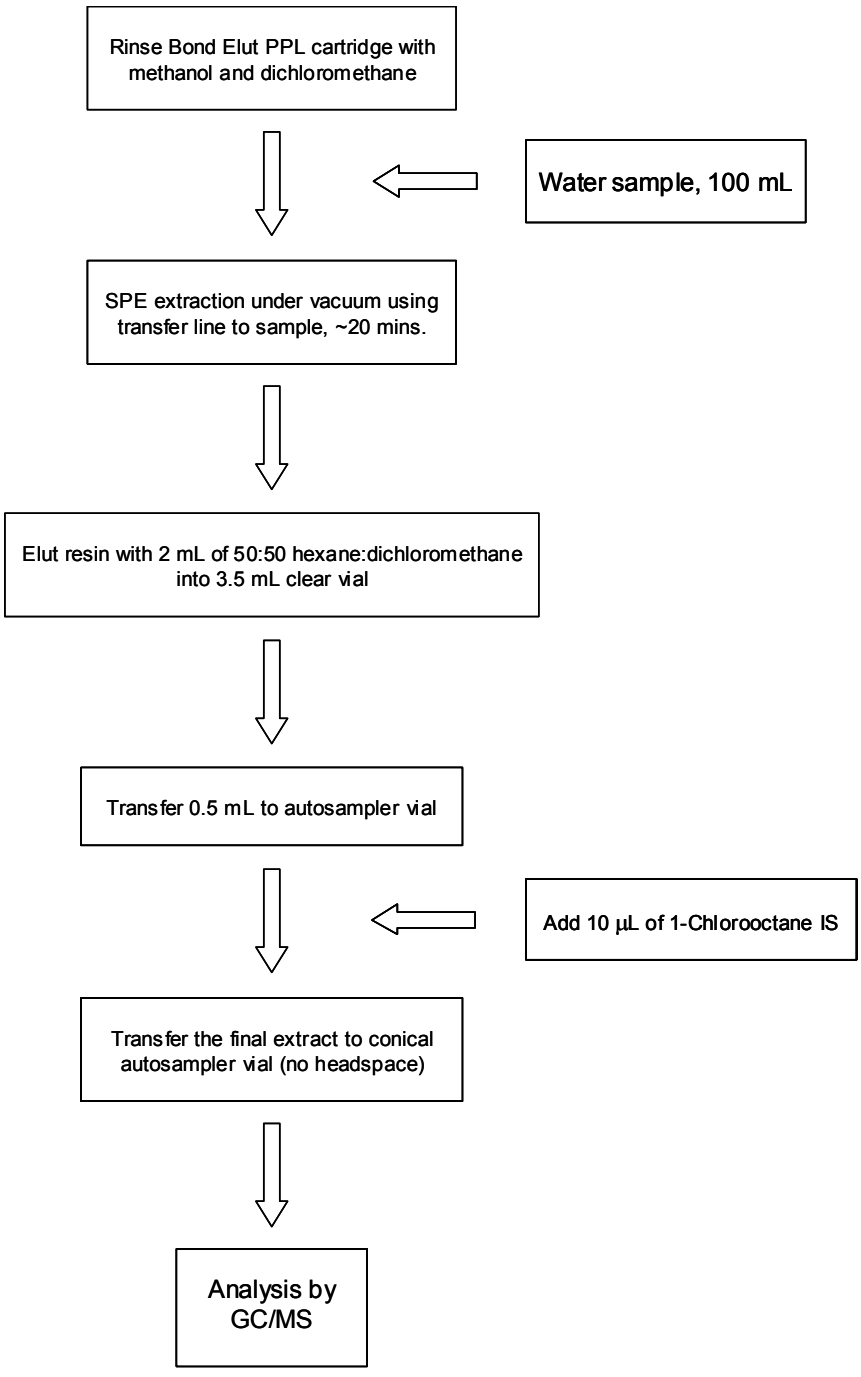

Figure 1. Summary of the SPE-GC/MS method used for analyzing 35+ DBPs in drinking water.

Six 3-mL SPE cartridges were conditioned by adding two 3 mL aliquots of methanol to the cartridge and allowing it to drain under vacuum, followed by two 3 mL aliquots of dichloromethane (Mallinckrodt Baker Inc., Paris, Kentucky). The samples were then attached to the vacuum manifold using the Teflon tubing and tube adapters. The flow rates were between 2 and 7 mL/minute for all samples for complete passage of the water through the sorbent. The vacuum lines were closed individually upon completion of the water transfer. To avoid loss of compounds, the vacuum was not applied to the sorbents any longer than necessary once the water had eluted.

The Teflon tubing from each sample cartridge was removed and the vial rack inserted with six 3.5-mL collection vials. Two mL of a 1:1 mixed solvent system of hexane (Aldrich Chemical Co., THM grade, Milwaukee, WI) and dichloromethane was used as the elution solvent and placed at the top of the sorbent. (It was not possible to use MtBE as a solvent, due to the Varian ion trap mass spectrometer being located in a MtBE-free environment in the laboratory). The individual manifold valves were opened and 10 drops were allowed to pass through the sorbent material. The six samples were eluted sequentially, 10 drops at a time, until no solvent was left in the cartridge. To complete the procedure, 0.5 mL of the top portion phase was transferred to an autosampler vial capped with a Teflon-lined septum. Ten µL of a 10 mg/L 1-chlorooctane standard (Chem Service, West Chester, PA) was added as the internal standard.

Standards and Check Sample

One advantage of a sector-based mass spectrometer is the dynamic range that can be achieved. Unlike an ion trap mass spectrometer, ions are separated in space and do not suffer from so-called "space charge" phenomena. Beginning with the first St. Louis/East St. Louis sample set (January 2001), a protocol was established that included standards made at the following levels: 1.0, 2.5, 5.0, 10, 20, 30, 40, 50, 60, 75, and 100 µg/L in pure water and adjusted to pH 3.5 (for initial analyses using the TS-250 sector mass spectrometer). These higher values (up from 40 µg/L previously) were used to bracket some of the higher THM concentrations that were seen at some earlier utilities. It was not feasible to spike a mixed set of DBPs for any given standard because of software processing limitations. Any higher concentration data points that were skewing the calibration curve or causing undesirable effects were eliminated. Using this method, very linear curves were produced for most of the 43 compounds analyzed by SPE-GC/MS.

The “check standard” can either be a newly extracted standard or a reinjection of one of the calibration standards. For the early utilities, the original calibration standards were used as check standards because it was very important to make sure that the instrument response had not drifted over the extended runs of the instrument (up to 38 hours). The final check was typically a 50 µg/L or 40 µg/L standard that was used to prove the instrument was still responding correctly. In this way, the check standard was certifying the run, and not necessarily the method.

New calibration standards were required to address the inability to use MtBE as the primary solvent for the SPE method. Migrating the method to the Varian ion trap mass spectrometer also set restrictions on the concentration range of standards that could be run on the instrument to avoid saturation of the trap and potential carryover to subsequent samples. Careful evaluation of the ion trap's sensitivity at full scan led to the following recommendations for standard concentrations: 0.25, 0.50, 1.0, 2.5, 5.0, 7.5, 10, 15, 20, 30, and 40 µg/L. Only the

range 0.25 µg/L to 30 µg/L would be used for calibration purposes because of a ten-point limit with the Star Workstation software. The 40 µg/L standard would be used for optional processing should THM concentrations exceed this range. This became an acceptable protocol because all DBP concentrations typically were below 40 µg/L, with the exception of chloroform, which was later dropped from the SPE method due to co-elution with the 1:1 hexane:methylene chloride solvent system. The final check standard and all sample spikes were at a level of 10 µg/L.

Gas Chromatography

Prior to June 2001, when the TS-250 sector mass spectrometer was used, the primary column was a DB-1, 30-m, 0.25-mm ID column with a 1-µm film thickness (J & W Scientific/Agilent, Folsom, CA). The Optic 2, an advanced programmable temperature injector unit, was used to develop the EPA method in conjunction with the TS-250 mass spectrometer. The unit comes with its own injector replacement for the Hewlett Packard 5890 GC and controls the flow of helium carrier gas, the injection temperature, and the split valves. The Optic 2 injector was set at 110 ^{o}C and was operated in a splitless mode with a head pressure of 8.0 psi on the column. Injection volume was 3 µL. The temperature program followed EPA Method 551.1: 1) Hold at 35 ºC for 22 min; 2) increase to 145 ºC at 10 ºC/min and hold at 145 ºC for 2 min; and 3) increase to 225 ºC at 20 ºC/min and hold at 225 ºC for 10 min.

After June 2001, when the Saturn ion trap mass spectrometer was used, the primary column was a DB-1, 30-m, 0.25-mm ID column with a 1-µm film thickness (J & W Scientific/Agilent, Folsom, CA). The Model 1079 injector was set at 90 ^{o}C and was operated in a splitless mode. Injection volume was 3 µL. The temperature program was changed to match the LLE-GC/ECD method being developed: 1) Hold at 35 ºC for 23 min; 2) increase to 139 ºC at 4 ºC/min; and 3) increase to 301 ºC at 27 ºC/min and hold at 301 ºC for 5 min. This program will be referred to as the updated GC program.

Mass Spectrometry

Electron ionization (EI) spectra show similar fragmentation patterns depending on the class of compound (Table 1). Using a defined sample list and methodology, software is capable of integrating individual channels to extract out the peaks of interest. After peak integration, the resulting areas are used to form calibration curves for each compound, which can then be applied to unknown samples.

Selected ion monitoring was used to achieve greater sensitivity with the TS-250 mass spectrometer. Because the DBPs measured are less than a few hundred Daltons in mass and contain similar functional groups, it was possible to monitor selected ion traces that comprised common fragment ions for all the compounds. This provided a significant enhancement in sensitivity for the older TS-250 sector mass spectrometer.

Table 1. Fragmentation matrix for DBPs measured using selected ion monitoring. A bold "X" indicates the quantitation ion; "x_c" is the confirmation peak. A strike through the x indicates a false peak.

Compound	Identified Fragment in EI Spectrum																							
	40	43	49	74	75	77	79	83	91	93	108	117	118	119	120	121	127	130	154	163	173	175	198	207	219	251	267
Halomethanes																											
Chloroform			x_c					X																			
Bromodichloromethane			x				x_c	X									x										
Dibromochloromethane			x				x		x_c	x							X										
Bromoform							x		x_c	x											X	x					
Tribromochloromethane		x	x				x_c		x	x								x						X		x	
Bromochloroiodomethane							x										X					x_c					
Dichloroiodomethane			x					X									x_c					x					
Dibromoiodomethane							x		x	x							x_c				X	x			x		
Chlorodiiodomethane																	x_c					X					x
Bromodiiodomethane							x										x_c								X		x
Iodoform																	X										x_c
Haloacetonitriles																											
Bromoacetonitrile	x						x_c		x	x				X		x											
Chloroacetonitrile	x				X	~~x~~																					
Dichloroacetonitrile			x_c	X	x	x																					
Bromochloroacetonitrile			x	X	x	x	x						x														
Dibromoacetonitrile							x_c		x	x			X		x												
Trichloroacetonitrile			x_c		x						X																
Tribromoacetonitrile							x_c		x	x		x	x	x									X				
Bromodichloroacetonitrile			x	x	x		x		x	x	X	x		x				x	x_c								
Dibromochloroacetonitrile			x	x_c	x		x		x	x		x	x	x	x				X				x				
Haloketones																											
Chloropropanone		X	x_c																								
1,1-Dichloropropanone		X	x					x		x_c																	
1,3-Dichloropropanone		x	x_c			X	~~x~~																				
1,1,1-Trichloropropanone		X	x					x_c			x			x			x										
1,1,3-Trichloropropanone			x			X	~~x~~	x_c																			
1,1,3,3-Tetrachloropropanone			x					X															x				
1,1,1,3,3-Pentachloropropanone			x					X				x_c		x		x											
1-Bromo-1,1-dichloropropanone		X	x			x	x	x									x_c			x							
1,1-Dibromopropanone		X					x		x	x					x						x_c	x					
1,3-Dibromopropanone		x								x_c						X											
1,1,1-Tribromopropanone		X					x		x_c	x											x	x				x	
1,1,3-Tribromopropanone		x					x		x	x_c					x	X					x	x					
1,1,3,3-Tetrabromopropanone															X						x_c	x					
Haloacetaldehydes																											
Dichloroacetaldehyde			X			x		x_c																			
Bromochloroacetaldehyde			X				x		x	x							x	x_c									
Tribromoacetaldehyde							x_c		x	x											X	x				x	
Halonitromethanes																											
Chloronitromethane			X																								
Bromonitromethane		x					x_c			X																	
Dichloronitromethane								X																			
Dibromonitromethane		x_c					x		x	x											X	x					
Chloropicrin			x_c			x						X		~~X~~		x											
Bromopicrin							x		x_c	x																X	
Bromodichloronitromethane			x_c				x		x	x										X							
Dibromochloronitromethane			x				x_c		x	x														X			
Misc. Compounds																											
Carbon tetrachloride			x_c									X		~~X~~		x											
Benzyl chloride									X																		

Sample Preservation

As samples are taken in the field, it is necessary to stop any further DBP formation from occurring by adding a quenching agent that can remove residual oxidants. In previous work, dilute solutions of ascorbic acid (AA) or ammonium chloride (AC) were added directly to the sample vial or bottle. This method works well, provided that the containers are not allowed to sit idle for more than a few days. Additionally, past studies have found that by adjusting the pH of the sampled water, many DBPs can be stabilized for several weeks, giving a much larger window of opportunity for analysis and establishing a better holding time for refrigerated storage.

The method parameters chosen for this study were 31 mg/L of ascorbic acid and enough sulfuric acid to lower the pH to 3.5. A solution of 16 mg/L of ascorbic acid was deemed necessary to remove 3.0 mg/L of chloramines residual, so 31 mg/L of ascorbic acid in each bottle was chosen to have a safety factor. An experiment was performed on Weymouth effluent water from the Weymouth Water Treatment Plant (La Verne, CA) using clear 44-mL vials with 1.4 mg of ascorbic acid (31 mg/L) and 5 drops of 0.25 M H_2SO_4 added. The 5 drops were enough to fully dissolve the ascorbic acid powder. After several days, however, the contents of the vials proved ineffective for quenching fresh samples of water. This posed a problem because the ascorbic acid in the acidic solution was degrading. As a result, the ascorbic acid and sulfuric

acid would have to be separated. Separate additions of ascorbic acid and sulfuric acid was also wise because it would be difficult to know the appropriate dose of acid to achieve the required pH for water utilities where the buffering capacity of the water was unknown. It was decided that an acid kit, which would include an eyedropper bottle with dilute sulfuric acid and pH test strips, would accompany each set of ice chests sent to the utilities, so that the sampler operators could add the necessary acid in the field. The quenching agent, ascorbic acid, in its granular form, would be added to each container at the Metropolitan Water District of Southern California (MWDSC) before shipping. For the 125 mL bottles filled for SPE-GC/MS analysis, two 2 mg scoops were used to achieve the ~4.0 mg and a solution concentration of 31 mg/L.

Each utility was given a detailed set of instructions and told not to rinse out the bottles (because they contained preservative). Only vials and bottles containing a red cap would require pH adjustment with acid. This situation worked out well because when unforeseen delays arose for the utility sampling, the bottles could be kept for several weeks both before the sampling and after the sampling without compromising the DBP preservation. When samples returned to the laboratory, their pH was re-checked and adjusted if necessary.

Ice Chest Containers

When each of the ice chests was opened, there was a set of paperwork immediately on top (sampling instructions, sample collection sheets, and a return Federal Express label). There was a sheet attached to the inside of each ice chest identifying it as belonging to the MWDSC and labeling the appropriate utility to which it was sent. Additional information included the identification of ice chests intended for simulated distribution system (SDS) samples or assimilable organic carbon (AOC) samples. The large ice chests contained four blue ice packs. The small ice chests contained one or two ice packs, depending on space. All ice packs were shielded from the sample bags by Styrofoam, peanut-filled plastic bags. It was important to isolate the cold packs from the samples to prevent freezing of the water and breakage.

The sulfuric acid solution containers were placed in small white boxes located usually along with the SDS ice chests. These acid kits included an eyedropping amber bottle, two additional plastic eyedroppers in case of breakage, and a set of pH test strips.

RESULTS AND DISCUSSION

Detection Limits

TS-250 Mass Spectrometer. Because the TS-250 instrument was older and was subject to drift during the course of a day's analysis, calibration standards were run with each set of samples to insure the most accurate results. A set of three 10 µg/L standards, comprising 20 of the DBPs, were extracted using SPE and analyzed the same day on three separate occasions. The results were interpreted for daily standard deviation and for the overall standard deviation for all 9 samples. The overall standard deviation was multiplied by 2.896 (student t-value for 8 degrees of freedom at 98% confidence) to get the approximate method detection level (Table 2).

A daily precision of 1.1 µg/L was observed for samples that underwent off-line SPE. However, when comparisons were made of data taken over multiple days, this variance increased to 2.2 µg/L. Overall detection limits were set at 3 µg/L because of the requirement that

standards be run on a daily basis. This limit appeared reasonable because the instrument was capable of detecting 1 µg/L levels.

The solid phase extraction technique is probably at its limit for reproducibility (for low ppb levels). SPE, unlike P&T, is performed manually over the course of several hours. Human error will play some role in the extraction process, but there is also a significant time segment where the sample is either exposed to a hood environment or direct vacuum, which can potentially contribute to the loss of some compounds.

Errors in quantitation of samples can also occur due to the SIM scan speed of the magnet. For SIM acquisition, the dwell time for each m/z measurement must be sufficiently long to adequately sample the ion population, but sufficiently short to collect as many samples per eluting peak as possible. By setting a residence time of 50 msec per m/z measured and allowing time for the magnet to switch to next mass, there is a necessary scan time of 2.17 seconds/scan. Often, this amounts to only 5 to 8 samples per chromatographic peak, which can cause errors because a peak area approximated by only 5 to 8 data points will be inherently less accurate than one sampled by many more points to give better peak resolution.

Table 2. Detection limit study for selected compounds showing both daily and overall standard deviations for a typical 10 µg/L standard

Compound	RT	A	B	C	D	E	F	G	H	I	Daily Std. Deviation			AVE	SD	RSD	Estimated
	(min.)	4/10	4/10	4/10	4/12	4/12	4/12	4/18	4/18	4/18	4/10	4/12	4/18	Conc.	AVE	%	MDL, ug/L
Chloroform	5.98	9.0	9.4	9.7	5.9	6.2	6.3	8.6	9.5	10.1	0.4	0.2	0.8	8.3	1.7	20	5
Dichloroacetaldehyde	6.20	17.7	15.2	16.2	13.7	13.0	13.9	9.6	11.5	11.2	1.3	0.5	1.0	13.6	2.6	19	7
Chloroacetonitrile	7.46	9.9	12.7	14.7	11.7	13.7	13.3	8.4	12.2	12.4	2.4	1.1	2.3	12.1	1.9	16	6
Chloropropanone	8.15	6.2	7.1	13.3	12.1	12.8	13.5	11.6	11.7	13.9	3.9	0.7	1.3	11.4	2.8	25	8
Trichloroacetonitrile	8.80	10.3	10.5	10.7	5.6	6.1	5.9	7.7	8.5	8.9	0.2	0.3	0.6	8.2	2.0	25	6
Dichloroacetonitrile	10.17	10.7	11.1	12.1	8.3	10.0	10.4	7.5	9.0	10.9	0.7	1.1	1.7	10.0	1.5	15	4
Bromodichloromethane	10.50	9.3	9.7	10.4	5.8	6.9	6.8	7.8	8.9	10.3	0.6	0.6	1.3	8.4	1.7	20	5
1,1-Dichloropropanone	12.70	9.1	9.6	10.1	9.2	10.3	10.9	8.0	9.9	11.1	0.5	0.9	1.6	9.8	1.0	10	3
Bromoacetonitrile	14.50	10.6	12.5	13.9	11.9	13.8	15.5	6.5	9.7	11.8	1.7	1.8	2.7	11.8	2.7	23	8
Chloropicrin	19.81	10.5	10.2	11.1	4.6	5.7	5.9	6.9	8.4	9.4	0.5	0.7	1.3	8.1	2.4	29	7
Dibromochloromethane	20.61	10.3	10.5	11.4	5.8	7.4	7.6	6.5	9.1	10.7	0.6	1.0	2.1	8.8	2.0	23	6
Bromonitromethane	21.00	11.6	12.3	13.7	8.3	11.9	13.5	5.9	9.2	10.6	1.1	2.7	2.4	10.8	2.6	24	7
Bromochloroacetonitrile	21.26	11.7	11.9	12.8	7.9	9.8	10.0	6.4	8.4	9.9	0.6	1.2	1.8	9.9	2.1	21	6
1,1,1-Trichloropropanone	26.38	11.9	12.2	12.9	9.0	10.4	10.9	6.3	8.6	10.0	0.5	1.0	1.9	10.2	2.1	20	6
1,3-Dichloropropanone	27.14	12.5	13.9	14.4	11.2	12.0	13.5	4.8	8.7	9.6	1.0	1.2	2.6	11.2	3.1	27	9
Bromoform	28.12	10.9	11.2	12.4	6.8	8.7	8.9	6.4	8.7	10.3	0.8	1.2	2.0	9.4	2.0	21	6
Dibromoacetonitrile	28.48	12.3	12.6	13.3	7.9	9.5	10.0	6.4	7.8	9.2	0.5	1.1	1.4	9.9	2.4	24	7
1,1,3-Trichloropropanone	30.75	16.4	14.8	15.4	11.3	11.6	10.8	8.3	9.9	9.0	0.8	0.4	0.8	11.9	2.9	24	8
Benzyl Chloride	32.66	10.3	10.6	11.6	6.9	8.1	8.4	5.9	7.1	7.8	0.7	0.8	1.0	8.5	1.9	22	6
Iodoform	37.86	12.4	12.7	13.3	7.2	8.2	8.2	10.2	9.6	9.3	0.5	0.6	0.5	10.1	2.2	22	6
								Averages			**1.0**	**1.0**	**1.6**		**2.2**	**21.5**	**6.3**

Extraction Efficiency

The extraction efficiency of the Bond Elut sorbent was tested at three different standard concentrations, 10 µg/L, 25 µg/L, and 50 µg/L, to determine whether there were any sample loading concerns with the sorbent's capacity. Most of the anticipated values for DBPs in drinking water would be well below 50 µg/L. Compounds within the same compound family exhibited similar extraction efficiencies. The important observations were that recoveries were good (74% average) and higher concentrations of analytes, up to 500 µg/L, do not saturate the capacity of the Bond Elut sorbent.

Early Observations

VOC concentrations can become altered if excessive headspace or high temperatures are present. For analysis, the headspace was minimized by using 100 µL conical autosampler vials (that hold ~300 µL when filled to top) for storage, rather than the typical 1.4 mL autosampler vials. For samples that sit on top of the GC for extended runs, they are exposed to high temperatures. A Tekmar water bath circulating system was attached to the sample tray to remove some of the heat load. The water bath's temperature was set to maintain a temperature of 21.0 ^{o}C (about room temperature) on the sample tray, which minimized sample degradation/volatilization for extended runs. Chloroform and bromodichloromethane showed the most improvement for spike recovery.

The heavier iodo-THMs, haloacetonitriles, and halonitromethanes showed much reduced recoveries for 10 ppb-spiked samples. This was either an expected limitation for the SPE procedure, or the lower injection temperature used discriminated against these heavier (higher boiling point) compounds. Significantly raising the injection temperature, however, would have caused many more problems with degrading species. It was discovered later that some of these compounds (bromodichloro-, dibromochloro-, and tribromoacetonitrile, and bromodichloro-, dibromochloro-, and tribromonitromethane) were not preserved using ascorbic acid.

Several analytes were found to coelute on the GC. Bromochloroacetaldehyde (retention time of 12.6 min.) co-eluted with trichloroacetaldehyde, which was not present in the method, but has been seen in many samples and was part of the Information Collection Rule. Chloropicrin (retention time of 21.8 min.) co-eluted with bromodichloroacetonitrile. An easy separation was achieved by using different quantitation masses -- m/z 117 for chloropicrin and m/z 108 for bromodichloroacetonitrile. The m/z 117 contribution from bromodichloroacetonitrile, if present, was negligible and small enough to ignore.

Tribromoacetaldehyde (retention time of 32.8 min.) co-eluted with tribromoacetonitrile. An alternate quantitation peak, m/z 251, was chosen for tribromoacetaldehyde, at reduced sensitivity, to effect a clean separation from tribromoacetonitrile and other nearby species. Bromonitromethane was sandwiched between dibromochloromethane and bromochloroacetonitrile, which did not allow baseline resolution for that quantitation channel, m/z 93.

Dibromoiodomethane, 1,3-dibromopropanone, tribromoacetaldehyde, and tribromoacetonitrile all eluted within 0.1 min of each other. Alternate channels eliminated major overlaps, but sensitivity was reduced. Chloro-, 1,1-dichloro-, 1,1,1-trichloro-, 1,1-dibromo-, 1-bromo-1,1-dichloro-, and 1,1,1-tribromopropanone were difficult to quantitate because of

common fragmentation patterns produced. The highest ion abundance came from m/z 43 ($COCH_3$), which showed a low level persistent background throughout the run. Another co-eluting system -- dibromoacetonitrile/bromodichloronitromethane (retention time of 33.9 min.) -- was eliminated by using different mass channels. Improved chromatography or the use of a different polarity column could also correct this problem.

Choice of Analytical Columns

CP-1301 Column. The CP-1301 column was installed on the TS-250 mass spectrometer to evaluate its performance for separating the targeted DBPs. The GC temperature program was the latest that MWDSC had been using, with the exception that this column could not go beyond a maximum temperature of 250 ^{o}C. This lowered maximum temperature caused a lower overall sensitivity for late eluting compounds.

Peaks that were not baseline-resolved included dichloronitromethane and dibromochoromethane, bromoacetonitrile and dichloroiodomethane, and bromochloronitromethane and bromoform. Another difficult problem was that of co-eluting species, which for the CP-1301 column included: chloroform + others, carbon tetrachloride + others, dichloroacetonitrile + bromodichloroacetonitrile, 1,1-dibromopropanone + bromochloroiodomethane, and dibromoiodomethane + benzyl chloride. Peaks for dichloroacetaldehyde, bromochloracetaldehyde, trichloroacetaldehyde, tribromonitromethane, and 1,1,3,3-tetrabromopropanone were not found, or, they were problematic for analysis using this column/setup. Bromodichloronitromethane and dibromochloronitromethane were not included in this mixture analyzed. Figure 2 shows the CP-1301 column performance for the targeted DBPs.

DB-5 Column. A DB-5 column was installed on the TS-250 mass spectrometer and was used to analyze the same spiking mixture. There were a lot of co-eluting peaks, although it was clear that trichloroacetaldehyde and bromochloroacetaldehyde were well separated. Another benefit of this column was that there was better signal-to-noise, compared to the CP-1301 column, particularly at the high end of the chromatogram where degradation of compounds and column bleed is normally a problem.

Peaks that were not baseline resolved included bromochloronitromethane and 1,1,1-trichloropropanone; 1,1,3-trichloropropanone and tribromochloromethane; and 1,1,1-tribromopropanone and bromodiiodomethane. Co-eluting peaks included dichloroacetaldehyde + others; chloroacetonitrile + trichloroacetonitrile; bromonitromethane + bromochloroacetonitrile; dibromoiodomethane + tribromoacetonitrile + benzyl chloride; and chlorodiiodomethane + 1,1,3,3-tetrachloropropanone.

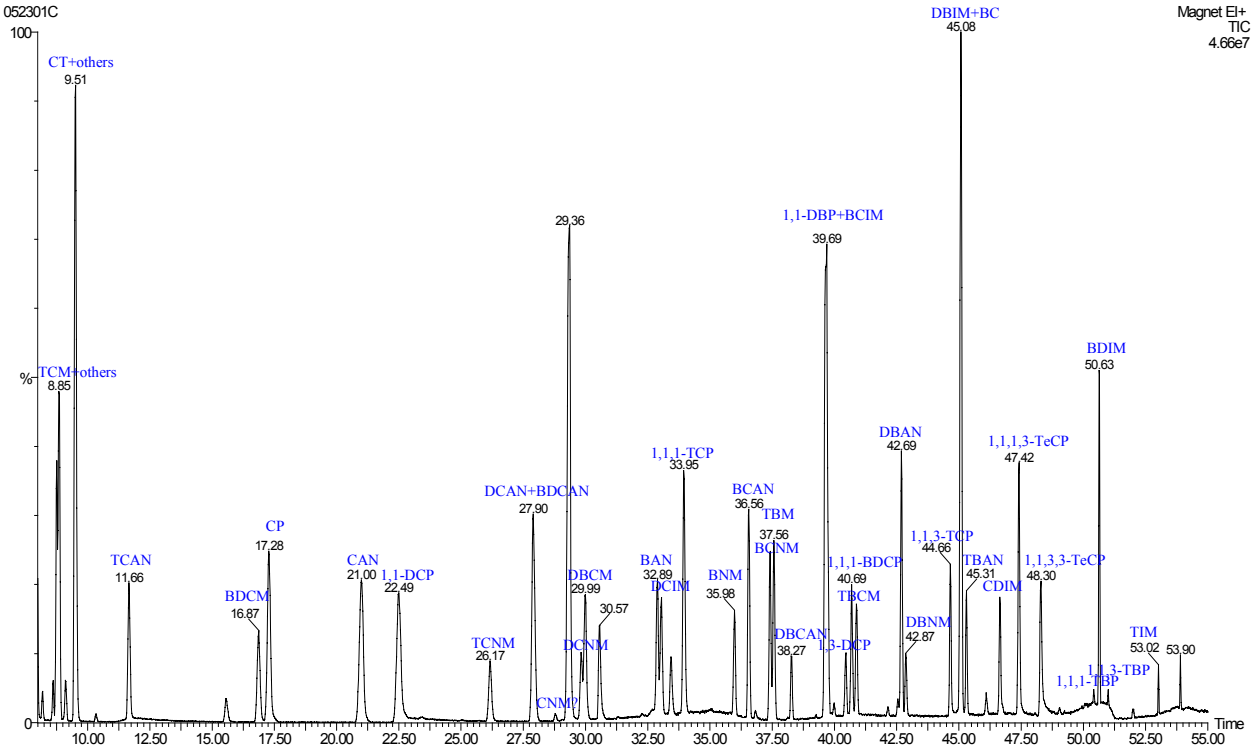

Figure 2. CP-1301 column performance using full DBP set. Compounds not detected include dichloroacetaldehyde, bromochloroacetaldehyde, tribromoacetaldehyde, tribromonitromethane, and 1,1,3,3-tetrabromopropanone. Compound abbreviations are found in Table 3.

DB-1 Column. As a comparison between the DB-5 column and a DB-1 column, the two columns are profiled side-by-side in Figure 3**,** which shows unambiguous peak identities when converting between the two chromatograms. As a general rule, the DB-1 column was preferred because, in conjunction with individual mass traces, it allowed for the separation of all the targeted DBPs, except for the trichloroacetaldehyde-bromochloroacetaldehyde conflict. In general, DB-1 improvements over DB-5 included: a) separation of chloroacetonitrile and trichloroacetonitrile, b) separation of bromonitromethane and bromochloroacetonitrile, c) separation of bromochloronitromethane and 1,1,1-trichloropropanone, d) separation of 1,1,3-trichloropropanone and tribromochloromethane, e) partial separation of dibromoiodomethane, tribromoacetonitrile, and benzyl chloride, f) separation of chlorodiiodomethane and 1,1,3,3-tetrachloropropanone, and g) separation of 1,1,1-tribromopropanone and bromodiiodomethane.

DB-624 Column. The DB-624 column used on the Varian Saturn ion trap mass spectrometer was very similar in polarity to the CP-1301 column tested. It is the column currently used by MWDSC for the EPA Method 524.2 purge-and-trap analyses. Many of the heavier DBPs, such as the halonitromethanes were not well recovered from this column, partially due to the polarity and lowered maximum temperature. The DB-624 column was replaced with a DB-1 column to achieve the same performance, as was being done for the LLE-GC-ECD and SPE-GC/MS (TS-250 mass spectrometer) methods. The replacement option made it necessary

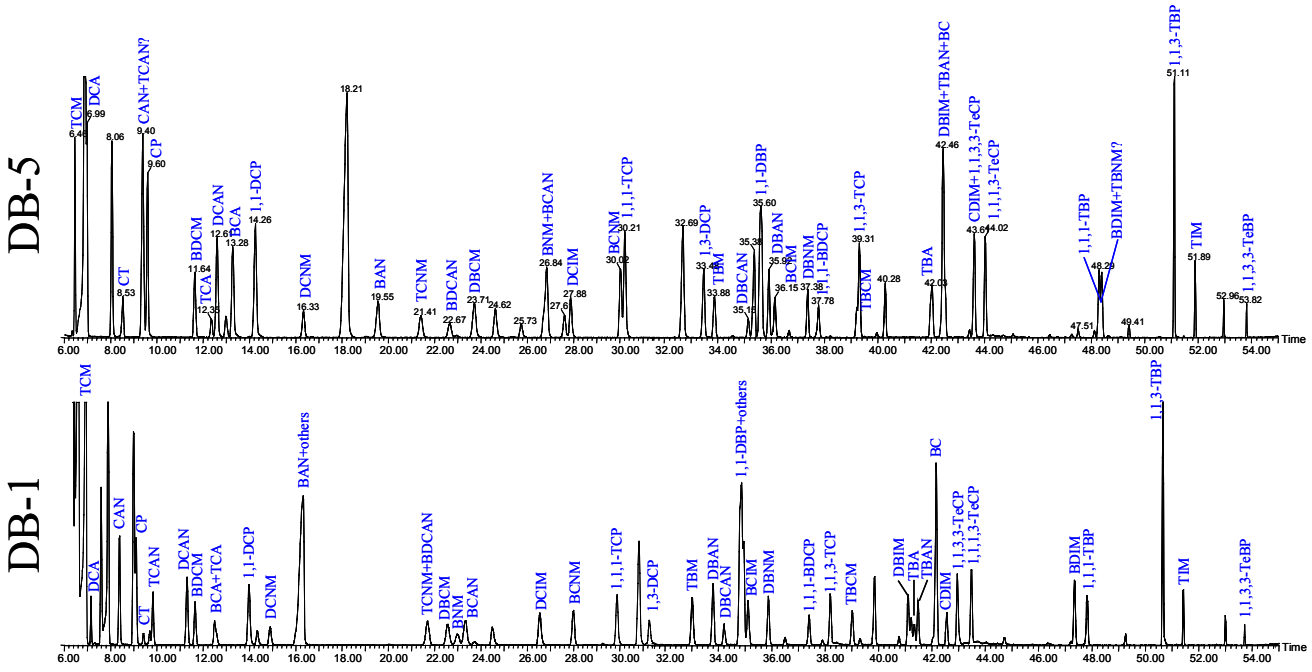

Figure 3. DB-5 column versus DB-1 column performance using full DBP set.

to re-evaluate purge-and-trap operation with a DB-1 column for a more limited set of compounds.

Improved Temperature Program

The updated GC temperature program was officially adopted in June 2001 for the SPE-GC/MS method used on the TS-250 mass spectrometer and all subsequent work on the Saturn ion trap mass spectrometer. The updated GC temperature program, along with a lower injection temperature of 90 ^{o}C was used for the latest set of stock solutions to get new retention times for all of the DBPs (Table 3).

In attempting to translate the retention times obtained from the older results to those found by utilizing the updated GC program, it was noted that simple linear equations can be used to approximate new retention times. During the first 23 min of the temperature programs, both results are the same because both hold the GC oven at 35 ^{o}C for the isothermal portion of the programs. The correlation of the retention times after 23 min is not a mirror image because of the differences in ramp rates between the two temperature programs (see **Gas Chromatography** section above). Figure 4 shows the two linear approximations that can be used for estimating the new GC retention times. The equation $y = 0.9972x + 0.0699$ for the 0 to 23 minute portion of the graph is synonymous with $y = x$, with a very small offset.

Table 3. VG TS-250 mass spectrometer quantitation ions for selected ion monitoring and elution order before and after update to GC program

Compound	Abbreviation	Quantitation m/z	Confirmation m/z	TS-250 Retention Time, Minutes (MtBE, 551.1 GC Program)	TS-250 Retention Time, Minutes (MtBE, Updated GC Program)
Chloroform	TCM	83	49	6.80	6.92
Dichloroacetaldehyde	DCA	49	83	7.04	7.10
Chloroacetonitrile	CAN	75	77	8.36	8.47
Chloropropanone	CP	43	49	9.11	9.12
Carbon Tetrachloride	CT	117	49	9.38	9.47
Trichloroacetonitrile	TCAN	108	49	9.79	9.85
Dichloroacetonitrile	DCAN	74	49	11.42	11.38
Bromodichloromethane	BDCM	83	79	11.69	11.73
Chloronitromethane	CNM	49	N/A	-----	12.42
Bromochloroacetaldehyde	BCA	49	130	12.57	12.57
1,1-Dichloropropanone	DCP	43	93	14.06	14.08
Dichloronitromethane	DCNM	83	N/A	15.01	14.95
Bromoacetonitrile	BAN	119	79	16.16	16.10
Chloropicrin	TCNM	117	49	21.83	21.83
Bromodichloroacetonitrile	BDCAN	108	154	21.90	21.92
Dibromochloromethane	DBCM	127	91	22.68	22.73
Bromonitromethane	BNM	93	79	23.25	23.10
Bromochloroacetonitrile	BCAN	74	N/A	23.29	23.52
Dichloroiodomethane	DCIM	83	127	25.25	26.67
Bromochloronitromethane	BCNM	129	79	26.03	28.05
1,1,1-Trichloropropanone	1,1,1-TCP	43	83	27.08	30.00
1,3-Dichloropropanone	1,3-DCP	77	49	27.80	31.38
Bromoform	TBM	173	91	28.75	33.12
Dibromoacetonitrile	DBAN	118	79	29.05	33.88
Bromodichloronitromethane	BDCNM	163	49	-----	33.87
Dibromochloroacetonitrile	DBCAN	154	74	29.32	34.28
1,1-Dibromopropanone	1,1-DBP	43	173	29.66	34.88
Bromochloroiodomethane	BCIM	127	175	29.80	35.18
Dibromonitromethane	DBNM	173	43	30.10	35.93
1-Bromo-1,1-dichloropropanone	1,1,1-BDCP	43	127	30.88	37.45
1,1,3-Trichloropropanone	1,1,3-TCP	77	83	31.22	38.25
Tribromochloromethane	TBCM	207	79	-----	39.10
Dibromochloronitromethane	DBCNM	207	79	-----	40.92
Dibromoiodomethane	DBIM	173	127	32.68	41.17
Tribromoacetaldehyde	TBA	251	173	32.75	41.40
Tribromoacetonitrile	TBAN	198	79	32.82	41.53
Benzyl chloride	BC	91	N/A	33.09	42.22
Chlorodiiodomethane	CDIM	175	127	33.36	42.62
1,1,3,3-Tetrachloropropanone	1,1,3,3-TeCP	83	N/A	33.46	43.00
1,1,1,3-Tetrachloropropanone	1,1,1,3-TeCP	77	49	33.70	43.53
Bromopicrin	TBNM	251	91	35.36	46.48
Bromodiiodomethane	BDIM	219	127	35.94	47.42
1,1,1-Tribromopropanone	1,1,1-TBP	43	251	36.14	47.90
1,1,3-Tribromopropanone	1,1,3-TBP	121	93	37.63	50.70
Iodoform	TIM	127	267	38.31	51.47
1,1,3,3-Tetrabromopropanone	1,1,3,3-TeBP	120	173	40.48	53.75

The interconversion between the two GC programs was helpful for determining where peaks would appear in a chromatogram, and it could be used to check the location of new peaks or impurities. The software method used for processing all SIM data was updated on 6/5/01 to reflect these new retention times, as well as the new correction factors for the latest set of stock solutions.

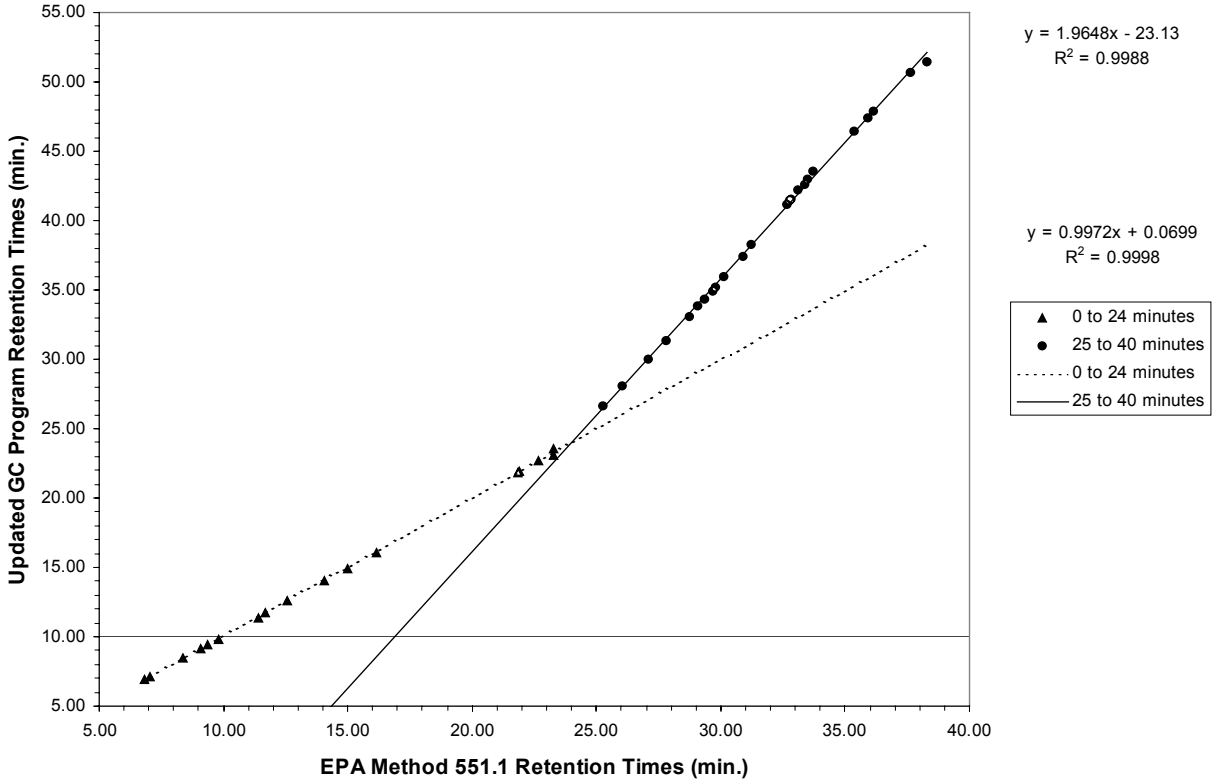

Figure 4. Correlation of retention times before and after GC program update.

Problematic Compounds

All subsequent work utilized the DB-1 column for compound separation. Chloronitromethane was found to co-elute with bromochloroacetaldehyde (and trichloroacetaldehyde). There was no solution available at this time (Figure 5). It may be possible to analyze for bromochloroacetaldehyde using only m/z 130 at about 40% of the sensitivity of the m/z 49 peak. There was not, however, sufficient quantities of bromochloroacetaldehyde to warrant further methods development on the bromochloroacetaldehyde and trichloroacetaldehyde co-elution.

Chloropicrin co-eluted with bromodichloroacetonitrile. Selection of different mass channels can eliminate this conflict (Figure 6). Bromodichloroacetonitrile and trichloronitromethane can be separated on the DB-5 column. The analysis of bromodichloroacetonitrile by SPE-GC/MS was later dropped because it required ammonium chloride for a quenching agent and preservative.

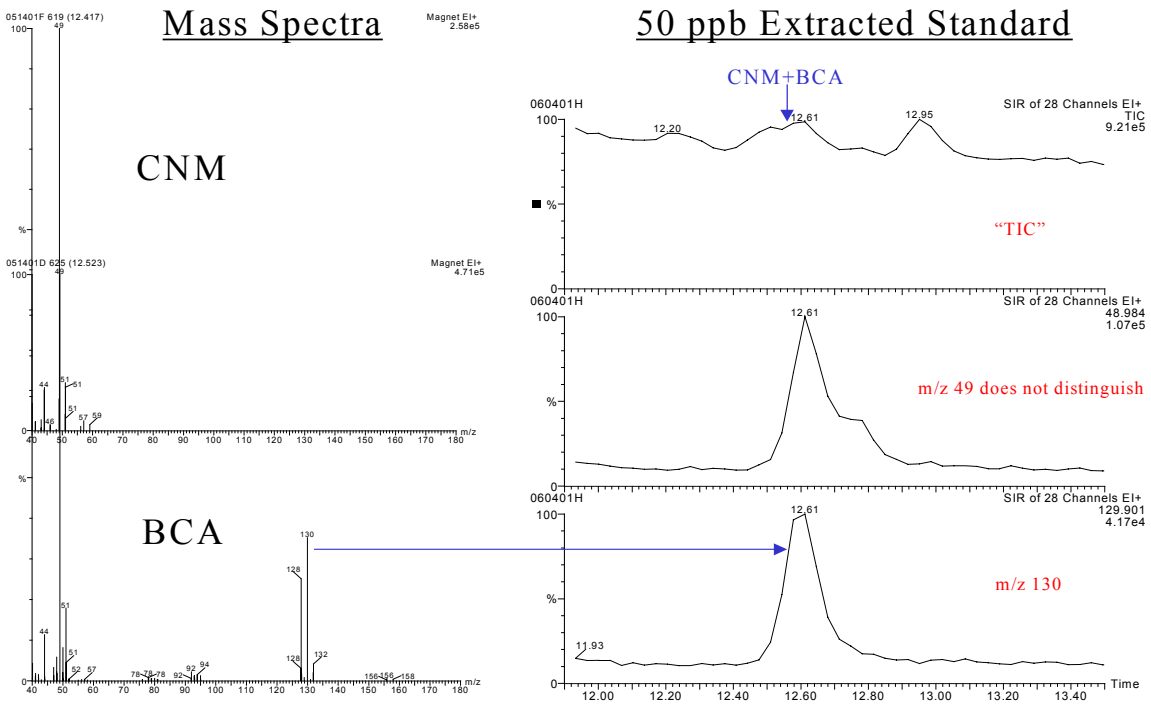

Figure 5. Chloronitromethane (CNM) co-elutes with bromochloroacetaldehyde (BCA) (which co-elutes with trichloroacetaldehyde (TCA)). Chloronitromethane is not amenable to SPE-GC/MS analysis.

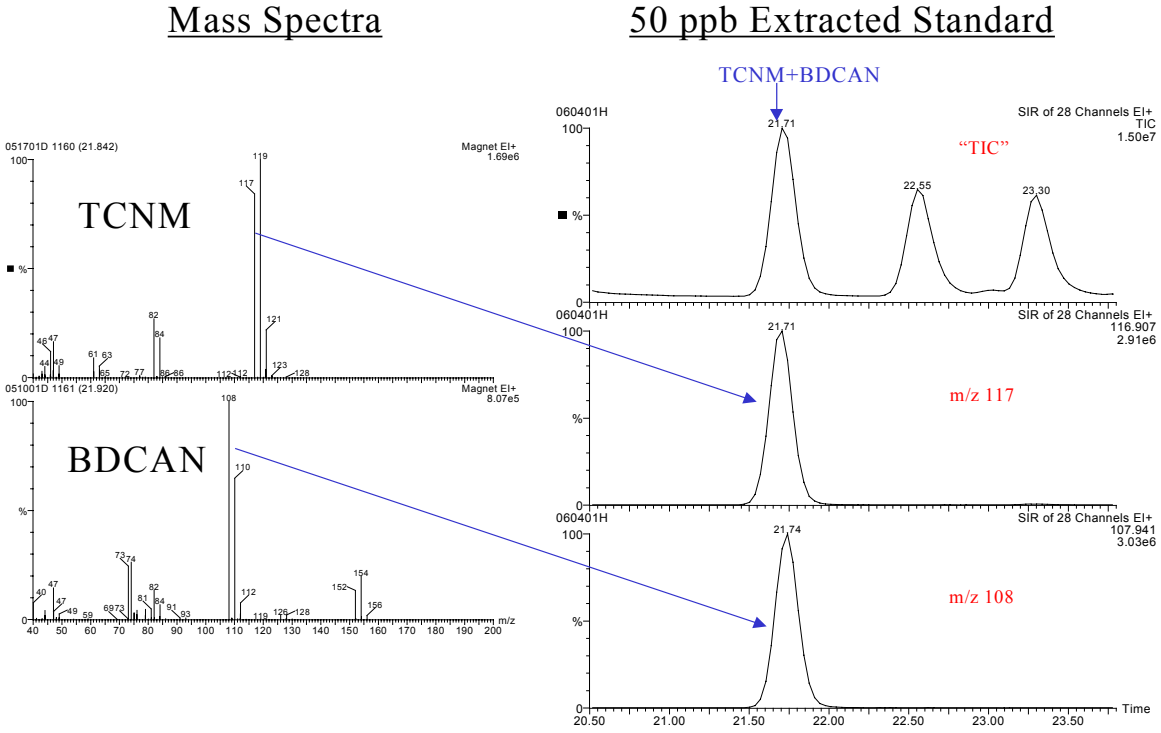

Figure 6. Chloropicrin (TCNM) co-elutes with bromodichloroacetonitrile (BDCAN). Both are amenable to SPE-GC/MS analysis.

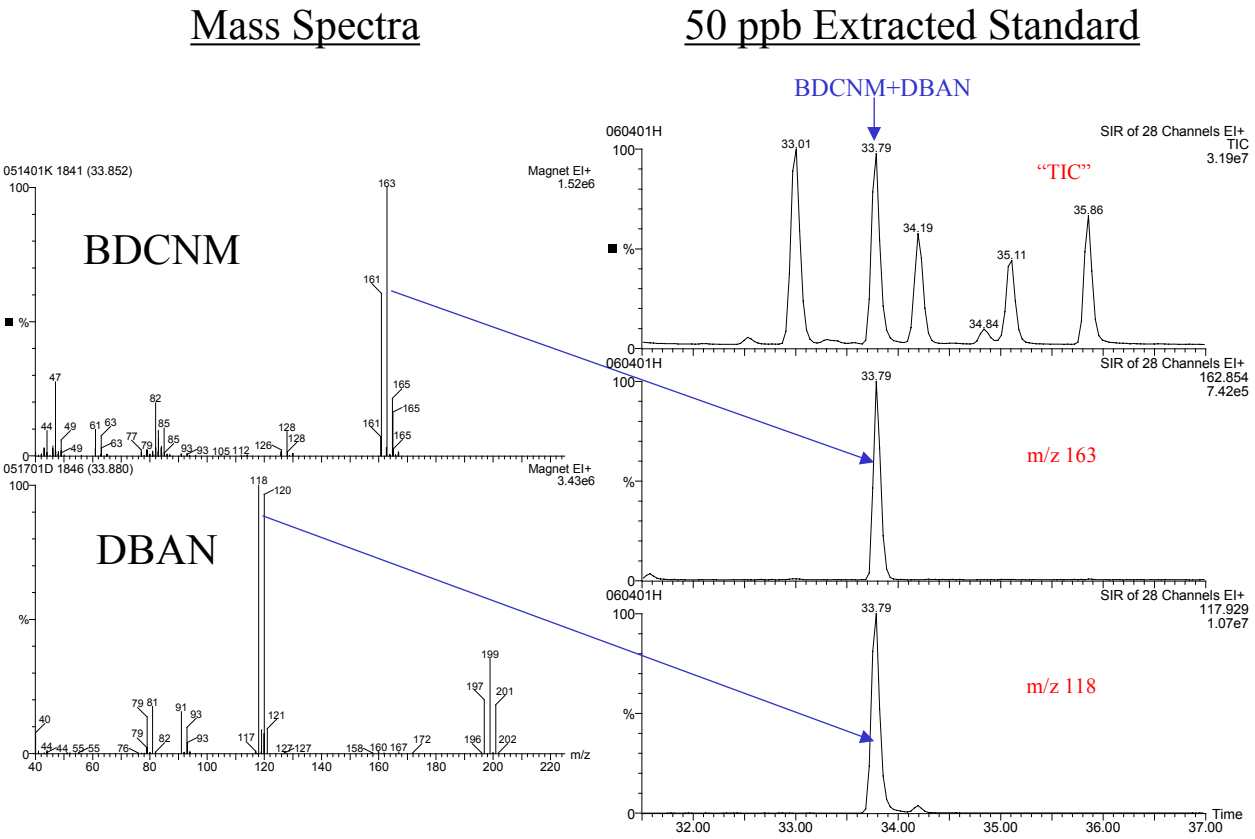

Figure 7. Bromodichloronitromethane (BDCNM) co-elutes with dibromoacetonitrile (DBAN). Both are amenable to SPE-GC/MS analysis.

Bromodichloronitromethane co-eluted with dibromoacetonitrile. Selection of alternate mass channels eliminates a conflict (Figure 7). However, bromodichloronitromethane was later dropped from the SPE method because it too required ammonium chloride as a quenching agent and preservative.

Holding Study

As was stated in the **Early Observations** section of this chapter, certain heavier haloacetonitriles and halonitromethanes showed consistently poor quantitation in earlier work on this project. Before the final year of sampling was to begin, it was necessary to revisit the choice of ascorbic acid as a general quenching agent and preservative for all DBPs that were being studied by SPE, LLE, P&T, and SPME methods. Many of these compounds were not available during the initial methods development period. Thus, an experiment was carried out to evaluate the stability of DBPs stored with ascorbic acid at a pH of 3.5.

The results were surprising because it was discovered that six compounds were not amenable to this ascorbic acid/pH 3.5 combination. To summarize the results by DBP class:

THMs -	No problems through Day 21.
Iodo-THMs -	No problems through Day 21.
Haloacetonitriles -	No problems through Day 21, except bromodichloro-, dibromochloro-, and tribromoacetonitrile showed no recovery between Day 0 and Day 3 (Figure 8).
Chloropropanones -	No problems through Day 21. 1,1-Dichloropropanone was difficult to quantitate.
Bromopropanones -	No problems through Day 21. 1,1,3-Tribromopropanone had a slow decay.
Halonitromethanes -	No problems through Day 21, except Bromodichloronitromethane, dibromochloronitromethane, and tribromonitromethane showed no recovery.
Haloacetaldehydes -	Difficult to quantitate. Tribromoacetaldehyde had fast decay.
Miscellaneous -	Both carbon tetrachloride and benzyl chloride had slow decays.

According to the plots of concentration vs. time (Figure 8), it appeared as if the following DBPs were highly unstable in the presence of ascorbic acid at pH 3.5: bromodichloro-, dibromochloro-, and tribromoacetonitrile, and bromodichloro-, dibromochloro-, and tribromonitromethane. Previous research has shown that trichloroacetonitrile can undergo base-catalyzed hydrolysis, but it is stable at acidic pH. The brominated versions of some of these DBPs (i.e., tribromoacetonitrile, bromodichloroacetonitrile, and dibromochloroacetonitrile) may be even more unstable and may break down in the presence of ascorbic acid. However, tribromonitromethane was stable at pH 4 in the presence of ammonium chloride, so it was possible that heavy, brominated DBPs may be stable in the presence of ammonium chloride at pH 3.5.

A new holding study was carried out to evaluate ammonium chloride as a quenching agent/preservative at pH 3.5. Ascorbic acid at pH 3.5 was tested in parallel on DBPs of interest (e.g., bromodichloro-, dibromochloro-, and tribromoacetonitrile, and bromodichloro-, dibromochloro-, and tribromonitromethane). The hypothesis was confirmed, and additional sample bottles containing ammonium chloride quenching agent/preservative were added for the LLE-GC-ECD method. These six compounds were dropped from the SPE method because of the additional work load that would have been involved in sampling and extraction.

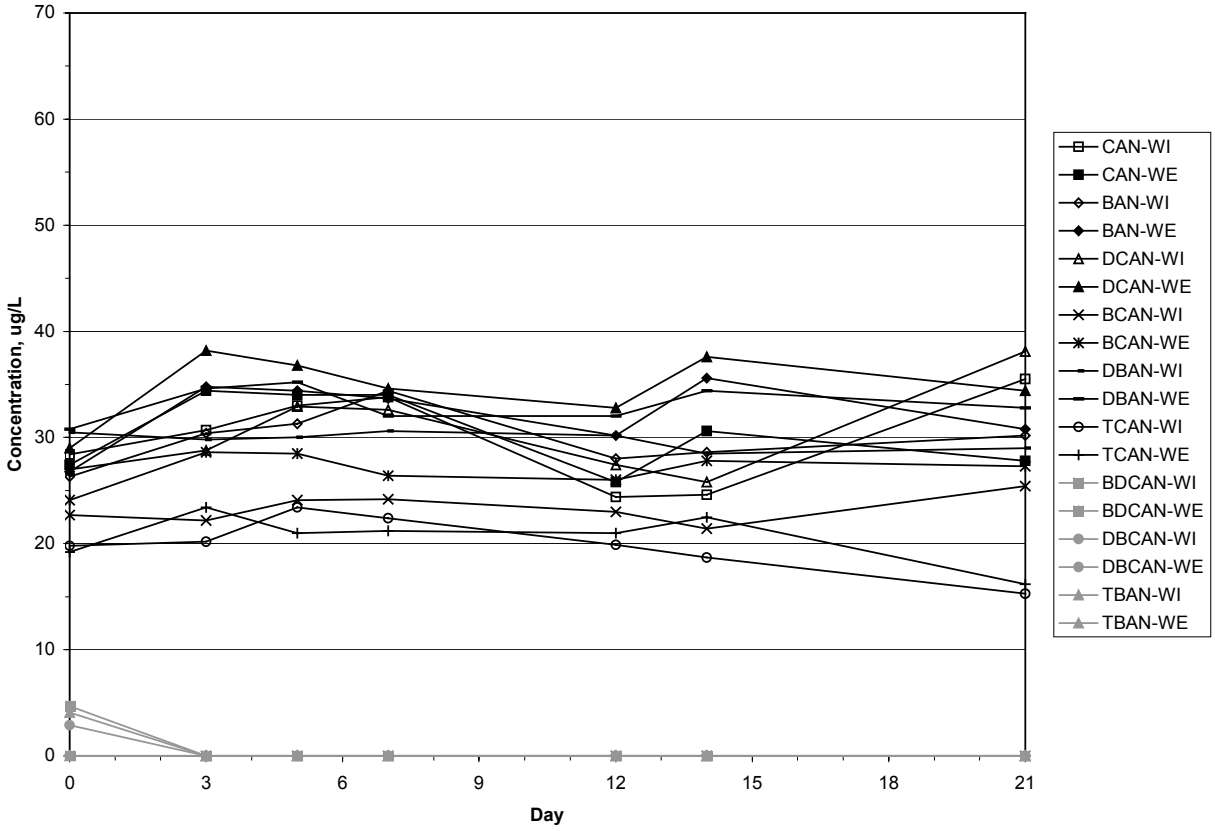

Figure 8. Ascorbic acid/pH 3.5 holding study results for haloacetonitriles (Weymouth filtration plant influent and effluent).

Migration to Saturn Ion Trap Mass Spectrometer

The SPE method was implemented on the ion trap mass spectrometer as a backup system in the event that the TS-250 mass spectrometer would become unusable for the project. If, at the end of this additional methods development period, the ion trap results were much better, then the SPE method would be permanently migrated to the Saturn 2000 ion trap mass spectrometer for all subsequent work. Restrictions to this work included: a) not using MtBE as the extraction solvent, and b) keeping the instrument as "stock" as possible for easy switch-over to purge-and-trap operation. Most of the initial testing occurred during late June 2001, when the performance of the existing DB-624 GC column and alternative solvents were tested. It was found that unless the original procedure was kept intact, from development with the TS-250 mass spectrometer, it would be difficult to achieve similar results. From previous work comparing different GC columns, a switch to the preferred DB-1 column was necessary. Because of the extra efforts involved in switching columns frequently, it was hoped that the DB-1 column could be used for both SPE and P&T analysis on the same instrument. Initial work would include optimizing some instrumental parameters, automating the system, running full calibration curves (0.5 - 30 µg/L), and injecting a suite of samples to establish a preliminary MDL. The results of this SPE work on the ion trap mass spectrometer showed that low-level detection was possible for almost all of the compounds that were part of the original SPE technique performed on the TS-250 instrument.

Results for chloroform, dichloroacetaldehyde, chloroacetonitrile, and chloropropanone could not be obtained because they co-eluted with the hexane solvent that was now part of the solvent extraction system. Of the solvents listed below, *n*-hexane was a logical choice based on the boiling point of the solvents. If the solvent is too volatile, the extraction process would become more difficult because SPE extractions occur under vacuum. Unfortunately, hexane is very non-polar and does not remove as many DBPs from the Bond Elut sorbent material. A mixed solvent system of 50:50 hexane/methylene chloride allowed full extraction of the DBPs, and, at the same time, avoided bringing MtBE and larger amounts of $MeCl_2$ into the VOC room, where they are routinely determined as part of the VOC method (Table 4).

Solvents*	Boiling Point (^oC)	Comments
Ethyl ether	34.6	
Pentane	36.1	
Methylene chloride	39.8	VOC compound
Carbon disulfide	46.5	
Methyl *tert*-butyl ether	55.2	VOC compound
Chloroform	61.2	VOC compound
n-Hexane	69.0	
Benzene	80.1	VOC compound
Cyclohexane	80.7	
Iso-octane	99.3	
Toluene	110	VOC compound

*Recommended for non-polar columns (100% methyl or 5% phenyl, 95% methyl)

Compound Notes

Dichloroacetonitrile had a co-elution problem with an unknown impurity that seemed to be present in the standards. The co-elution also occurred when MtBE was used as the extraction solvent on the TS-250 instrument, but there was not sufficient resolution to resolve the co-eluting peak from dichloroacetonitrile, and the two peaks were integrated together to produce a systematic error.

Bromonitromethane was a minor problem for quantitation because it eluted between dibromochloromethane and bromochloroacetonitrile, both of which have small m/z 93 contributions to bromonitromethane's main quantitation mass channel. On the TS-250 instrument, this problem could be solved by manually re-integrating the peaks.

Chloronitromethane and bromochloracetaldehyde were eliminated from the SPE method because of their co-elution on the DB-1 column with chloral hydrate (TCA) and each other.

Table 4. Varian Saturn 2000 performance with 1:1 Hexane/$MeCl_2$ solvent system and updated GC program. Shaded compounds were later removed from the SPE method.

Compound	Saturn 2000 Retention Time Using Updated GC Program	Quantitation m/z	Confirmation m/z	Lowest Standard Estimate (Ion Trap, DB-1, Splitless)
Chloroform	*Blocked by solvent*	83	49	*Blocked by solvent*
Dichloroacetaldehyde	*Blocked by solvent*	49	83	*Blocked by solvent*
Chloroacetonitrile	*Blocked by solvent*	75	77	*Blocked by solvent*
Chloropropanone	*Blocked by solvent*	43	49	*Blocked by solvent*
Carbon Tetrachloride	9.40 min.	117	49	0.50 ppb
Trichloroacetonitrile	9.69 min.	108	49	0.50 ppb
Dichloroacetonitrile	10.78 min.	74	49	0.75 ppb
Bromodichloromethane	11.15 min.	83	79	0.75 ppb
Chloronitromethane	*Co-elution Problem*	49	N/A	*Co-elution Problem*
Bromochloroacetaldehyde	*Co-elution Problem*	130	N/A	*Co-elution Problem*
1,1-Dichloropropanone	13.19 min.	43	93	1.0 ppb
Dichloronitromethane	13.95 min.	83	48	2.5 ppb
Bromoacetonitrile	14.91 min.	119	79	?
Chloropicrin	20.14 min.	117	49	1.0 ppb
Bromodichloroacetonitrile	20.18 min.	108	154	1.0 ppb
Dibromochloromethane	20.94 min.	127	208	0.50 ppb
Bromonitromethane	21.29 min.	93	79	?
Bromochloroacetonitrile	21.64 min.	74	155	0.50 ppb
Dichloroiodomethane	25.08 min.	83	127	?
Bromochloronitromethane	26.62 min.	129	79	0.75 ppb
1,1,1-Trichloropropanone	28.66 min.	43	83	1.0 ppb
1,3-Dichloropropanone	30.08 min.	77	49	1.0 ppb
Bromoform	31.80 min.	173	254	0.50 ppb
Dibromoacetonitrile	32.58 min.	118	79	0.50 ppb
Bromodichloronitromethane	32.61 min.	163	49	0.50 ppb
Dibromochloroacetonitrile	33.05 min.	154	74	0.50 ppb
1,1-Dibromopropanone	33.66 min.	43	173	1.0 ppb
Bromochloroiodomethane	33.90 min.	127	175	0.50 ppb
Dibromonitromethane	34.68 min.	173	43	0.75 ppb
1-Bromo-1,1-dichloropropanone	36.28 min.	43	127	2.5 ppb
1,1,3-Trichloropropanone	37.07 min.	77	83	0.75 ppb
Tribromochloromethane	37.89 min.	207	79	0.75 ppb
Dibromochloronitromethane	39.76 min.	207	79	?
Dibromoiodomethane	39.99 min.	127	173	0.75 ppb
Tribromoacetaldehyde	40.24 min.	251	N/A	?
Tribromoacetonitrile	40.39 min.	198	79	0.75 ppb
Benzyl chloride	41.09 min.	91	126	0.50 ppb
Chlorodiiodomethane	41.44 min.	175	127	0.50 ppb
1,1,3,3-Tetrachloropropanone	41.88 min.	83	111	2.5 ppb
1,1,1,3-Tetrachloropropanone	42.10 min.	77	49	0.50 ppb
Bromopicrin	43.64 min.	251	172	2.5 ppb
C8-Cl Internal Standard	44.40 min.	91	N/A	N/A
Bromodiiodomethane	46.23 min.	219	127	0.50 ppb
1,1,1-Tribromopropanone	46.77 min.	43	251	?
1,1,3-Tribromopropanone	49.89 min.	121	93	1.0 ppb
Iodoform	50.69 min.	127	267	0.50 ppb
1,1,3,3-Tetrabromopropanone	53.06 min.	120	173	?

1,1,1,3-Tetrachloropropanone showed an unrecoverable co-elution with an impurity late in the chromatographic run (retention time of 42.1 min.). There was no solution to this problem, so poor quality assurance (QA) data was obtained for this compound, following migration to this method.

1,1,3,3-Tetrabromopropanone (retention time of 53.1 min.) exhibited poor quantitation for standards and was the latest eluting compound of all the DBPs studied. Either 1,1,3,3-tetrabrompropanone was slowly degrading or quantitation of this compound was made difficult because of poor signal-to-noise in this section of the chromatographic run, when the GC oven was doing its final ramp to 301 ^{o}C. The baseline rises significantly about 52 min into the run.

Multiple Quantitation Ions

The main obstacle for quantitation of SPE results was low signal-to-noise of the chromatographic peaks. The electron capture detector is inherently more sensitive for detection for halogenated compounds (as low as 0.10 ppb). SPE and P&T are comparable for minimum reporting levels, generally 0.20 to 0.25 ppb. The peaks are often much sharper and more distinct using P&T because of a lack of solvent and full injection of the sample aliquot.

A new strategy of using multiple quantitation ions for improving SPE sensitivity was tested. In the past, the SPE method used the most optimum ion channel for high abundance and

minimal interference problems from other peaks. In this new strategy, the original quantitation ion was added to the next-largest ion that was a significant contribution to the EI mass spectrum. This provided up to a two-fold improvement for some compounds. About one-third of the compounds showed improvement, with a previous reporting level of 1.0 µg/L now becoming 0.50 µg/L.

MDL and Sample Reporting

All of the remaining 35 compounds gave results comparable to or better than those obtained in the past using the TS-250 instrument. In several cases, the lowest calibration standards could be dropped to 0.25 µg/L. (In previous work, the lowest calibration point was 1 µg/L, and a reasonable MDL was established at 3 µg/L).

The ten calibration standards for the Varian ion trap were at concentrations of 0.25, 0.50, 1.0, 2.5, 5.0, 7.5, 10, 15, 20, and 30 µg/L. After calibration curves had been established, the data files for 0.25 µg/L - 5.0 µg/L standards were duplicated and processed as if they were actual samples to check the accuracy and integrity of the calibration curves. Table 5 shows these results. If the reported values were within 30% of the theoretical values, then the results were designated in bold type, and the lowest, reliable values to report are shown in a shaded highlight. As an example, the results for a recent Alameda County Water District sampling on 3/19/02 showed that the values used for SPE results reporting could be set much lower than those produced from a simple MDL comparison (Table 5). Because this was such an important survey study, and real world results are often below 5 µg/L for any given DBP, it was necessary to extract all available information that we could from this SPE method.

Success with Migration of SPE Technique to Ion Trap

The SPE technique was successfully implemented on the Saturn 2000 ion trap mass spectrometer. Full-scan mode on the Saturn ion trap provided more mass spectral information and improved the sensitivity over the TS-250 instrument. The ion trap mass spectrometer provided full automation and overnight runs, along with more reliable operation. Because both the SPE and P&T methods used the same instrument for analysis, comparison of results was much better. Because of these advantages, the Saturn 2000 ion trap mass spectrometer was used for all subsequent samplings.

Comparison of SPE to P&T and LLE

The pursuit of multiple analytical techniques for the Nationwide DBP Occurrence Study led to a complementary scheme for data analysis and interpretation -- the liquid-liquid extraction technique would be the primary method used for quantitation, and other techniques such as P&T, SPE, or SPME could provide true confirmation of a compound's presence. Not all the techniques could analyze for each compound. Table 6 shows the comparison of results using SPE, P&T, and LLE techniques. The results were very consistent. Because this is only a comparison of

how SPE results compare to the other techniques, many of the compounds that were part of this study, but were not amenable to SPE, were intentionally left off the table.

Table 5. Minimum reporting levels (MRLs) for Alameda County Water District sampled on 3/19/02. A concentration in bold represents values that lie within the ± 30% range. Shading represents the lowest reportable level for this study set.

Compound	Quantitation Ions	0.25 ug/L (0.175 - 0.325) Range	0.50 ug/L (0.350 - 0.650) Range	1.0 ug/L (0.700 - 1.300) Range	2.5 ug/L (1.750 - 3.250) Range	5.0 ug/L (3.500 - 6.500) Range	Minimum Reporting Level	MDL Comparison
Halomethanes								
BDCM	83+85		0.701	**0.835**	**2.355**	**4.034**	1.0 ppb	4 ppb
DBCM	127+129	**0.229**	**0.643**	**0.860**	**2.488**	**3.910**	0.25 ppb	6 ppb
TBM	171+173		0.665	**0.953**	**2.659**	**4.221**	1.0 ppb	5 ppb
TBCM	207+209	**0.219**	**0.476**	**0.818**	**2.119**	7.445	0.25 ppb	5 ppb
DCIM	83+85	**0.250**	**0.534**	**0.845**	**2.417**	**4.406**	0.25 ppb	4 ppb
BCIM	127+129	**0.253**	0.665	**0.842**	**2.316**	**4.068**	0.25 ppb	4 ppb
DBIM	127+173			**0.774**	**2.244**	**4.424**	1.0 ppb	3 ppb
CDIM	127+175		**0.481**	**0.701**	**2.381**	**4.516**	0.50 ppb	4 ppb
BDIM	219+221				**1.990**	**5.899**	2.5 ppb	4 ppb
TIM	127+267				**1.968**	**4.014**	2.5 ppb	4 ppb
Haloacetonitriles								
BAN	119+121			**1.027**	**2.450**	8.820	1.0 ppb	12 ppb
DCAN	74		1.095	0.539	**2.876**	3.317	2.5 ppb	6 ppb
BCAN	74+76		**0.592**	**0.842**	**2.461**	**3.963**	0.50 ppb	5 ppb
DBAN	118+120		**0.544**	0.697	**2.370**	**3.798**	0.50 ppb	4 ppb
TCAN	108+110		**0.537**	**0.793**	**2.341**	**3.708**	0.50 ppb	3 ppb
Haloketones								
1,1-DCP	43+63+83				**2.935**	3.351	2.5 ppb	5 ppb
1,3-DCP	77+79				**2.014**	**4.154**	2.5 ppb	5 ppb
1,1-DBP	43+79+173		0.888	**1.012**	**2.334**	**4.229**	1.0 ppb	5 ppb
1,1,1-TCP	43+97+125		**0.595**	**1.031**	**2.961**	**4.024**	0.50 ppb	4 ppb
1,1,3-TCP	77+83				**2.441**	**3.504**	2.5 ppb	7 ppb
1,1,1-BDCP	43+97+125			**1.119**	**2.949**	**3.953**	1.0 ppb	4 ppb
1,1,1-TBP	43+79+251				**1.989**	**4.235**	2.5 ppb	9 ppb
1,1,3-TBP	121+123					**3.848**	5.0 ppb	11 ppb
1,1,3,3-TeCP	83+85				**1.830**	**3.505**	2.5 ppb	8 ppb
1,1,1,3-TeCP	77+79						>> 5 ppb	12 ppb
1,1,3,3-TeBP	120+122						>> 5 ppb	8 ppb
Haloacetaldehyde								
TBA	172+173				**2.543**	**6.380**	2.5 ppb	8 ppb
Halonitromethanes								
BNM	95					**5.092**	5.0 ppb	10 ppb
DCNM	83+85	0.401	0.678	**1.083**	**2.111**	**3.778**	1.0 ppb	10 ppb
BCNM	127+129					**4.220**	5.0 ppb	8 ppb
DBNM	171+173		**0.640**	**1.039**	**2.250**	**3.999**	0.50 ppb	7 ppb
TCNM	117+119		**0.509**	**0.923**	**2.473**	**4.095**	0.50 ppb	4 ppb
Misc. Compounds								
CT	117+119			**1.035**	**1.978**	**6.515**	1.0 ppb	4 ppb
BC	91+126	**0.192**	**0.552**	**0.841**	**2.138**	7.811	0.25 ppb	4 ppb
1,1,2,2-TeBCE	141+299				1.463	**5.821**	5.0 ppb	Not Available

Table 6. Comparison of results for SPE, P&T, and LLE analysis for Alameda County Water District. Patterned boxes denote that the compound was not reported for that method.

Alameda County Water District 3/19/02	MRL	Treated Tank Effluent (MSJWTP)			Finished Water (MSJWTP)			Dist. System/Average (MSJWTP)			SDS Average (MSJWTP)			Clearwell Effluent (TP2)			Finished Water (TP2)			Dist. System/Average (TP2)			SDS Average (TP2)		
	ug/L	SPE ug/L	P&T ug/L	LLE ug/L	SPE ug/L	P&T ug/L	LLE ug/L	SPE ug/L	P&T ug/L	LLE ug/L	SPE ug/L	P&T ug/L	LLE ug/L	SPE ug/L	P&T ug/L	LLE ug/L	SPE ug/L	P&T ug/L	LLE ug/L	SPE ug/L	P&T ug/L	LLE ug/L	SPE ug/L	P&T ug/L	LLE ug/L
Halomethanes																									
Bromodichloromethane	1.0	17.32	17.12	N/A*	22.91	19.27	N/A*	19.77	21.91	N/A*	26.84	23.52	N/A*	2.10	2.02	N/A*	2.40	2.84	N/A*	3.74	4.93	N/A*	4.18	4.54	N/A*
Dibromochloromethane	0.25	7.85	4.8	N/A*	9.62	5.34	N/A*	8.99	5.65	N/A*	9.99	5.78	N/A*	2.38	0.97	N/A*	2.87	1.78	N/A*	5.25	3.51	N/A*	5.46	3.38	N/A*
Bromoform	1.0	(0.78)	0.67	N/A*	(0.91)	0.69	N/A*	(0.90)	0.82	N/A*	(0.92)	0.84	N/A*	(0.65)	[0.49]	N/A*	(0.79)	0.76	N/A*	2.21	2.3	N/A*	2.43	2.37	N/A*
Tribromochloromethane	0.25																								
Dichloroiodomethane	0.25	1.35	1.61	3.7	1.75	2.04	2.6	2.02	3.07	1.8	2.41	3.26	2.3			2.0			2.5			1.4			
Bromochloroiodomethane	0.25	0.88	1.3	1.6	1.00	1.5	1.1	0.87	1.2	1.3	1.08	1.66	1.5							+			+		
Dibromoiodomethane	1.0	+	0.51		+	0.6		+	[0.44]		(0.34)	0.54													
Chlorodiiodomethane	0.50	+		0.9	+		0.7	+		1.1	+		1.2												
Bromodiiodomethane	2.5																								
Iodoform	2.5																								
Haloacetonitriles																									
Bromoacetonitrile	1.0																								
Dichloroacetonitrile	2.5	(0.96)	1.35	7.5	(0.97)	1.41	7.2	(1.20)	1.43	6.6	(1.49)	1.58	7.7			0.7			0.7			1.3			1.2
Bromochloroacetonitrile	0.50	0.95		1.1	0.95		1.8	1.10		1.0	1.17		1.2	+			+		0.8	(0.41)		2.2	(0.34)		1.6
Dibromoacetonitrile	0.50	(0.28)		0.7	0.70		1.1	(0.36)		0.7	(0.33)		0.8	+		0.5	+		0.6	(0.36)		1.1	(0.28)		0.4
Trichloroacetonitrile	0.50																								
Haloketones																									
1,1-Dichloropropanone	2.5		1.06	3.3	(0.72)	0.92	2.1		0.52	1.9		[0.49]	2.0			1.2			1.1			1.5		0.56	2.4
1,3-Dichloropropanone	2.5															0.2									
1,1-Dibromopropanone	1.0																								
1,1,1-Trichloropropanone	0.50	1.46	3.68	5.6	2.01	3.71	6.0	1.40	2.32	4.2	1.66	2.42	4.3	+		0.9	(0.28)		0.8			0.6			0.3
1,1,3-Trichloropropanone	2.5																								
1,1,1-Bromodichloropropanone	1.0	+			+		0.9									0.1			0.2						
1,1,1-Tribromopropanone	2.5																								
1,1,3-Tribromopropanone	5.0						0.1									0.5									
1,1,3,3-Tetrachloropropanone	2.5																								
1,1,1,3-Tetrachloropropanone	>> 5																								
1,1,3,3-Tetrabromopropanone	>> 5																								
Haloacetaldehydes																									
Tribromoacetaldehyde	2.5			0.4			0.1									0.8			0.5						
Halonitromethanes																									
Bromonitromethane	5.0																								
Dichloronitromethane	1.0	+		0.3	+		0.2	+		0.2	+		0.3							+		0.2			0.3
Bromochloronitromethane	5.0						0.3												0.1			0.2			
Dibromonitromethane	0.50																		0.1						
Trichloronitromethane	0.50	(0.25)		0.3*	+		0.6*	(0.40)		1.2*	0.53		1.5*							+		0.8*	(0.33)		0.9*
Misc. Compounds																									
Carbon tetrachloride	1.0																								
Benzyl Chloride	0.25																								
1,1,2,2-Tetrabromochloroethan	5.0																								

+ Compound is present but could not be quantitated.
* High spike recovery.

CONCLUSIONS

There was no one universal method that could be used to analyze all targeted DBPs. LLE-GC-ECD is the most universal of all the techniques, but it does not provide the definitive results that a mass spectrometric technique provides. Of the two mass spectrometry techniques examined (P&T-GC/MS and SPE-GC/MS), P&T-GC/MS excelled at measuring volatiles and benefited from being a solvent-less technique. SPE, on the other hand, can make use of a variety of sorbents to target specific families of compounds or to provide general screening results, as was the case for this study.

The solid phase extraction technique was developed to incorporate as many compounds as possible. To this end, we achieved our goal. In future work, we hope to improve upon the technique by taking advantage of many new sorbents that have appeared on the market, which offer improved extraction efficiencies that should provide lower detection limits. We are also pursuing an on-line solid phase extraction apparatus that will remove the need for an operator to extract the cartridges by hand, which should improve reproducibility. A fully automated on-line SPE system would offer the flexibility to screen many compounds, ranging from volatiles to semi-volatiles, with full mass spectrometric detection and limited user intervention.

LIQUID-LIQUID EXTRACTION-GAS CHROMATOGRAPHY-ELECTRON CAPTURE DETECTION METHOD

INTRODUCTION

Different versions of the gas chromatographic (GC) method were used during the course of this disinfection by-product (DBP) occurrence project since the method was still undergoing major development during the utility sampling phase. A short description of the final version of the method will be given, followed by a history highlighting some of the major changes that occurred during the method development. The method changes improved the scope and quality of the method over the development period.

METHOD SUMMARY

The basic method used GC with a salted liquid-liquid extraction (LLE) procedure to quantitate and confirm 47 drinking water DBPs (Figure 1). For this method, two different GC columns were operated simultaneously (DB-1 and DB-5), which permitted the separation and quantitation for all of the analytes. The method included two different internal standards used as reference peaks. Samples were collected in two analytical fractions; however each fraction used the same sample preparation method. The two analytical fractions were used to accommodate the use of two different chemical preservatives (ascorbic acid and ammonium chloride). The method required two separate extractions and two GC injections of each sample to achieve the quantitation for all 47 DBPs. Sample preparation included collection of a 30 mL volume of sample, salting with 11 g of sodium sulfate and 1 g of copper sulfate, and extraction with 3 mL of methyl *tertiary*-butyl ether (MtBE). A mechanical platform shaker was used for automated sample extraction. The copper sulfate enhanced analyte recovery and aided in the extract transfer process. An autosampler injected sample extracts onto a split-splitless GC injection port, and a two-channel data system simultaneously collected the two chromatograms for each injection.

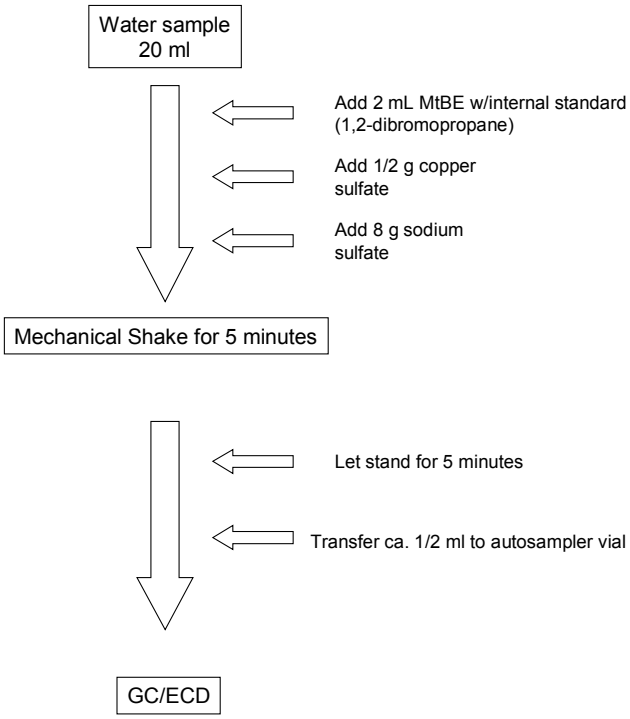

Figure 1. Summary of the LLE-GC-ECD method.

Sample Preparation

A 30 mL glass syringe was used to transfer samples into 40 mL glass vials. Daily procedural calibration standards were prepared with each set of samples using acidified reagent water. Sample matrix spikes and sample duplicates were prepared with each sample set. The MtBE extraction solvent contained two different internal standards. Because the MtBE was prepared with the internal standard, additional steps of adding the internal standard to each sample extract was eliminated. After 3 mL of MtBE was added, 11 g of dried sodium sulfate and 1 g of copper sulfate were added. The sample was capped and shaken briefly by hand before placing into a sample holder. After the solvent and salt were added to all of the samples, they were shaken using a vortex mixer for 11 min. A disposable Pasteur pipette was used to transfer approximately 2 mL of extract evenly between the two autosampler vials. One vial was stored in a freezer as a backup extract, and the other vial was was used for analysis.

Gas Chromatography Method

This GC method accomplished the separation and quantitation of 47 drinking water DBPs. The method involved the simultaneous analysis of one sample injection on two different analytical columns. The two different columns were attached to one injection port, allowing each sample to be analyzed by a GC equipped with two electron capture detectors (ECD). The two channels of data were collected simultaneously and processed sequentially. Unlike previous GC methods where one column is used as the primary analytical column for quantitation and a secondary column is used as a confirmation column, this method used both columns as primary analytical columns, with each column also used for confirmatory analysis. Using two different analytical columns allowed coeluting peaks to be resolved.

Two sets of samples collected from the each location because two different sample preservatives were required. Forty-one compounds were preserved and collected using ascorbic acid (AA). Ammonium chloride (AC) was used to preserve six other compounds (tri-halonitromethanes) that could not be preserved using ascorbic acid. Both the ammonium chloride and the ascorbic acid fractions were analyzed using the dual primary column analysis method. When analyzing the ascorbic acid fraction, one column could separate 25 compounds, and the other column could separate the other 16 compounds. Some compounds could be resolved on both columns, while other compounds could be resolved only on one of the columns. When a compound was separated on both columns, one column was used as the primary quantitation column, and the other column used for confirmation. Table 1 lists which DBPs coelute for each column. Ascorbic acid was used as a preservative for all sampling locations. Later in the study, ammonium chloride was used as a preservative for a smaller subset of those same sampling locations

When ammonium chloride-preserved samples were analyzed using the dual primary column analysis, 4 compounds could be resolved on one column, and the other two on the other column. Both columns were used for confirmation, as described for ascorbic acid-preserved samples. Ammonium chloride-preserved samples were extracted and analyzed using the same LLE procedure and GC conditions as for ascorbic acid-preserved samples.

Four separate GC software methods were developed to allow all 47 compounds to be analyzed. The 47 compounds were analyzed by producing four different chromatograms and calibrating most of the compounds twice. Data processing was done in pairs for each analytical fraction to enable cross-checking between columns. This aided in the analyte identification and detection process.

The primary column "A" was a DB-1 (J & W Scientific/Agilent, Folsom , CA, 30-m, 0.25- mm ID, 1-µm film thickness); primary column "B" was a DB-5 (J & W Scientific/Agilent, Folsom, CA, 30-m, 0.25-mm ID, 1-µm film thickness). Both analytical columns were installed onto a single GC injector (Model 3600, Varian Analytical Instruments, Walnut Creek, CA). The GC was equipped with two ECDs and an autosampler (Varian Analytical Instruments, Walnut Creek, CA). The autosampler injected 4.7 µL of extract onto a Model 1077 split-splitless injector operated in the splitless mode. The "A" and "B" channel ECD outputs were connected to a PE Nelson 970 interface (Perkin Elmer Corp., San Jose, CA).

Table 1. Gas chromatographic interferences for disinfection by-product analysis[a]

	DB-1 (10 coelutions)	**DB-5 (14 coelutions)**
1	cnm+bca+tca	can+tcan
2	tcnm+bdcan	Cnm+11dcp
3	1133tecp+13dbp	Bnm+bcan
4	dban+bdcnm	113tcp+tbcm
5	(ban+i)^	tba+dbim
6		bc+tban
7		1133tecp+cdim
	^ ban appears to coelute with an interference peak	
	Shouldered Peaks*	**Shouldered Peaks**
1	bnm & bcan & i	tca & dcan
2	13dcp & i	11dbp & dban & bcim
3	tbm & i	Bdim & i
4	bcim & 11dbp	
5	dbim & i	
6	111tbp & i	
	*i=unknown interference	

[a] Compound Abbreviations are Shown in Table 3

The GC operating conditions shown in Table 2 were optimized to enhance sensitivity. A low injection temperature of 87 °C was used to minimize degradation of thermally labile compounds. A large injection volume of 4.7 µL was chosen to increase sensitivity. Column flow rates and other conditions were adjusted to maximize resolution and detection for each compound.

Table 2. Gas chromatograph operating conditions

GC Temperature Program:											
	Temperature (°C):	35		139		301					
	Rate (°C/minute):		4		27						
	Time (minutes):	23		0		5					
Flow rates:	Helium carrier gas at 35°C	DB-1 Column = 2.3 ml/min									
		DB-5 Column = 1.3 ml/min									
	Head Pressure 14.3 psi										
Rear Injector Varian model 1077 capillary split/splitless											
	Split ratio = 12										
	Injector temperature = 87 °C										
	Injection mode splitless										
	Split valve program 0.89 min (relay=2)										
Detector Varian Nickel 63 Electron Capture Detector (ECD)											
	Two regular size ECD's (model # 02-001972-00)										
	Operating Temperature = 297 °C										
	Make-up gas Nitrogen at 29.3 mL/min										
	Autozero on										
	Range 10										
Varian model 8200 Autosampler											
	Injection Volume = 4.7 uL										
	Solvent plug size= 0.1 uL										
	Slow injection rate= 2.3 uL/sec										
	Upper air gap and lower air gap selected										
	Viscosity = 4										
	Resevoir pressure= 27psi										
	Resevoir solvent= MtBE										
Other Parameters											
	Thermal stabilize time=1.07 min										
	Column standby temperature= 117 °C										
	Column A and B installed:	A=J&W DB-1, 30 meter, 0.25 mm I.D., 1 micron film thickness									
		B=J&W DB-5, 30 meter, 0.25 mm I.D., 1 micron film thickness									
	GC= Varian model 3600										
	A central laboratory gas manifold system supplies nitrogen and helium gas										
	Dual channel data aquisition 1 volt input to model 970 PE Nelson Interface/Buffer										
	Chromatography Software PE Turbochrome Navigator (ver4.1) 1987-1995										

Calibration and Data Processing

Two sets of calibration standards were prepared from five different intermediate stock solutions (Table 3). The ascorbic acid spiking solutions contained the first 41 compounds (Table 3), and used 7 different concentration points (over the range of 0.1 – 80 µg/L) for the calibration curve. An additional high concentration point was added for THM analyses to enable the concentration range to extend to 120 µg/L (ppb). Ammonium chloride spiking solutions contained 6 compounds (trihalonitromethanes) (Table 3), and used 7 different concentration points (over the range of 0.5 – 20 µg/L) for the calibration curve. Calibration standards were prepared daily from stock solutions. Standards and blanks were prepared in pH-adjusted, distilled water (adjusted to 3.5 with concentrated sulfuric acid). Direct standards (non-extracted standards) were also prepared with each daily batch of extractions. Individual stock solutions were prepared on an annual basis, intermediate stock solutions were prepared quarterly, and spiking solutions were prepared bimonthly. All sample extracts and standard solutions were stored in the freezer at -11 °C.

Method Development Highlights

A short chronology of the major steps in the method development will be discussed. Each step is included because it has affected the type and quality of the project data. The variations in methods used over the project period can help to identify differences in the data over the utility sampling period.

The GC method development started in December 1998 and continued through the end of the utility sampling phase (April 2002). From February 1999 to August 2000, initial GC-ECD, purge-and-trap-GC/MS, and solid phase microextraction (SPME)-GC/MS methods were developed. In October 2000, due to operational problems with the Varian 3500A GC, two other GCs (a Varian 3500B and a Varian 3600) were configured for the dual column-GC-ECD analyses. Between February and March 2001, adjustments were made to the GC temperature program to achieve better separations. Higher quality-control spike concentrations of THM standards (50 ppb) were also made during this time. In March 2001, 9 additional compounds were added to the GC method (dichloronitromethane, bromochloronitromethane, tribromonitromethane, 1,1-dibromopropanone, 1-bromo-1,1-dichloropropanone, 1,1,1-tribromopropanone, 1,1,3-tribromopropanone, 1,1,1,3-tetrachloropropanone, and bromodichloroacetonitrile). Between May and July 2001, the extraction method was improved to increase the concentration factor and improve analyte recoveries. At this point, ammonium chloride was also introduced as a second preservation chemical, and the remaining 4 analytes were added to the method (tetrabromochloroethane, dibromochloronitromethane, bromodichloronitromethane, and chloronitromethane), for a total of 47 analytes. An additional internal standard (2-bromo-1-chloropropane) was also added to aid in analyte identification.

Table 4 shows the improved recoveries that were accomplished by the adjustments in the LLE-GC-ECD method. Table 5 shows the method reporting limits (MRLs) for the LLE-GC-ECD method compared to the SPE-GC/MS and P&T-GC/MS methods. In general the LLE-GC-ECD method reporting limits were the same or lower than other methods (Table 5).

Table 3. Stock standard calibration preparation

btl	#	Compounds		Stk Date	Stk ppm	Chk Date	Purity	Adj conc	uL in 1mL ACN	conc ppm
A		**100ppm THM & 551B mix**								
1	1	chloroform	tcm	11/28	2000		99+	2000	**50**	100.0
2	2	bromodichloromethane	bdcm		Supelco			ppm		
3	3	chlorodibromomethane	cdbm		4-8140u					
4	4	bromoform	tbm		MeOH					
1	5	Dichloroacetonitrile	dcan	11/28	2000		99+	2000	**50**	100.0
2	6	bromochloroacetonitrile	bcan		Supelco			ppm		
3	7	dibromoacetonitrile	dban		4-8046					
4	8	trichloroacetonitrile	tcan		acetone					
5	9	1,1-dichloropropanone	1,1-dcp		551b					
6	10	1,1,1-trichloropropanone	1,1,1-tcp		dbp					
7	11	chloropicrin	tcnm		mix					
1	12	1,1,2,2-tetrabromo-1-chloroethane	tebce	9/28	3700	6/29	78.7	2912	**35**	101.9
B		**100ppm Halomethane mix**								
1	13	Bromochloroiodomethane	bcim	4/6	3400	5/16	96.4%	3300	**32.0**	105.6
2	14	Dichloroiodomethane	dcim	4/6	2100	5/16	90.2%	1900	**54.0**	102.6
3	15	Dibromoiodomethane	dbim	4/6	3500	5/16	99.0%	3500	**28.6**	100.0
4	16	Chlorodiiodomethane	cdim	4/6	3900	5/17	68.3%	2650	**38.0**	100.7
5	17	Bromodiiodomethane	bdim	4/6	4800	5/16	93.8%	4500	**23.0**	103.5
6	18	Iodoform	tim	4/5	6900	5/17	99.0%	6900	**15.0**	103.5
7	19	Tribromochloromethane	tbcm	4/6	4200	5/16	94.9%	4000	**26.0**	104.0
C		**100ppm Halo(acetonitrile & acetaldehyde) mix**								
1	20	Bromoacetonitrile	ban	9/28	4400	5/10	99+%	4400	**23.0**	101.2
2	21	Chloroacetonitrile	can	4/5	2000	5/10	99+%	2000	**50.0**	100.0
3	22	Dichloroacetaldehyde	dca	4/6	4600	5/14	99.0%	4600	**24.0**	110.4
4	23	Bromochloroacetaldehyde	bca	7/17	2400	7/19	54.1%	1298	**78.0**	101.3
5	24	Tribromoacetaldehyde	tba	4/6	3200	5/14	99.0%	3200	**32.0**	102.4
6	25	chloral	tca	9/23	1000		99+%	1000	**100.0**	100.0
D		**100ppm Haloketone mix**								
1	26	Chloropropanone	cp	4/10	2100	5/14	98.0%	2050	**50.0**	102.5
2	27	1,3-Dichloropropanone	1,3-dcp	4/5	6500	5/14	99.0%	6500	**15.4**	100.1
3	28	1,1,3-Trichloropropanone	1,1,3-tcp	4/5	1900	5/15	99.6%	1900	**54.0**	102.6
4	29	1,1,3,3-Tetrachloropropanone	1,1,3,3-tecp	4/6	2000	5/15	99.0%	2400	**42.0**	100.8
5	30	1,1,1,3-Tetrachloropropanone	1,1,1,3-tecp	4/6	2200	5/15	92.4%	2050	**50.0**	102.5
6	31	1-Bromo1,1dichloropropanone	1-b1,1dcp	4/6	2700	5/15	77.6%	2100	**50.0**	105.0
7	32	1,1-Dibromopropanone	1,1-dbp	6/29	1800	5/15	94.0%	1700	**60.0**	102.0
8	33	1,1,1-Tribromopropanone	1,1,1-tbp	4/6	2600	5/15	97.0%	2500	**40.0**	100.0
9	34	1,1,3-Tribromopropanone	1,1,3-tbp	6/29	2200	5/15	97.6%	2150	**48.0**	103.2
10	35	1,1,3,3-Tetrabromopropanone	1,1,3,3-tebp	4/6	6400	5/15	99.0%	2000	**50.0**	100.0
E		**100ppm Halonitromethanes + bc mix**								
1	36	Chloronitromethane	cnm	9/28	5300	5/14	99.0%	5300	**19.0**	100.7
2	37	Bromonitromethane	bnm	4/5	3100	5/14	99.0%	3100	**34.0**	105.4
3	38	Dichloronitromethane	dcnm	4/5	2900	5/14	99.0%	2900	**36.0**	104.4
4	39	Bromochloronitromethane	bcnm	4/10	1950	5/14	97.4%	1900	**54.0**	102.6
5	40	Dibromonitromethane	dbnm	4/5	3600	5/14	97.1%	3500	**30.0**	105.0
6	41	Benzyl chloride	bc	4/5	2300	5/14	99+%	2300	**44.0**	101.2
F		**30ppm AC Mix**								
1	42	Bromopicrin	tbnm	4/5	3300	5/14	99.0%	3300	**9.1**	30.0
2	43	Tribromoacetonitrile	tban	4/6	3700	5/14	99.0%	3700	**8.1**	30.0
3	44	Bromodichloroacetonitrile	bdcan	4/6	2400	5/10	94.8%	2300	**13.1**	30.1
4	45	Dibromochloroacetonitrile	dbcan	4/10	3500	5/14	42.1%	1500	**20.0**	30.0
5	46	Bromodichloronitromethane	bdcnm	4/5	3800	5/14	99.0%	3800	**8.0**	30.4
6	47	Dibromochloronitromethane	dbcnm	4/5	4400	5/14	99.0%	4400	**6.9**	30.4

Table 4. Improved extraction method comparison showing increased compound recoveries

	tcm	can	cp	TCAN	DCAN	BDCM	tca	dcnm	BAN	bdcan	bnm	bcan	
A Method	107	516	137	2093	2022	1489	2690	418	7537	4115	2502	2793	
B Method	74	272	86	1065	1172	310	1674	176	2077	1598	506	526	
% Improved	**45**	**90**	**59**	**97**	**73**	**380**	**61**	**138**	**263**	**158**	**394**	**431**	
	dcim	bcnm	111tcp	13dcp	TBM	dban	dbcan	11dbp	dbnm	111dcbp	113tcp	tbcm	dbim
A Method	257	3388	2030	1159	291	2547	875	3876	2912	577	945	102	29
B Method	118	2082	632	427	173	1441	249	2911	1899	169	262	49	14
% Improved	**118**	**63**	**221**	**171**	**68**	**77**	**251**	**33**	**53**	**241**	**261**	**108**	**107**
	TBA	tban	BC	CDIM	1133tecp	1113tecp	tbnm	BDIM	111tbp	113tbp	tim	1133tebp	
A Method	294	1653	12	101	184	1868	2	265	184	1834	247	96	
B Method	129	621	6	47	73	431	1	107	71	1249	76	47	
% Improved	**128**	**166**	**100**	**115**	**152**	**333**	**100**	**148**	**159**	**47**	**225**	**104**	
A Method	Extract 30 mL sample with 3 mL MtBE + CuSO4+ Na2SO4 - 11 min shake												
B Method	Extract 20 mL sample with 4ml MtBE + Na2SO4 only - 5 min shake												

CONCLUSIONS

The GC method produced various levels of data quality, as it was developed throughout the sampling period. The GC method became more reliable and robust over the development period. The final method was capable of measuring the 47 DBP analytes in this study.

Table 5. Method reporting limit comparison of three analytical methods

			GC-LLE		SPE		P&T	
No.	Compounds	symbol	mrl	count	mrl	count	mrl	count
A	**100ppm THM & 551B mix**							
1	chloroform	tcm	0.5	1			0.2	1
2	bromodichloromethane	bdcm	0.1	2	0.5	1	0.2	2
3	chlorodibromomethane	dbcm	0.1	3	0.5	2	0.5	3
4	bromoform	tbm	0.1	4	2.5	3	0.5	4
1	Dichloroacetonitrile	dcan	0.1	5	5	4	0.2	5
2	bromochloroacetonitrile	bcan	0.1	6	0.5	5	1.0	6
3	dibromoacetonitrile	dban	0.1	7	.5	6		
4	trichloroacetonitrile	tcan	0.1	8	0.5	7		
5	1,1-dichloropropanone	1,1-dcp	0.1	9	1	8	0.5	7
6	1,1,1-trichloropropanone	1,1,1-tcp	0.1	10	1	9	0.5	8
7	chloropicrin	tcnm	0.1	11	0.5	10	1.0	9
1	1,1,2,2-tetrabromo-1-chloroethane	tebce	0.5	12	2.5	11		
B	**100ppm Halomethane mix**							
1	Bromochloroiodomethane	bcim	5.0	13	1	12	0.5	10
2	Dichloroiodomethane	dcim	0.5	14	1	13	0.5	11
3	Dibromoiodomethane	dbim	0.5	15	1	14	0.5	12
4	Chlorodiiodomethane	cdim	0.1	16	2.5	15	0.5	13
5	Bromodiiodomethane	bdim	0.5	17	5	16	0.5	14
6	Iodoform	tim	2.0	18	2.5	17		
7	Tribromochloromethane	tbcm	0.5	19	0.5	18		
C	**100ppm Halo(acetonitrile & acetaldehyde) mix**							
1	Bromoacetonitrile	ban	0.1	20	5	19	2.5	15
2	Chloroacetonitrile	can	0.1	21			0.2	16
3	Dichloroacetaldehyde	dca	0.5	22				
4	Bromochloroacetaldehyde	bca	0.5	23				
5	Tribromoacetaldehyde	tba	0.1	24	5	20		
6	chloral	tca	0.1	25				
D	**100ppm Haloketone mix**							
1	Chloropropanone	cp	0.1	26			0.5	17
2	1,3-Dichloropropanone	1,3-dcp	0.1	27	2.5	21		
3	1,1,3-Trichloropropanone	1,1,3-tcp	0.1	28	2.5	22		
4	1,1,3,3-Tetrachloropropanone	1,1,3,3-tecp	0.1	29	5	23		
5	1,1,1,3-Tetrachloropropanone	1,1,1,3-tecp	0.1	30	5	24		
6	1-Bromo1,1dichloropropanone	1-b1,1dcp	0.1	31	1	25		
7	1,1-Dibromopropanone	1,1-dbp	0.5	32	0.5	26	0.5	18
8	1,1,1-Tribromopropanone	1,1,1-tbp	0.1	33	5	27		
9	1,1,3-Tribromopropanone	1,1,3-tbp	0.1	34	5	28		
10	1,1,3,3-Tetrabromopropanone	1,1,3,3-tebp	0.5	35	5	29		
E	**100ppm Halonitromethanes + bc mix**							
1	Chloronitromethane	cnm		36			0.5	19
2	Bromonitromethane	bnm	0.1	37	2.5	30		
3	Dichloronitromethane	dcnm	0.1	38	0.25	31	0.5	20
4	Bromochloronitromethane	bcnm	0.1	39	2.5	32		
5	Dibromonitromethane	dbnm	0.1	40	0.5	33		
6	Benzyl chloride	bc	2.0	41	0.25	34	0.5	21
F	**30ppm AC Mix**							
1	Bromopicrin	tbnm	0.5	42				
2	Tribromoacetonitrile	tban	0.5	43				
3	Bromodichloroacetonitrile	bdcan	0.5	44				
4	Dibromochloroacetonitrile	dbcan	0.5	45				
5	Bromodichloronitromethane	bdcnm	0.5	46				
6	Dibromochloronitromethane	dbcnm	0.5	47				

CLOSED-LOOP STRIPPING ANALYSIS METHOD

Closed-loop stripping analysis (CLSA) has been successfully applied in the past for the determination of volatile organic compounds (VOCs) of intermediate molecular weight, including many taste-and-odor species. Typically, the compounds are stripped from 1 L of water by a recirculating stream of air, and trapped on a carbon filter cartridge. Extraction of the cartridge to a small, 20 µL volume produces unusually high concentration factors of 50,000:1 – enough to quantitate low ng/L levels. Although originally scheduled for the U.S. Environmental Protection Agency (USEPA) disinfection by-product (DBP) study, this technique proved less than desirable for continued research given the emerging successes of both solid phase extraction (SPE) and solid phase microextraction (SPME) techniques. It was discontinued during the Summer of 1999.

EXPERIMENTAL

Instrumentation

The instrument used for this work was a VG TS-250 medium resolution mass spectrometer (VG Tritech, Manchester, England) equipped with a Digital PDP-11/53 computer (Digital Equipment Corporation, Maynard, MA). Samples were injected using a CTC A200S autosampler (Leap Technologies, Chapel Hill, NC). A HP 5890 (Hewlett-Packard, Palo Alto, CA) gas chromatograph was used for separations and partially controlled by an Optic 2 injector (AI Cambridge, Cambridge, England).

Chromatography

A DB-1 column was used (30-m, 0.25-mm ID, 1-µm film thickness) (J&W Scientific/Agilent, Folsom, CA). The GC oven temperature program used was based on EPA Method 551.1 (an initial temperature of 35 ^{o}C, which was held for 22 min, followed by an increase at a rate of 10 ^{o}C/min to 145 ^{o}C, which was held for 2 min; followed by an increase at a rate of 20 ^{o}C/min to 225 ^{o}C, which was held for 15 min).

General Procedure

The procedure for CLSA was taken from Standard Methods for the Examination of Water and Wastewater (20th ed., 1998). For standards, 900 mL of organic pure water (OPW) was placed into a 1-L glass stripping bottle. Seventy-two grams of sodium sulfate were added with rapid mixing until the salt was mostly dissolved. The sample was then spiked with a cocktail mix, covered, placed into a water bath at room temperature (22 ^{o}C), and stripped for 2 hours. The 1.5 mg carbon filter was extracted with dichloromethane, carbon disulfide (CS_2), or methyl *tertiary* butyl ether (MtBE) and brought to a final volume of 20 µL, if needed. The infinitesimally small sample was transferred into a special conical-shaped autosampler vial for storage. After a 2 µL injection to the GC, the remaining extract was covered with a fresh Teflon cap and stored in the freezer for future reference. A detailed description of the method can be also found at Krasner *et al*. (1983).

RESULTS AND DISCUSSION

Initial DBP Testing - Extraction Efficiency

Stripping efficiencies can be optimized by adjusting stripping time, temperature, and use of salt to increase the ionic strength of the water. A preliminary check of DBP compatibility was done using a mixture of DBPs spiked in organic pure water. The spiking mix (5 µL of the 200 ppm mixture) was added to 900 mL of pure water to give an actual concentration of 1.1 µg/L in the water. At 100% analyte recovery, this is equivalent to a 50-ppm unextracted standard. Stripping time was two hours.

Table 1. Extraction efficiency of select DBPs

Compound	RT (min)	No Salt CS_2	No Salt CS_2 DUP	72 g Salt CS_2	72 g Salt CS_2 DUP	72 g Salt $MeCl_2$	72 g Salt $MeCl_2$ DUP
chloroacetonitrile	7.3	ND	ND	ND	ND	ND	ND
chloropropanone	7.9	ND	ND	ND	ND	ND	ND
carbon tetrachloride	8.7	**6%**	ND	ND	**9%**	**3%**	**15%**
bromoacetonitrile	15.2	ND	ND	ND	ND	ND	ND
dichloroiodomethane	24.8	**14%**	**15%**	**24%**	**19%**	**25%**	**44%**
1,3-dichloropropanone	27.5	ND	ND	ND	ND	ND	ND
bromochloroiodomethane	29.6	**37%**	**23%**	**50%**	**36%**	**44%**	**71%**
1,1,3-trichloropropanone	31.0	ND	ND	ND	ND	ND	ND
chlorodiiodomethane	33.2	**37%**	**22%**	**49%**	**40%**	**57%**	**76%**
bromodiiodomethane	35.7	**26%**	**19%**	**60%**	**40%**	**47%**	**61%**
hexachloropropanone	37.4	ND	ND	ND	ND	ND	ND
iodoform	38.1	**8%**	**6%**	**22%**	**14%**	**21%**	**24%**

This preliminary check of the CLSA method pointed out potential problems that would need to be addressed. First, the results were highly irreproducible for duplicate analyses without any internal standard. The sample concentrations listed in Table 1 were obtained from raw area counts of the compound peaks. There can be many variables introduced during the stripping procedure to cause such a wide variance in results, such as minute air leaks in the stripping apparatus, differences in the filter flow rates (age of filter, contamination), temperature differences during stripping, and analyte loss during the final extraction. For some haloketones and haloacetonitriles (chloropropanone, 1,3-dichloropropanone, 1,1,3-trichloropropanone, chloroacetonitrile, and bromoacetonitrile), there were no detectable recoveries. For the iodinated THMs and carbon tetrachloride, results showed that the use of salt improved the stripping efficiency. Also, dichloromethane was a better solvent compared to carbon disulfide.

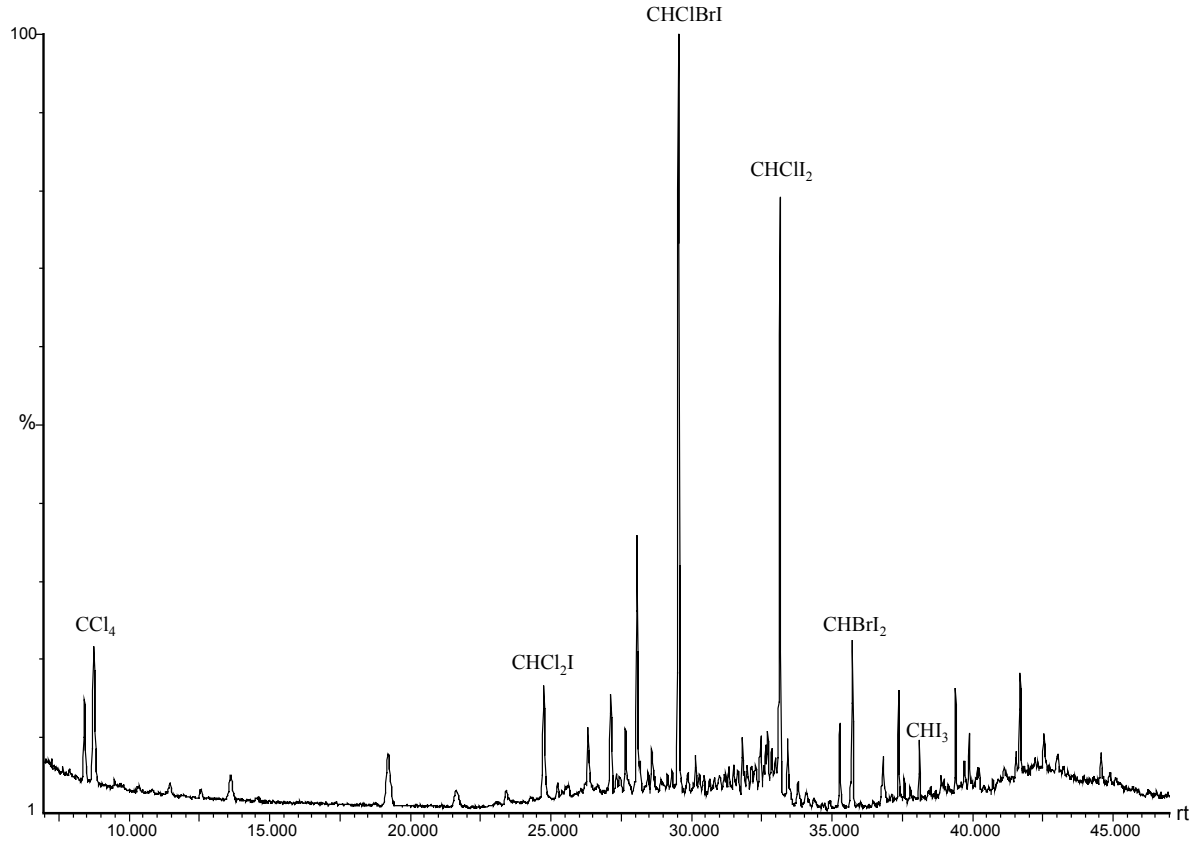

Figure 1. Two-hour closed-loop stripping analysis of iodinated THMs and carbon tetrachloride. Elution solvent was dichloromethane.

Figure 1 shows the best case scenario for iodo-THMs and carbon tetrachloride, utilizing 72 grams of sodium sulfate and dichloromethane for extraction. Stripping time was 2 hours.

Traditional DBPs

Initial attempts to apply closed-loop stripping analysis to the new DBPs that are part of this project failed to yield immediate results for any compounds other than iodinated species and carbon tetrachloride. The targeted compounds included chloropropanone, 1,3-dichloropropanone, 1,1,3-trichloropropanone, hexachloropropanone (later found to immediately hydrolyze in water), bromoacetonitrile, and chloroacetonitrile.

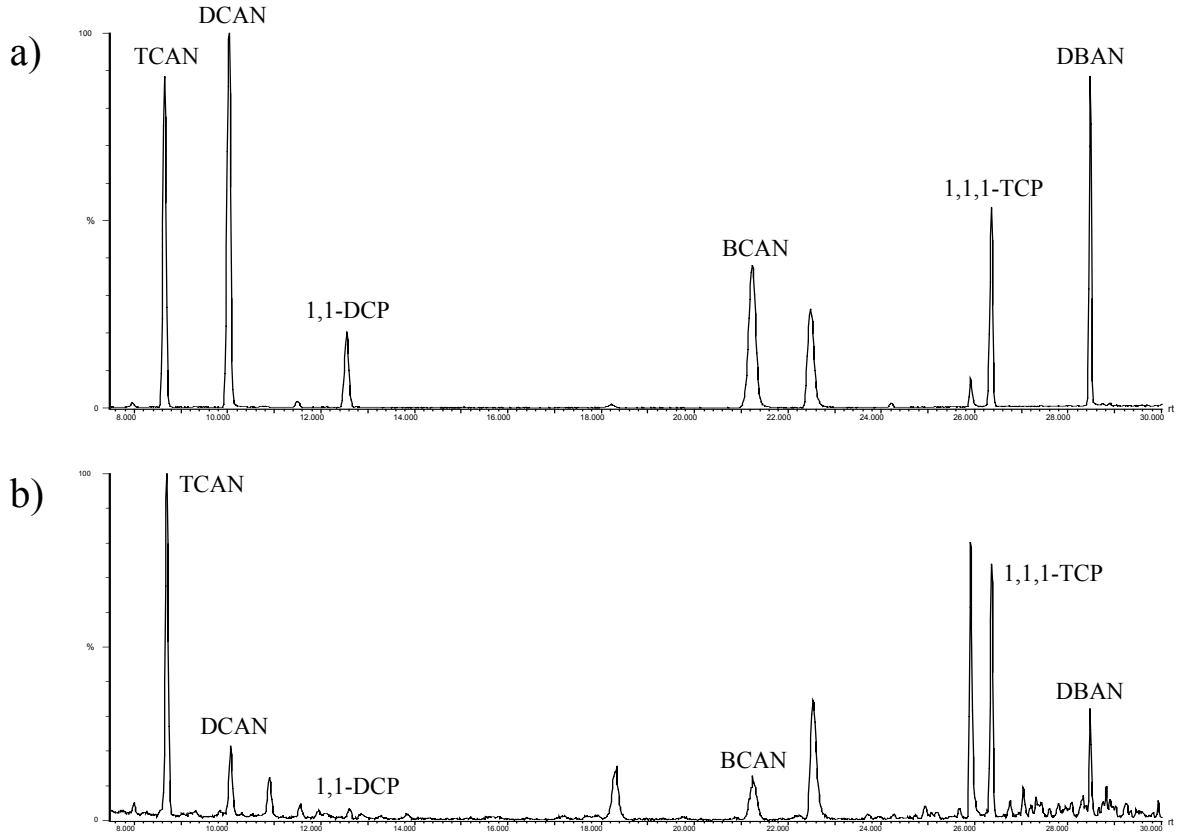

Figure 2. a) Direct injection of 200 ppm of DBP mixture for comparison. b) CLSA extract of DBP mixture in MtBE.

It was suggested that some of the EPA method 551.1 DBPs should be attempted since there was some evidence that it should be possible to strip these compounds (Croue and Reckhow 1989). Therefore, the following standards were obtained and analysed by CLSA: dichloro-, dibromo-, and trichloroacetonitrile, and 1,1-dichloro-, and 1,1,1-trichloropropanone. Results from these compounds were more promising. A series of experiments was performed to evaluate the effect of extraction solvent and stripping time for the compounds. All of the compounds were spiked both with the DBP mixture and an added 1-chlorooctane internal standard/surrogate. For consistency and ease of results interpretation, all samples were stripped on the same apparatus and on the same day. Three solvents were tested, including MtBE, dichloromethane, and carbon disulfide. A 30-min stripping time was also evaluated as an alternative to the traditional 1-2 hour time.

The MtBE solvent peak eluted at 4 min and continued until about 5.5 min, with tailing. Quantitative peaks occurred after 7 min and continued throughout the 50-min run. The 1-chlorooctane internal standard eluted at 34 min and was not shown in Figure 2. All peaks were identified using their NIST library mass spectra.

Overall, MtBE was best at removing the compounds from the carbon filter, followed by $MeCl_2$, and then CS_2. An additional benefit of using MtBE is that it allows extracts to be run on a GC equipped with an electron capture detector (ECD), which is not possible for chlorinated solvents. In addition, it was confirmed that a 1-hour strip was preferred over a 30-min strip time,

although there is a point of diminishing returns. Generally, anything over two hours does not increase analyte recoveries significantly.

The use of higher stripping temperatures improved stripping efficiency. However, attempts at 40 ^{o}C were unsuccessful because of moisture condensation onto the carbon filter. Despite attempts to heat the entire air system using heater tape to avoid cold spots, the large volume of humid air moving through the system inevitably spoiled any attempts to produce successful results. Commercially-designed systems (e.g. Mass Evolution, Inc., Houston, TX) can use slightly wider glass cartridge holders and heating blocks to allow higher temperature operation.

CONCLUSIONS

At the start of this work, many of the DBPs that were planned for the Nationwide DBP Occurrence Study had yet to be received. This work represents only a portion of the compounds that could have been tested. But, based on these preliminary results, it seems unlikely that CLSA would have been a good universal screening device for new DBPs (i.e. limited compatibility, large sampling requirement, poor reproducibility). Table 2 lists the compounds tested and whether they were amenable to closed-loop stripping analysis.

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Croué, J.-P., and D. A. Reckhow. Destruction of chlorination byproducts with sulfite. *Environmental Science & Technology* 23(11):1412 (1989).

Krasner, S. W., C. J. Hwang, and M. J. McGuire. *Water Science & Technology* 15: 127 (1983).

Munch, D. J., and D. P. Hautman. Method 551.1. Determination of ChlorinationDisinfection Byproducts, Chlorinated Solvents, and Halogenated Pesticides/Herbicides in Drinking Water by Liquid-Liquid Extraction and Gas Chromatography with Electron Capture Detection. *Methods for the Determination of Organic Compounds in Drinking Water, Supplement III,* EPA-600/R-95/131. Cincinnati, OH: U.S. Environmental Protection Agency, 1995.

Standard Methods for the Examination of Water and Wastewater, 20th ed.; American Public Health Association: Washington, D.C., 1998.

Table 2. Summary of compounds tested for closed-loop stripping analysis

Compound	CLSA Extraction?
Iodomethanes	
Dichloroiodomethane	YES
Bromochloriodomethane	YES
Dibromoiodomethane	YES
Chlorodiiodomethane	YES
Bromodiiodomethane	YES
Triiodomethane (iodoform)	YES
Haloacetonitriles	
Chloroacetonitrile	NO
Bromoacetonitrile	NO
Dichloroacetonitrile	YES
Bromochloroacetonitrile	YES
Dibromoacetonitrile	YES
Trichloroacetonitrile	YES
Haloketones	
Chloropropanone	NO
1,1-Dichloropropanone	NO
1,3-Dichloropropanone	NO
1,1,1-Trichloropropanone	YES
1,1,3-Trichloropropanone	NO
Misc. Compounds	
Carbon tetrachloride	YES

PURGE-AND-TRAP GAS CHROMATOGRAPHY/MASS SPECTROMETRY METHOD

The method used for the analysis of volatile organic compounds (VOCs) and volatile and semi-volatile disinfection by-products was a purge-and-trap (P&T) gas chromatography (GC)/ mass spectrometry (MS) method based on U. S. Environmental Protection Agency (USEPA) Method 524.2 (Figure 1). The methods development included the addition of several volatile and semi-volatile DBPs and some changes to the GC conditions (i.e., analytical column and column temperature program).

EXPERIMENTAL

Instrumentation

The instrument used was a Varian Saturn 2000 mass spectrometer (Varian Analytical Associates Inc., Walnut Creek, CA) equipped with a 3800 gas chromatograph (GC). A Tekmar LSC2000 concentrator (Tekmar Co., Cincinnati, OH) and a Varian Archon P&T autosampler (Varian) were used for automated sampling.

Sample Preparation

Information about the analytical standards used for this P&T method are outlined in Table 1. Standard mixes were obtained from Ultra Scientific (North Kingstown, RI), which contained the following compounds at a level of 5000 µg/mL each in acetone: dichloro-, bromochloro-, dibromo-, and trichloroacetonitrile, 1,1-dichloro- and 1,1,1-trichloropropanone, and chloropicrin. The trihalomethane mix (Ultra Scientific) contained chloroform, bromodichloromethane, dibromochloromethane, and bromoform at a level of 5000 µg/mL each in methanol. Each of the VOCs was prepared from separate, individual solutions containing chloromethane, bromomethane, dibromomethane, bromochloromethane, carbon tetrachloride, methyl *tertiary* butyl ether, and methyl ethyl ketone, all of which were obtained from Supelco (Bellefonte, PA) at either a 2000 or 5000 µg/mL level. An EPA Method 524.2 Fortification Solution (Supelco) contained the internal standards for this analysis, fluorobenzene (FB), and the surrogates, 4-bromofluorobenzene (BFB) and 1,2-dichlorobenzene-d_4 (1,2-DCP-d_4), at concentrations of 2000 µg/mL each in methanol. The other target DBPs were obtained in the highest purity available from sources listed in Table 1.

Stock Solutions from Neat Compounds

For all of these new, target DBPs that were being investigated in this project, stock solutions were prepared by either of two different methods. First, those DBPs that were prepared from pure, neat compound as follows. An accurately measured portion of 1.0 mL of methanol solvent (Burdick & Jackson, purge and trap grade, Muskegon, MI) was placed into a capped 2.0 mL autosampler vial and weighed. Approximately 2-3 µL of the neat compound was pulled into a cleaned syringe and spiked into the solvent after piercing the septum. The additional weight by difference, between 2-5 mg, was used to calculate the concentration of each compound. The septum caps were changed before storage. Alternatively, those DBPs that were solid were prepared by weighing the standard in the autosampler vial and adding solvent.

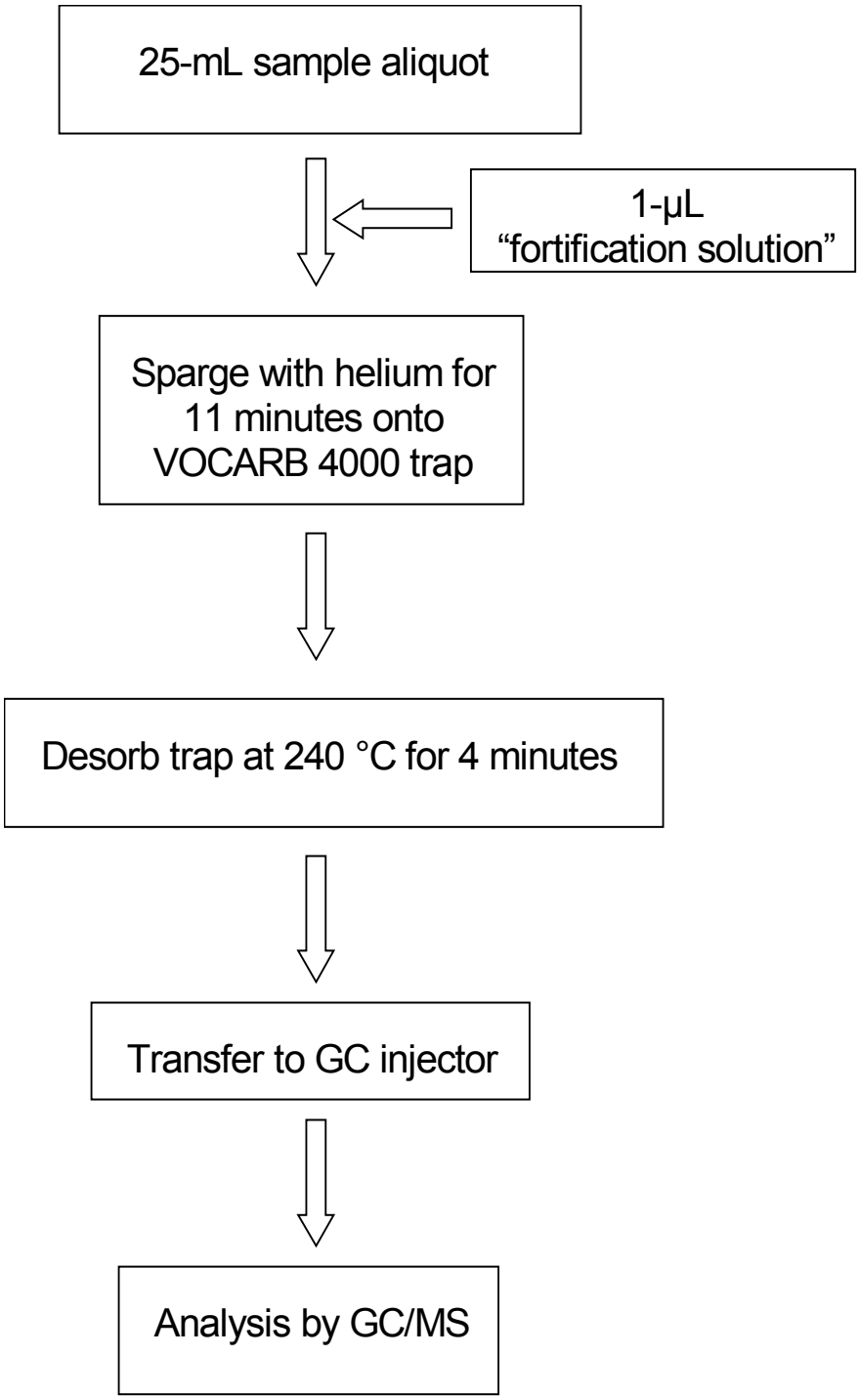

Figure 1. Summary of the Purge and Trap-GC/MS method used for analyzing DBPs in drinking water.

Standard Spiking Solutions

A standard DBP spiking solution was prepared by diluting all of the target compounds to a final volume of 1 mL of methanol (Burdick & Jackson). Table 2 outlines the concentrations and volumes of the standard solutions used to prepare the DBP spiking solution. This solution was used to prepare P&T calibration standards.

Internal Standard and Surrogates

The internal standard and surrogates were prepared as follows. Into a 5-mL volumetric flask was measured 4.5 mL of methanol. A 62.5 µL aliquot of the "fortification solution" was added to the methanol and the volume brought up to 5 mL. This solution was then transferred to the Archon autosampler standard solution reservoir. The Archon autosampler then adds a 1 µL standard addition to the sample water prior to purge-and-trap concentration for a final concentration of 1 µg/L.

Calibration Standards and Check Samples

Calibration standards were prepared at the levels of 0.2, 0.5, 1.0, 2.5, 5.0, 10, 20, and 40 µg/L. An appropriate amount of the DBP spiking solution was added to a 50-mL volumetric flask containing purified water (Ultra Resi-analyzed, J.T. Baker, Phillipsburg, NJ). This solution was then transferred to a 40-mL vial containing 2 drops of 1 M H_2SO_4 to bring the pH down to 3-3.5, then capped with an open-top cap and Teflon-silicon septa. Calibration standards were prepared every time a set of samples was analyzed, approximately every two weeks.

Check standards were analyzed at the beginning and end of each analytical run. These check standards were prepared in the same way as calibration standards, but at the 5 or 10 µg/L level.

Table 1. P&T-GC/MS DBP target analyte sources

Compound Class/DBP	Source	Compound Class/DBP	Source
THM Mix	Ultra Scientific[a]	Halonitromethanes	
Chloroform		Chloronitromethane	Can Syn[e]; Helix
Bromodichloromethane		Bromonitromethane	Aldrich
Dibromochloromethane		Dichloronitromethane	Can Syn; Helix
Bromoform			
		Haloacetonitriles	
551B Mix	Ultra Scientific	Chloroacetonitrile	Aldrich
Dichloroacetonitrile		Bromoacetonitrile	Aldrich
Bromochloroacetonitrile			
Dibromoacetonitrile		VOCs	
1,1-Dichloropropanone		Chloromethane	Supelco[g]
1,1,1-Trichloropropanone		Bromomethane	Supelco
Chloropicrin		Dibromomethane	Supelco
		Bromochloromethane	Supelco
Iodomethanes		Carbon tetrachloride	Supelco
Dichloroiodomethane	AGBAR[b]	MTBE	Supelco
Bromochloroiodomethane	AGBAR	MEK	Supelco
Dibromoiodomethane	AGBAR		
Chlorodiiodomethane	AGBAR	Miscellaneous	
Bromodiiodomethane	AGBAR	Benzyl chloride	Fluka
Haloketones		Internal Standard	
Chloropropanone	Aldrich[f]	Fluorobenzene	Supelco
1,3-Dichloropropanone	Aldrich		
1,1,3-Trichloropropanone	Fluka[h]	Surrogates	
1,1-Dibromopropanone	UNC[c]; Helix[d]	4-Bromofluorobenzene	Supelco
		1,2-Dichlorobenzene-d_4	Supelco

[a]Ultra Scientific (North Kingstown, R.I.)
[b]AGBAR: Aigues of Barcelona (Spain)
[c]UNC: Synthesized by University of North Carolina at Chapel Hill
[d]Helix Biotech (New Westminster, B.C., Canada)
[e]Can Syn: Synthesized by Can Syn Chem Corp. (Toronto, ON, Canada)
[f]Aldrich (St. Louis, Mo.)
[g]Supelco (Bellefonte, Pa.)
[h]Fluka (St. Louis, Mo.)

Table 2. Standard spiking solution preparation

Compound	Abbrev. Name	Conc. (mg/L)	Purity	Adjusted Conc. (mg/L)	Actual Transfer Vol. (uL) 50 mg/L Std	Final Concentration (50 mg/L Std)
THM/551B Mix						
Chloroform	TCM	5000	99+%	5000	10	50
Bromodichloromethane	BDCM	5000	99+%	5000	10	50
Dibromochloromethane	DBCM	5000	99+%	5000	10	50
Bromoform	TBM	5000	99+%	5000	10	50
EPA 551B Mix						
Dichloroacetonitrile	DCAN	5000	99+%	5000	10	50
Bromochloroacetonitrile	BCAN	5000	99+%	5000	10	50
Dibromoacetonitrile	DBAN	5000	99+%	5000	10	50
1,1-Dichloropropanone	1,1-DCP	5000	99+%	5000	10	50
1,1,1-Trichloropropanone	1,1,1-TCP	5000	99+%	5000	10	50
Chloropicrin	TCNM	5000	99+%	5000	10	50
Iodomethane Mix						
Dichloroiodomethane	DCIM	3500	93.3%	3250	17	55.25
Bromochloroiodomethane	BCIM	5200	96.7%	5050	9.9	49.995
Dibromoiodomethane	DBIM	3400	97.2%	3300	15	49.5
Chlorodiiodomethane	CDIM	4200	86.3%	3600	14	50.4
Bromodiiodomethane	BDIM	4800	91.5%	4400	11	48.4
Haloacetonitrile Mix						
Chloroacetonitrile	CAN	3700	99+%	3700	13.5	49.95
Bromoacetonitrile	BAN	5700	99+%	5700	9	51.3
Haloketone Mix						
Chloropropanone	CP	2700	98.1%	2650	19	50.35
1,3-Dichloropropanone	1,3-DCP	4100	99+%	4100	12	49.2
1,1,3-Trichloropropanone	1,1,3-TCP	3500	97.7%	3400	15	51
1,1-Dibromopropanone	1,1-DBP	3300	94.1%	3100	16	49.6
Halonitromethane Mix						
Chloronitromethane	CNM	2700	98.8%	2650	19	50.35
Bromonitromethane	BNM	5200	99+%	5200	10	52
Dichloronitromethane	DCNM	5000	99+%	5000	10	50
Miscellaneous						
Benzyl chloride	BC	3100	99+%	3100	16	49.6
Volatiles Mix						
Chloromethane	ClMe	2000	99+%	2000	25	50
Bromomethane	BrMe	2000	99+%	2000	25	50
Dibromomethane	DBM	2000	99+%	2000	25	50
Bromochloromethane	BCM	2000	99+%	2000	25	50
Carbon Tetrachloride	CCl4	5000	99+%	5000	10	50
MtBE		2000	99+%	2000	25	50
MEK		2000	99+%	2000	25	50

Gas Chromatography

A DB-624 GC column was used (30-m, 0.25-mm ID, 1.4-µm film thickness) (J & W Scientific/Agilent, Folsom, CA). The 1079 injector was set at 220 °C with a split ratio of 30:1. The column temperature program used was developed for a wide range of VOCs: an initial oven temperature of 35 °C, which was held for 4 minutes, followed by an increase at a rate of 4 °C/min to 50 °C, with no time hold, followed by an increase at a rate of 10 °C/min to 175 °C, which was held for 2 min, then a final increase at a rate of 20 °C/min to 200 °C, which was held for 1.5 min. The total temperature run time was 25 min. This temperature program was used until January 2002.

For analyses performed after June 2001, a DB-1 GC column was used (30-m, 0.25-mm ID, 1-µm film thickness) (J & W Scientific/Agilent), and the 1079 injector was set at 220 °C with a split ratio of 20:1. The same column temperature program that was used with the DB-624 column was used with the DB-1 column. A modified temperature program was used beginning in January 2002 to match the work that was developed for the LLE-GC/ECD method: isothermal column temperature at 35 ºC held for 23 min, followed by an increase at a rate of 4 ºC/min to 139 ºC, with no time hold, followed by an increase at a rate of 27.7 ºC/min to a final temperature of 250 ºC, which was held for 5 min. Total run time was 58.0 min.

Mass Spectrometry

Electron ionization (EI) was used on the Saturn GC/mass spectrometer. Table 3 outlines the mass spectrometer parameters used for this method.

Purge-and-Trap (P&T) Analysis

The P&T concentration was carried out using the Varian Archon autosampler, which prepared a 25 mL aliquot of sample for transfer to the Tekmar LSC 2000 concentrator. The 40-mL sample vials were placed in the Archon autosampler, where a 25-mL aliquot was taken. Prior to transfer to the LSC 2000, 1 µL of the "fortification solution" was added. Once the sample was transferred to the LSC 2000 concentrator, it was sparged for 11 min at room temperature with helium, at a flow rate of 15 mL/min, onto a VOCARB 4000 trap (Supelco). The analysis continued with a desorption preheating of the trap to 240 °C and final desorption of the sample for 4 min. At this point the sample was then "injected" onto the Varian GC attached to the Saturn mass spectrometer.

Sample Preservation

Samples were collected in nominal 40-mL vials with Teflon-faced silicon septa and polypropylene open-top screw caps. The sample vials were filled with 1.4 mg of ascorbic acid to quench any residual oxidant present at the time of sampling. A solution of freshly prepared sulfuric acid was used to reduce the pH to within the 3-3.5 range to provide stability of the target analytes and was added prior to capping the sample bottle. This reduction in pH was necessary in order to eliminate the possibility of base-catalyzed hydrolysis that many of the target analytes are susceptible to at higher pH. Samples were stored during transit to the laboratory in ice chests with ice-packs to keep them cold. Upon arrival at the laboratory, the samples were placed in a 10 °C refrigerator for longer-term storage.

Table 3. Saturn ion trap mass spectrometer conditions

Segment 1	filament off, no data acquisition			
Segment 2	start time	1.0 min.		
	end time	50 min.		
	emission current	25 µA		
	scan time	1.00 sec		
	low mass	41 m/z		
	high mass	400 m/z		
	ionization mode	EI AGC [1]		
	ion preparation technique	none		
	EI auto mode:			
		Mass range	ion. storage level	ion. time factor
	scan segment 1	10 to 70	35 m/z	120%
	scan segment 2	71 to 78	35 m/z	70%
	scan segment 3	79 to 150	35 m/z	100%
	scan segment 4	151 to 650	35 m/z	68%
	maximum ionization time	25000 µsec		
	target TIC	30000 counts		
	prescan ionization time	100 µsec		
	background mass	45 m/z		
	RF dump value	650 m/z		

[1] AGC - automatic gain control

RESULTS AND DISCUSSION

Detection Limits

Detection limits were determined in two different ways. The first was strictly by observing the lowest level standard that could be seen and measuring the peak area counts. Based on a signal-to-noise ratio of 5 or greater, a detection limit was initially used. This technique resulted in a wide variety of observed levels for each of the target analytes. The second method used was a statistical evaluation of seven replicates run on two successive days. This method yielded significantly higher detection limits for the target analytes. The method detection limit (MDL) was determined for each analyte as follows:

MDL = t (S)
t = 2.65 (student t value for 13 degrees of freedom and 99 percent confidence level)

S = standard deviation of the 14 replicate analyses

These MDLs were used as minimum reporting levels (MRLs), except where the instrumental detection limit proved to be higher. Often, the MRLs corresponded to the lowest level standard on the calibration curve. Table 4 shows the DL and MDL for each of the P&T target compounds. Where NA is reported for a compound, the opportunity to calculate the MDL was not available, as the compound was added very late in the project for P&T analysis. This table shows that these compounds are amenable to P&T analysis.

Table 4. Detection limits for purge-and-trap DBP analysis

Compound	DL (µg/L)	MDL (µg/L)	Compound	DL (µg/L)	MDL (µg/L)
Chloroform	0.2	0.684	Chloromethane	0.2	0.903
Bromodichloromethane	0.2	0.732	Bromomethane	0.2	1.02
Dibromochloromethane	0.2	0.727	Dibromomethane	0.5	0.775
Bromoform	0.5	0.716	Bromochloromethane	0.5	0.654
			Carbon Tetrachloride	0.2	0.906
Dichloroacetonitrile	0.2	0.945	MtBE	0.2	0.721
Bromochloroacetonitrile	0.5	NA	Methyl ethyl ketone	0.5	0.617
Dibromoacetonitrile	0.5	NA			
1,1-Dichloropropanone	0.5	0.775	Chloropropanone	0.5	1.19
1,1,1-Trichloropropanone	0.5	0.755	1,3-Dichloropropanone	0.5	NA
Chloropicrin	0.5	NA	1,1,3-Trichloropropanone	0.5	NA
			1,1-Dibromopropanone	0.5	NA
Dichloroiodomethane	0.5	0.819			
Bromochloroiodomethane	0.5	0.748	Chloronitromethane	0.5	NA
Dibromoiodomethane	0.5	1.28	Bromonitromethane	0.5	NA
Chlorodiiodomethane	0.5	0.669	Dichloronitromethane	0.5	NA
Bromodiiodomethane	0.5	0.811			
			Chloroacetonitrile	0.2	0.775
Benzyl chloride	0.5	0.624	Bromoacetonitrile	2.5	1.12

DL = detection limit; MDL = method detection limit

Evaluation of Analytical Columns

A DB-624 column was initially installed on the Saturn GC/MS in the early phase of the project. This was due to the fact that the instrument was shared with another group analyzing VOCs for compliance purposes. As the project progressed, it was determined that other arrangements needed to be made in order to accommodate the addition of analyzing solid phase extraction (SPE) samples on the same instrument.

The DB-624 column is a medium polarity column and is the column used by the Metropolitan Water District of Southern California (MWDSC) for EPA Method 524.2 (P&T) for compliance VOC monitoring. An evaluation of this column compared to the DB-1 was necessary in order to determine whether it was suitable for the SPE method. It was determined, and discussed in further detail in the SPE section, that the DB-624 column was unsuitable for the SPE method.

A total ion chromatogram (TIC) comparison between the DB-624 column and a DB-1 column is shown in Figure 2. Because the DB-1 column showed significantly improved resolution of the analytes, it was determined that this column would be optimal for P&T analyses. One of the problems associated with the use of the DB-624 column was the coelution of some target compounds, such as chloropropanone and bromodichloromethane. This was not a problem with the DB-1 column.

Other Changes to P&T Method

Other changes to the P&T method included the use of only a selected list of VOCs combined with the other target DBPs. Initially the P&T method relied on the use of two separate sets of calibration standards and separate calibration curves. By paring down the VOC list to only the target VOCs of interest in this study and combining them with the target DBPs had some major advantages. One advantage was a simpler calibration step in which all of the P&T method compounds could be analyzed in a single P&T run. This eliminated the need to process sample data files twice. Also, the elimination of any coelution interferences between those VOCs that were part of a larger cocktail of analytes and some of the target DBPs. Some of the target DBPs that exhibited coelution problems were chloropropanone, bromodichloromethane, 1,1,1-trichloropropanone, chlorodiiodomethane, and bromochloroiodomethane. These compounds were difficult to separate from VOCs that were contained in the original cocktail of more than 60 VOC compounds. Chloropropanone and bromodichloromethane were resolved simply by changing to the DB-1 column.

Improved Temperature Program

An updated GC column temperature program was used beginning in January 2002. Figure 3 shows a TIC for a 10 µg/L standard analyzed with the updated column temperature program. This improvement allowed for better separation of the analyte peaks. The temperature program used was similar to the one used for the LLE and SPE analyses, except that a lower final temperature of 250 °C was used instead of 301 °C.

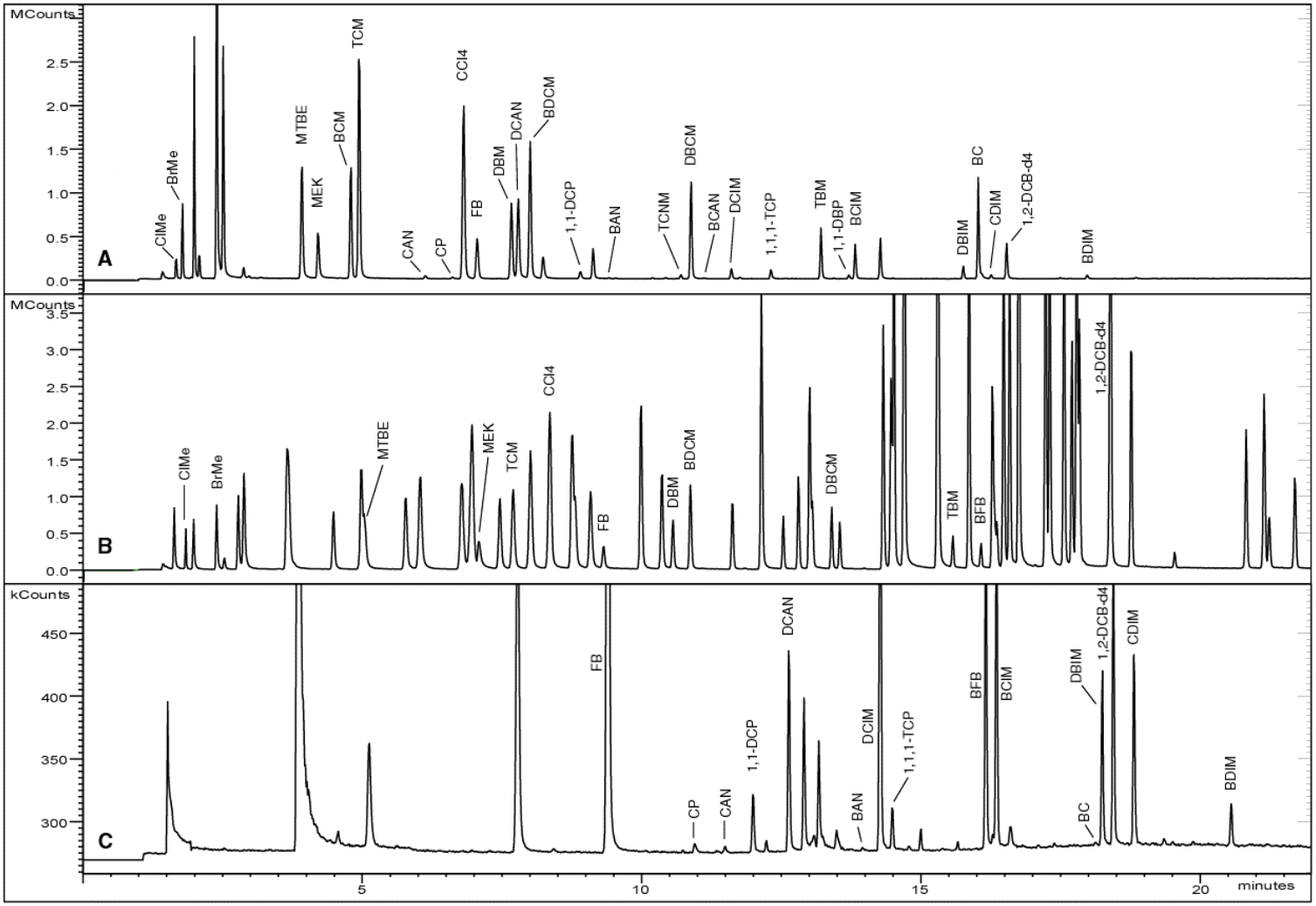

Figure 2. Comparison TIC between DB-624 and DB-1 columns for purge-and-trap analysis.
A) All target DBPs on DB-1 column; B) VOCs on DB-624 column; C) Target DBPs on DB-624 column.

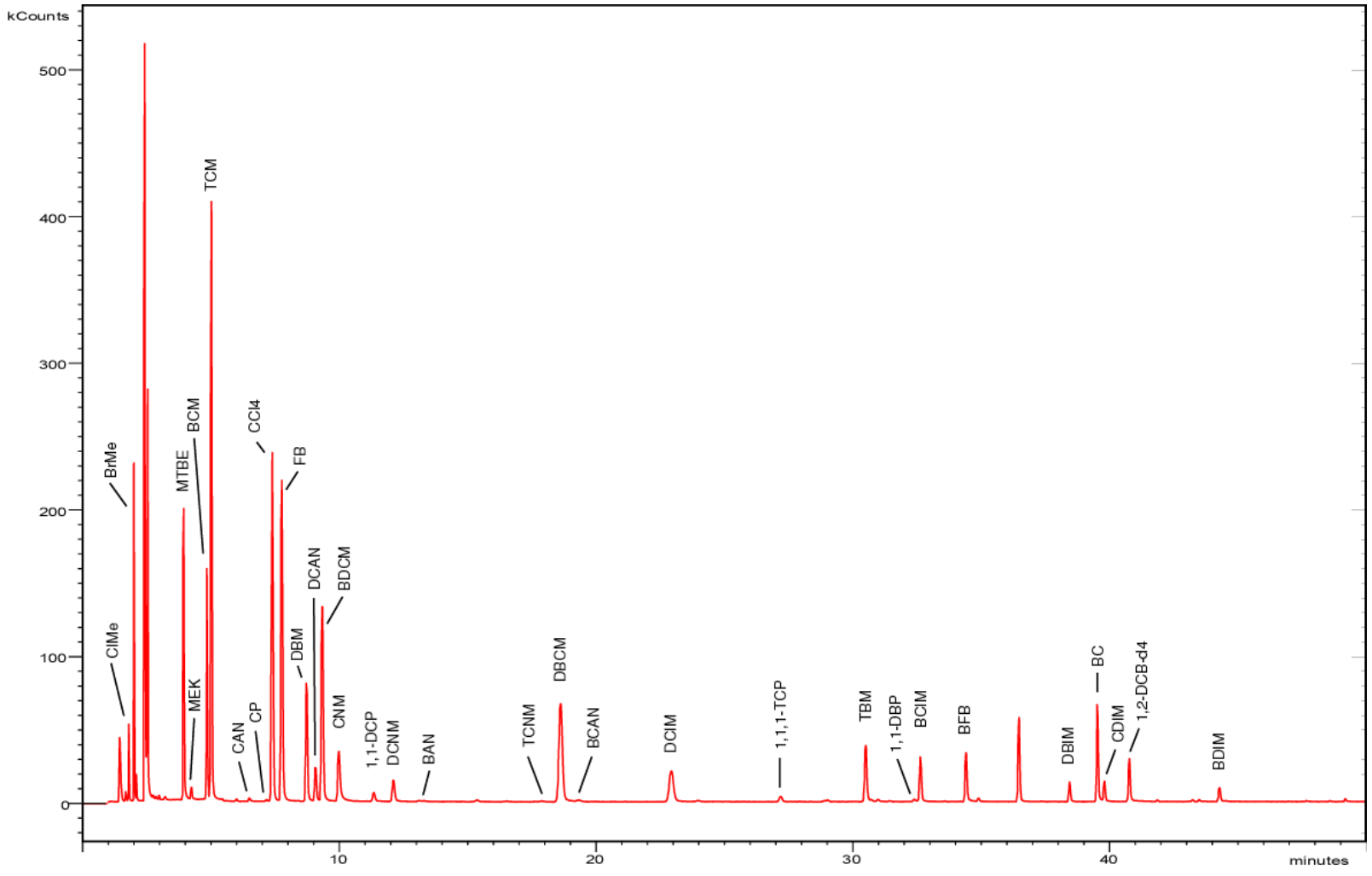

Figure 3. TIC for a 10 µg/L Purge-and-trap DBP/VOC standard on DB-1 column with extended column temperature program.

Holding Study

Sample stability data was used from previous work done using SPE or LLE methods, and was not repeated for the P&T analysis. The P&T analysis used the same sample bottles and preservation scheme as the SPE and LLE methods (ascorbic acid preserved) samples. To summarize these results by compound family:

VOCs -	Stable through Day 21.
THMs -	Stable through Day 21.
Iodo-THMs -	Stable through Day 21.
Haloacetonitriles -	Stable through Day 21
Chloropropanones -	Stable through Day 21.
Halonitromethanes -	Stable through Day 21.
Miscellaneous -	Benzyl chloride showed a slow decay.

Samples were generally analyzed within 2-3 days after receipt at MWDSC. This allowed for time to reanalyze samples if necessary and to allow for the instrument to be used for the SPE analyses later.

Improvements on the Saturn Ion-trap

One of the improvements made for the analysis of the P&T analytes was the use of multiple quantitation ions to increase the sensitivity. In previous analyses, a single ion was used to quantitate analyte peaks. The result of this change was an increase in selectivity for the target analytes.

CONCLUSIONS

EPA Method 524.2 was used as the basis for these analytes, but it was modified in such a way that an expanded list of compounds could be analyzed. The only real changes were the analytical column used and the column temperature program. The P&T concentrator parameters and the internal standard/surrogates remained the same. This P&T method was capable of analyzing for 32 DBPs as part of the Nationwide DBP Occurrence Study. Of those 32 compounds included in this method, 11 were originally analyzed as VOC compounds. The remaining 21 compounds represent additional compounds not normally associated with a P&T type of analysis. This P&T method allowed for confirmation of results obtained from SPE and LLE methods, as well as the solid phase microextraction method developed later.

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METHOD FOR HALOGENATED FURANONES (MX-ANALOGUES)

METHOD SUMMARY

For the Nationwide DBP Occurrence Study, a method was developed for the analysis of the following halogenated furanones: MX, MCA, BMX-1, BMX-2, and their *open* forms (see full names in Glossary; structures in Figure 1). This method evolved from the previous methods of Holmbom et al. (1981), Hemming et al. (1986), and Kronberg et al. (1988, 1991) which required large volumes of water for concentration onto XAD resins and lengthy processing times that endanger the stability of the MX-analogues. Because of their complexity, these methods do not incorporate adequate quality assurance (QA)/quality control (QC) components to validate their resulting data. In order to accurately assess the concentrations of MX-analogues in drinking water, a liquid-liquid extraction (LLE)-gas chromatography (GC)-electron capture detection (ECD) method was developed, which uses smaller sample volumes and shorter processing times to protect compound stability.

For the new method, the chlorine quenching agent, ammonium sulfate [100 μL of 40 mg/mL $(NH_4)_2SO_4$] was added to acid-washed amber glass sample bottles (250 mL) fitted with Teflon-lined screw caps prior to sending the bottles to the water treatment plants for duplicate sample collection. Field blanks filled with DIW were included. Sample bottles were returned to UNC in a cooler with ice packs, shipped by overnight delivery. Immediately upon arrival, or within 5 hours, the samples were removed from the cooler, and analyzed for MX and MCA after they had reached room temperature (the BMX analysis was performed one week following receipt of samples). The calibration samples were prepared on the day of extraction, at 0, 50, and 250 ng/L MX and MCA (or 0, 100, and 500 ng/L BMX-1,2,3) in DIW in 250 mL volumetric flasks. One sample from each plant was collected in a 1 L amber bottle to allow for a matrix spike sample (250 ng/L MX and MCA or 500 ng/L BMX-1,2,3).

Prior to extraction, each 250-mL sample was spiked with MBA as a surrogate standard at 250 ng/L, and acidified to pH 2 with sulfuric acid. Each sample was extracted twice with 50 mL of MtBE in a 500 mL glass separatory funnel. The combined extract was collected in a 125 mL amber bottle (fitted with a Teflon-lined screw cap) containing two approximately 8 g of calcium chloride ($CaCl_2$), and shaken to remove residual water dissolved in the MtBE. The extract was transferred (without $CaCl_2$) to a 250 mL round bottomed flask and reduced to a few mLs by rotary evaporation at 40°C. The reduced extract was transferred to a 20 mL centrifuge tube, with a few mL rinse of MtBE. This extract was further reduced to about 500 μL by nitrogen (N_2) gas. To this reduced MtBE extract was added 2 mL of 14% BF_3/MeOH, and the tube was sealed with a Teflon-lined screw cap. The solution was mixed and heated at 70°C for 4 hours in an oven. After returning to room temperature, the derivatization agent and pH were neutralized by adding 4 mL of 10% $NaHCO_3$, with mixing.

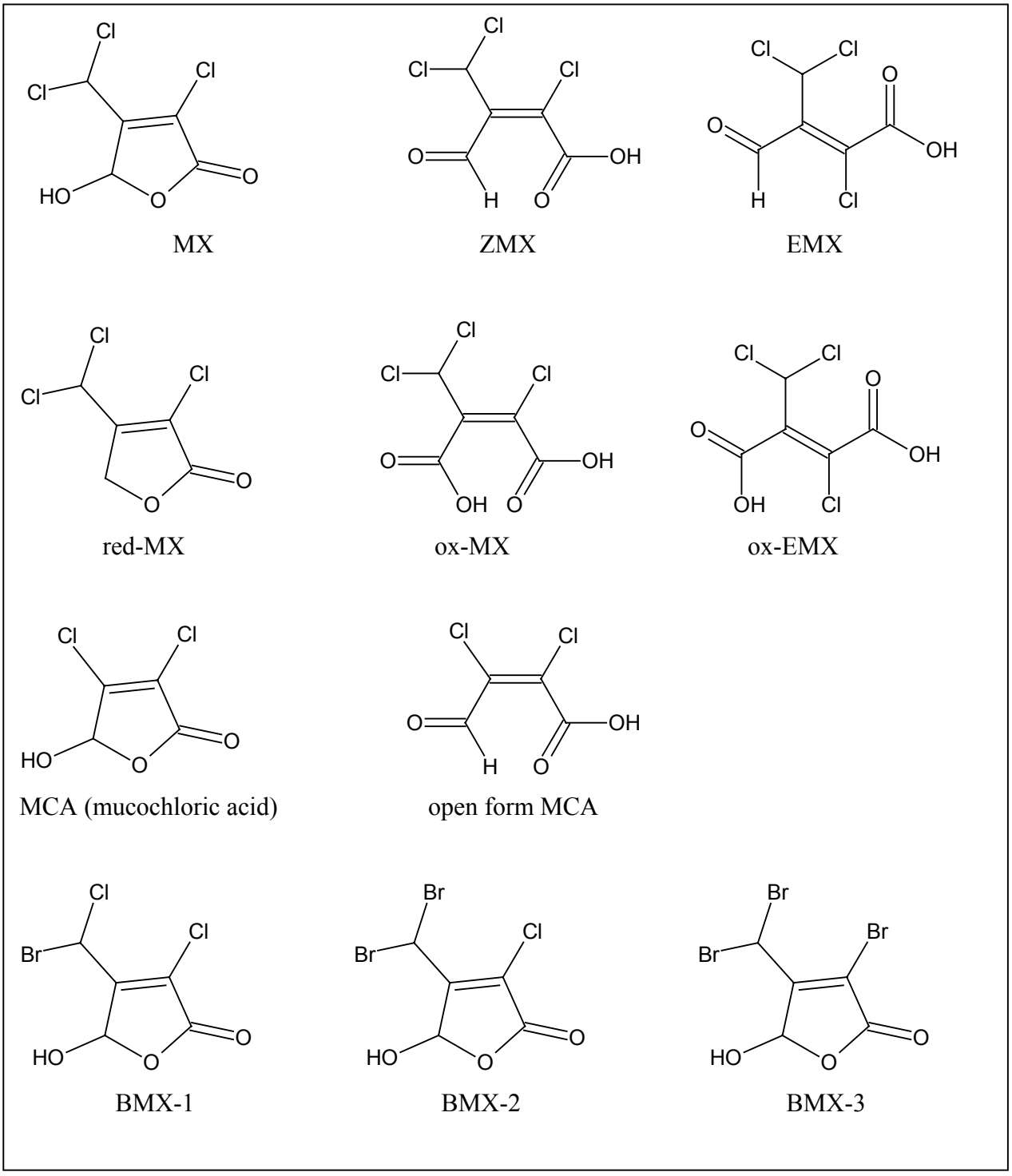

Figure 1. Structures of halogenated furanones (MX-analogues).

The MXR-analogues were back-extracted twice into 1 mL hexane. The combined 2 mL hexane extract was collected in a 10 mL centrifuge tube and reduced to <250 μL by N_2 gas. The internal standard hexachlorobenzene (HCB) was added (5 μL of 500 ng/mL HCB/hexane) to the hexane extract, which was brought to a final volume of 250 μL. The final hexane extract was transferred to an amber crimp-topped vial with a 300 μL glass insert for GC-ECD analysis. The MX and MCA samples were separated by gas chromatography on a HP-5MS column (30-m x 0.25 mm ID x 0.25 μm film thickness) at a temperature program of 105°C for 1 min, 2.5°C/min to 140°C, and 20°C/min to 280°C, with an injection temperature of 200°C and a detector temperature of 300°C. The BMX samples were separated by gas chromatography on a Phenomenex ZB5 column (60-m x 0.25 mm ID x 0.25 μm film thickness) at a temperature program of 100°C for 1 min, 20°C/min to 150°C, 1°C/min to 185°C, and 20°C/min to 280°C, with an injection temperature of 160°C and a detector temperature of 300°C. Calibration curves for each component were constructed using analyte area relative to the internal standard (HCB). Calculated concentrations of analytes were corrected by percent recovery in the matrix spike sample. Relative areas of the analytes to the surrogate standard (MBA) were not reliable for duplicate calibration samples.

Because method development continued during the first year of plant surveys, no halogenated furanone data is presented during the first two seasons. The plant data and discussion is included among the results for each utility elsewhere in this report. The minimum reportable limit for MX-analogues was 40 ng/L. Non-zero concentrations below 40 ng/L are given in parentheses, to indicate relative values extrapolated from the calibration curves.

INTRODUCTION

The detection of the disinfection by-product (DBP) 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX) in chlorinated drinking water in Finland in the early 1980's caused great concern in the scientific and public health communities because MX was found to account for 20-60% of the mutagenicity in chlorinated drinking water. Later research showed that MX was also carcinogenic to rats (at a dose of 400 μg MX per kg body mass per day) (Komulainen et al., 1997). Other compounds similar to MX (referred to as MX-analogues), including ZMX, EMX, red-MX, ox-MX, mucochloric acid (MCA), and brominated forms of MX--BMX-1, BMX-2, BMX-3 (Figure 1) have also been identified in drinking water.

Following the initial identification of MX in Finland (Kronberg and Vartiainen, 1988), MX and MX-analogues were also detected in drinking waters from the United States, the United Kingdom, Australia, Canada, Spain, China and Japan, in levels ranging from 0.1 to 90 ng/L (Andrews et al., 1990; Horth, 1990; Huixian et al., 1995; Meier et al., 1987; Simpson and Hayes, 1993; Simpson and Hayes, 1998; Smeds et al., 1995; Suzuki and Nakanishi, 1990; Wright et al., 2002). MX has been detected primarily in waters treated with chlorine, less so with the use of chlorine dioxide or chloramines, and very minimally in ozonated waters with post-chlorination (Holmbom and Kronberg, 1988).

The structural components responsible for the mutagenicity of MX are the $CHCl_2$ and Cl substituents in a *cis* arrangement on a carbon-carbon double bond (Figure 1). The mutagenity of these substituents is enhanced by incorporation into the 5-hydroxy-2(5H)-furanone *ring* system or an *open* structure that can readily transform to this ring system under the conditions of mutagenic testing (Ishiguro et al., 1987). Therefore, when comparing the relative mutagenicities of the MX-analogues (Figure 1), EMX, ox-EMX and MCA are less mutagenic than the other MX-analogues. The mutagenicity of halogenated furanones is also enhanced by the presence of the C-5 hydroxyl group (Kronberg and Franzen, 1993), making red-MX less mutagenic than MX (LaLonde et al., 1991). Bromine substitution with chlorine substituents can increase the toxicity of the compound, as found for THMs and the BMX-analogues (Bull, 1993; Ramos et al., 2000). The bromine substituents originate from natural bromide ions found in many coastal ground and surface waters.

While mutagenicity in *Salmonella* cannot be used to determine carcinogenicity in humans, MX is still considered a potential human carcinogen. Because MX and other analogues are highly mutagenic and there is very little occurrence data for them (particularly for the brominated-MX analogues), they received a high priority for inclusion in this Nationwide DBP Occurrence Study

ANALYTICAL METHOD DEVELOPMENT

Previous Methods

Method development for the detection of MX in drinking water began in the 1980's, at first catalyzed by Holmbom's identification of MX in kraft chlorination effluent (Holmbom et al., 1981). Soon after, Hemming et al. (1986) and Kronberg et al. (1988) detected MX in chlorinated drinking waters. The methods of Hemming et al. (1986) and Kronberg et al. (1988) became the key methods that were used to detect MX thereafter.

The stability of MX is very sensitive to the pH of an aqueous solution. The *ring* form is predominant at low pH, but as the pH rises, the ring opens to ZMX, which tautomerizes to EMX, and at higher pH levels (above pH 8), degrades to smaller products (Kronberg and Christman, 1989, Figure 2). Hemming et al. (1986) and Kronberg et al. (1988) adjusted the pH to stabilize the *ring* form. The extraction method consisted of acidification of a large volume sample (10 L), concentration on a mixture of XAD resins, elution with ethyl acetate, and solvent reduction to dryness by rotary evaporation and nitrogen gas. Methylation of the hydroxyl group on the MX ring structure was achieved by heating with sulfuric acid in methanol (Figure 3).

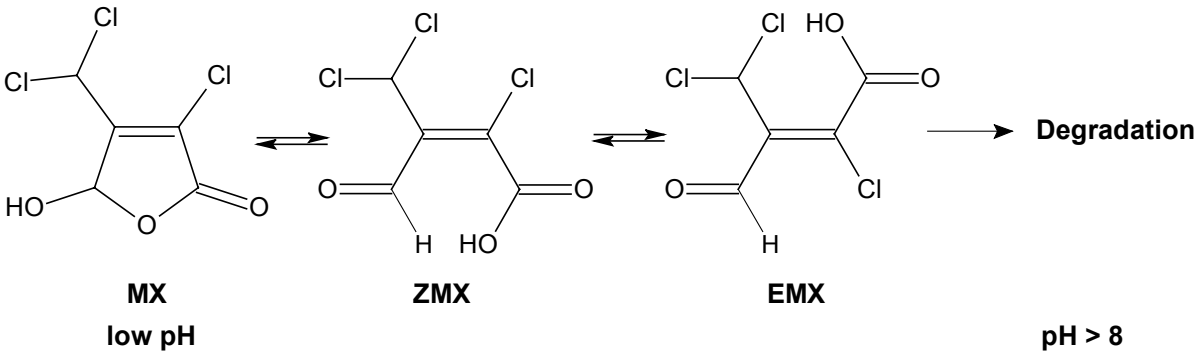

Figure 2. MX degrades as pH increases.

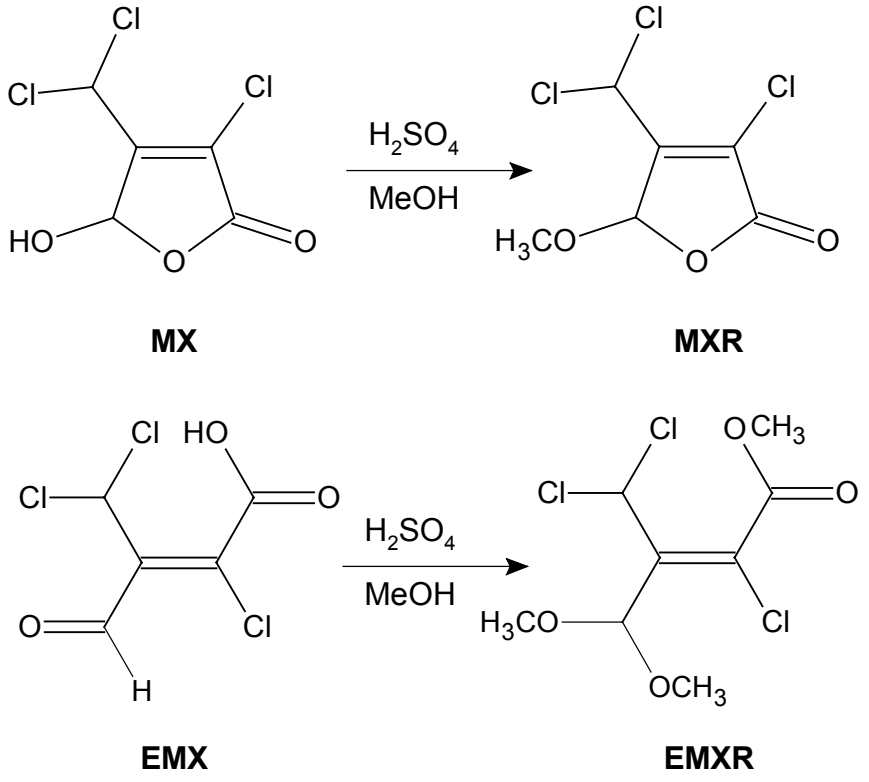

Figure 3. Methylation of MX-analogues with sulfuric acid in methanol.

Methylation converts the alcohol group on the MX ring to a methyl ether group, but the carboxylic acid groups of the *open* forms of MX (ZMX and EMX) are changed to esters, and the aldehyde groups to dimethyl acetal groups (Figure 3). Thus, to simplify naming the methylation products, they are all referred to as "esters," i.e. MX becomes MXR. The esterified MX (MXR) was recovered by neutralization with sodium bicarbonate aqueous solution, and back-extraction into hexane. The reduced hexane extract (100 μL) was analyzed by capillary gas chromatographic (GC) separation and high resolution mass spectrometric detection (HRMS), with a detection limit of 2 ng/L MX. In some cases, researchers used high performance liquid chromatography (HPLC) prior to methylation to remove natural organic carbon contaminants (Kronberg et al., 1985a; Meier et al., 1987). The HPLC separation involved first concentrating XAD extracts of drinking water to dryness by rotary evaporation, followed by soxhlet extraction with diethyl ether (Et_2O), extraction with 2% sodium bicarbonate to remove strong acids, acidification of the aqueous phase to pH 2 with HCl, re-extraction with Et_2O, transfer to 30% methanol/water, separation into 2 mL fractions by a C18 semi-prep column using a 30-100% methanol/water gradient, followed by a 100% hold for 10 min, methylation of the weak acid fractions, and detection of MXR-analogues by GC/MS (Meier et al., 1987). Other researchers applied a silica column clean-up step to the final hexane extract (Suzuki and Nakanishi, 1995), or multiple reaction monitoring during mass spectrometric detection (Simpson and Hayes, 1993) to isolate the MX-analogues from interfering co-contaminants such as natural organic matter (NOM).

Identification of MX-analogues. The structure of MX was first determined by HRMS, UV and IR spectroscopy (Holmbom et al., 1981). Padmapriya et al. (1985) reported the IR, UV, and ^{1}H NMR spectra for MX and MXR, and the ^{13}C NMR spectrum for MX. No identification spectra have been previously published for ZMX. Kronberg et al. (1988) identified EMX by its ^{1}H NMR and mass spectra, and EMXR by its mass spectrum. Kronberg et al. (1991) identified ox-EMX, ox-EMXR, ox-MXR and red-MX by their mass spectra. LaLonde et al. (1990) identified red-MX by its IR, ^{1}H NMR, and ^{13}C NMR spectra, and MCA by its ^{1}H NMR spectrum. Nawrocki et al. (2000) identified MCR by its mass spectrum. Lloveras et al. (2000) identified BMX-1, BMX-2, and BMX-3 by their ^{1}H NMR, ^{13}C NMR and mass spectra. Peters (1991) identified BMXR-1, BMXR-2, and BMXR-3 by their mass spectra.

Derivatization Efficiency. Kronberg et al. (1988) achieve derivatization of MX by addition of 2% sulfuric acid in methanol (H_2SO_4/MeOH, Figure 3), heated at 70°C for 1 hour. While the efficiency of this reaction has not been reported for the derivatization of MX, some researchers have compared the use of H_2SO_4/MeOH to other derivatization agents. Diazomethane (CH_2N_2) does not successfully methylate MX and its analogues (Kronberg et al., 1991). Although H_2SO_4/MeOH can adequately methylate MX, it cannot methylate the diacidic MX-analogues (ox-MX and ox-EMX). A 14% boron trifluoride methanol complex (BF_3/MeOH) solution, heated at 70°C for 12 hours, was successfully applied to ox-MX and ox-EMX (Kanniganti et al., 1992). Meier et al. (1987) claimed that the derivatization yield of EMX is related to the derivatization time (using Amberlite IR 120 sulfonated polystyrene cation exchange resin in methanol, in a sealed tube, at 70°C for 16-18 hours). Huixian et al. (1995) compared the MXR yield from derivatization with

saturated BF_3/MeOH to the method with 2% H_2SO_4/MeOH, and found that saturated BF_3/MeOH was the more efficient derivatization agent regardless of reaction time (1-8 hours at 95°C in water bath). Overall, BF_3/MeOH has shown to be the best derivatization agent, with reaction time significantly affecting the product yield.

Extraction Efficiency. Holmbom et al. (1984) evaluated a number of organic solvents and solid phases to extract MX from aqueous solutions; mutagenicity was measured as an indicator of MX recovery. Ethyl acetate (EtAc) completely extracted the mutagenicity (70-90%), while dichloromethane (50-70%) and pentane (<10%) recovered less of the mutagenicity. Rotary evaporation of EtAc extracts did not degrade the mutagenicity (even after 10 min at 40°C and 1.5 kPa). Adsorption of MX onto XAD-4 resin recovered similar amounts of mutagenicity as EtAc. Although MX can ionize in aqueous solution, anion-exchange solid phase materials are not appropriate for isolating MX from chlorinated aqueous samples. MX behaved as a neutral compound when applied to the anion exchange DEAE-Sepharose column due to the MX ring structure.

Acidification prior to resin adsorption (XAD-2/8 resin adsorption/acetone elution) was essential for adequate recovery of MX in the protonated form (Figure 2) from spiked water samples and to maintain the stability of MX at low pH (Meier et al., 1987). MX was measured in terms of mutagenicity assays. XAD-2/8 recovery of mutagenicity from acidified (pH 2), chlorinated MX-spiked drinking water samples was only 55% effective. Subsequent extraction and HPLC isolation recovered only 18% of the remaining MX, resulting in an overall 10% MX recovery through XAD-2/8 adsorption, Et_2O extraction, HPLC separation, and derivatization procedures. These percent recoveries were not taken into account when reporting MX concentrations, and no apparent method calibration solutions were analyzed to monitor recoveries at different MX concentrations. MX concentrations were determined relative to a derivatized MX standard by high resolution GC/MS analysis. Recoveries of MX from water samples buffered at higher pH levels (pH 8) were 0-1%; the high pH favors MX in the ionized form and does not promote extraction from aqueous solution. Poor extraction recovery of MX from drinking water onto XAD resins was also attributed to complexation with chlorinated humic materials. When evaluated separately, the methyl-methacrylate polymer XAD-8 recovered more MX than the styrene-divinyl benzene copolymer XAD-2 (92 vs. 22 % MX recovery) from a fortified deionized water sample (20 L, 50 ng/L MX) at pH 2; MX recovery was measured by mutagenicity (Schenck et al., 1990). MX recovery was also significantly enhanced by reducing XAD-8 adsorption time; a total sample collection time of 25 hours recovered 92 % MX, whereas 56 hours recovered only 38 % MX (see stability section).

The octanol-water partition coefficient, K_{ow}, is indicative of how much of an analyte is likely to partition out of water into a highly polar organic solvent. MX is fairly hydrophilic with a K_{ow} of 11.9 (mg/L octanol / mg/L water) at pH 2 (Holmbom et al., 1984). The K_{ow} value should be lower in neutral pH surface and drinking waters, and therefore MX is less susceptible to bioaccumulation in these waters. The K_{ow} of MX *open* (ZMX or EMX) in the neutral acid form was computed to be 1.16, using CLOGP, ver3.5 (Biobyte Inc., Pomona, CA) (DeMarini et al., 2000). The variability of these K_{ow} values is likely due to the difference between the *ring* and *open* forms of MX, and the pH considered.

Kronberg et al. (1991) used mucobromic acid (MBA, Figure 4) as an internal standard to assess recovery of MX-analogues through the derivatization process, by spiking MBA into the EtAc extract prior to derivatization (derivatization standard). However, MBA was determined to be an inappropriate surrogate standard (by spiking MBA into the original water sample prior to acidification and XAD adsorption) for the XAD/HPLC MX method (Simpson and Hayes, 1993), because MBA is more susceptible than MX to intermolecular hydrogen bonding with natural organics. The levels of MX recorded were corrected for recovery losses, based on separate MX method recovery experiments (average 10% recovery, consistent with Meier et al. 1987). Higher levels of total organic carbon (TOC) in drinking water have been associated with lower recovery of MX (Meier et al. 1987). The high K_{ow} (11.9 mg/mg) for MX, may indicate the likelihood that MX would strongly associate with NOM as a highly polar solvent, and not be easily extracted by XAD. The major loss of MX was seen in the HPLC fractionation steps (average 60% recovery in this step, Simpson and Hayes, 1993), but these steps are only necessary in high TOC waters. Multiple reaction monitoring (MRM) by mass spectrometry was investigated as an alternative method to HPLC for removal background natural organic interferences, and it showed some promise (Simpson and Hayes, 1993). MRM eliminates interference from co-extracting compounds by monitoring compound-specific metastable transitions between selected parent and daughter ions of the target analyte.

MBA *ring* **MBA *open***

Figure 4. Mucobromic acid (MBA) isomers.

Stability of MX-Analogues. MX hydrolysis, isomerization, and decomposition processes in aqueous solution are strongly dependent on pH (Holmbom et al., 1989). MX is stable at pH 2 but starts to degrade at pH 4 and above. Beyond pH 6.5, the water solubility of MX increases rapidly, due to ring opening and dissociation (tautomerization), as determined by extraction of aqueous MX solutions with ethyl acetate at different pH values (Holmbom et al., 1984). The degradation of MX at pH 5-7 correlates with the formation of EMX (Simpson and Hayes, 1993). However, EMX also degrades over time at neutral or alkaline pH (Holmbom and Kronberg, 1988). When acidified to pH 2, EMX completely converts to MX. The BMX-analogues also show tautomerization, degrading over time (48 hours) from the *ring* forms to the *open* forms and finally to degradation products, as measured in a pH 7.4 phosphate-buffered aqueous solution by HPLC/UV (Ramos et al., 2000), similar to MX in Figure 2.

Meier et al. (1987) measured the mutagenic activity of MX spiked distilled water samples at 4°C. It was constant at pH 2, 4, and 8 over 14 days, but declined to 30% at pH 6 after 14 days. At 23°C, the order of stability was pH 2 > pH 4 > pH 8 > pH 6, where pH 2 was constant. The loss of activity in pH 4-8 followed first-order decay kinetics. ZMX occurred in MX solutions buffered at pH 6, but less at pH 8 (stored for 7 days at 23°C). The pK_a value of MX was determined to be 5.3 by NMR spectroscopy (Streicher, 1987). However, the pK_a of MX *open* (ZMX or EMX) was computed to be 1.85, using the SPARC method (DeMarini et al., 2000). The variability of these two pK_a values is likely due to the difference between the *ring* and *open* forms of MX.

Meier et al (1987) determined the half-lives of MX in distilled water at 23°C to be 12.9 days at pH 4, 4.6 days at pH 8, and 2.3 days at pH 6, by measuring loss in mutagenicity. When MX was spiked into tap water samples buffered at pH 6 and 8, stored at 23°C, the same losses in mutagenicity were seen as those in distilled water. This work was confirmed by measuring MX concentration at pH 2-9 in MX spiked Milli-Q water by HPLC/UV analysis (Simpson and Hayes, 1993). Simpson and Hayes (1993) recovered 95% of the original MX in pH 2 Milli-Q water stored at 20°C after 14 days. At the same temperature, the half-life of MX at pH 8 (11.3 days) was much longer than that for pH 6 (5.4 days). However, at 23°C, the half-life of MX at pH 8 was 4.6 days. This agrees with rates of hydrolysis at pH 7.0 measured by Croué and Reckhow (1989) at 20ºC, $k = 0.9 \pm 0.5 \times 10^{-6}$ s^{-1} (~0.07 $days^{-1}$) and $t_{1/2} \sim 8.9$ days.

MX has been shown to degrade in the presence of increasing concentrations of chlorine (10-100 mg/L Cl_2), buffered at pH 8 (Schenck et al., 1990; Simpson and Hayes, 1993). The second order rate constant for MX degradation by chlorine was estimated to be 32.3 L mol^{-1} min^{-1}, based on the reaction rate over the first 10 min and initial concentrations of 20 mg/L MX and 40-120 mg/L Cl_2 (Schenck et al., 1990). MX degradation was also observed at lower residual chlorine concentrations (0.5-3 mg/L Cl_2) that might be practical levels found in drinking water treatment plant effluents. Chlorine and MX reacted at about a 5:1 molar ratio, and the reaction was complete within 1 day (Schenck et al., 1990). MX can be converted to EMX, ox-MX and ox-EMX in the presence of chlorine (Simpson and Hayes, 1993). However, in the presence of chloramine (10-100 mg/L NH_2Cl), MX converts to only EMX, due to the fact that chloramine is not as strong of an oxidizing agent as chlorine. EMX, ox-MX and ox-EMX were qualitatively identified as disinfection by-products, but their levels were not quantified in these studies.

Due to the MX degradation by chlorine, some researchers tried to quench the residual chlorine prior to MX analysis. Simpson and Hayes (1993) identified *L*-ascorbic acid (Figure 5, note similar furanone structure to MX) as the best quenching agent for MX, because nucleophiles in other quenching agents (e.g., sodium thiosulfate or sodium sulfite) destroy MX by removing chlorine atoms (Croué and Reckhow, 1989). The rates of decomposition of MX significantly increase in the presence of sulfite (100 μM) at 20ºC, $k = 22 \pm 3 \times 10^{-6}$ s^{-1} and $t_{1/2} \sim 8.7$ hours (Croué and Reckhow, 1989). Suzuki and Nakanishi (1990) suggest that quenching residual chlorine is unnecessary; after acidification, their samples were purged with nitrogen gas and the residual chlorine was reduced to 0.2 mg/L;

no difference in MX concentration was observed between purged and non-purged samples. However, considering the MX degradation by chlorine observed by Schenck et al. (1990), quenching of residual chlorine is necessary for a 0.3 mg/L chlorine residual and above.

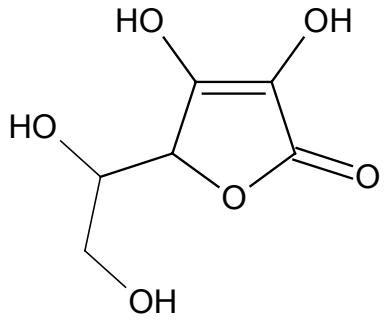

Figure 5. Structure of ascorbic acid (Vitamin C).

Summary of Current Methods for Analysis of MX-Analogues in Drinking Water

MX, ZMX, EMX, and MCA. The method of Kronberg et al. (1991) for extraction of MX, ZMX, EMX, and MCA from aqueous solutions involves first acidifying the solution to pH 2, passing the solution through a mixture of XAD-4 and XAD-8 resins (1:1), and eluting the adsorbed compounds with ethyl acetate (EtAc). However, liquid-liquid extraction has met with some success. By extracting 250 mL of a solution with successive 40, 20, and 20 mL volumes of diethyl ether, 77% of MX was recovered (Kanniganti et al., 1992). MBA was added to the EtAc extract as the derivatization standard. The EtAc extract was blown down to dryness, derivatized with 250 µL of 2% H_2SO_4/MeOH at 70ºC for 1 hour, neutralized with 2% $NaHCO_3$/deionized water (DIW), and extracted twice with 250 µL of hexane. The hexane extract was then concentrated down to 100 µL and decafluorobiphenyl was added as an internal standard. The extract was analyzed by gas chromatography on a DB-1 column (30m), with a temperature program of 110ºC for 3 min, 6ºC/min to 165ºC, and the resolved compounds detected by HRMS, single ion monitoring mode (Kronberg et al., 1991). The extract can also be separated on a DB-5 column (30-m x 0.25 mm ID x 0.25 µm film thickness), using the temperature program 50ºC for 1 min, 2.5ºC/min to 150ºC, 5ºC/min to 300ºC (Kanniganti et al., 1992).

red-MX. The method of Kronberg et al. (1991) for extraction of red-MX from aqueous solutions involves first acidifying the solution to pH 2, passing the solution through a mixture of XAD-4 and XAD-8 resins (1:1), and eluting the adsorbed compounds with ethyl acetate. Since the EtAc extract did not require derivatization, 2,3-dibromo-2(5H)-furanone (red-MBA) was added as an internal standard, and the extract was reduced to 100 µL with nitrogen gas. The EtAc extract was separated by gas chromatography on a DB-1 column (30 m), with a temperature program of 110ºC for 3 min, 6ºC/min to 165ºC. Red-MX is detected by HRMS based on retention time and most abundant ions: m/z 165 and 167 for $(M\text{-}Cl)^+$, 171 and 173 for $(M\text{-}CHO)^+$.

ox-MX and ox-EMX. The method of Kronberg et al. (1991) for extraction of ox-MX and ox-EMX from aqueous solution involves first acidifying the solution to pH 2, passing the solution through a mixture of XAD-4 and XAD-8 resins (1:1), and eluting the

adsorbed compounds with ethyl acetate. MBA was added to the EtAc extract as the derivatization standard. The EtAc extract was blown down to dryness, derivatized with 250 μL of 12% BF_3/MeOH at 100ºC for 12 hours, neutralized with 2% $NaHCO_3$/DIW, and extracted twice with 250 μL of hexane. The hexane extract was then concentrated down to 100 μL and decafluorobiphenyl added as an internal standard. The extract was analyzed by gas chromatography on a DB-5 column (60 m), with a temperature program of 160ºC for 3 min, 6ºC/min to 190ºC. Ox-EMX elutes immediately prior to ox-MX using GC/MS (HP5890 GC/VG 70-250 SEQ mass spectrometer, resolving power 1000). The LLE method using diethyl ether has also been applied successfully to these compounds (Kanniganti et al., 1992).

BMX-Analogues. The method for analysis of BMX-1, BMX-2, and BMX-3 is very similar to that of MX (Suzuki and Nakanishi, 1995). The BMX-analogues were measured in Japanese drinking waters by acidifying 10 L samples to pH 2, passing them through 50 mL XAD-8 resins, eluting with 150 mL EtAc, and concentrating down to 5 mL by rotary evaporation at 40°C. Three mL of this extract was spiked with 100 ng MBA as the derivatization standard, and evaporated to dryness with nitrogen (N_2) gas. The residue was methylated with 250 μL of 2% H_2SO_4/MeOH for 1 hour at 70°C, neutralized by 500 μL of 2% $NaHCO_3$/DIW, and extracted twice with 500 μL hexane. The hexane extract was then passed through a 500 mg Sep-Pak silica column, eluted with 1 mL hexane and 5 mL ethyl acetate:hexane (1:7), and only the last 4 mL fraction was collected and concentrated to 100 μL with N_2. Separation was achieved using a 30-m x 0.25 mm ID DB-5MS GC column, injection temperature 160°C, temperature program 50°C for 2 min, 50-120°C at 40°C/min, 120°C for 2 min, 120-135°C at 2°C/min, 135-180°C at 6°C/min, 180°C for 5 min. The components were detected by HRMS using a VG Autospec-Ultima mass spectrometer. Spike recoveries ranged from 71 to 122%.

The BMX compounds are susceptible to thermal degradation in the injection port of a GC. An injection temperature of 160°C produced a larger BMX-3 signal (HRMS) than 200°C, in a calibration range of 0-1000 pg/μL. Calibration solutions were made from standards of the esterified BMX compounds. Detection limits were also dependent on compound stability in the GC injection port. The detection limit for MX was 0.1 ng/L, whereas BMX-3 was 0.5 ng/L, using a 60,000:1 concentration factor. BMX-1 and BMX-2 showed intermediate thermal degradation (and intermediate detection limits) to MX and BMX-3.

Opportunities for Improvement of Existing Methods. A unified method needs to be developed for the analysis of all MX-analogues in drinking water in a single extract, which accounts for sample preservation and recovery of MX-analogues through each processing step. Routine analysis by GC-ECD instead of high resolution GC/MS would make the method more amenable for environmental and water treatment laboratories in the United States. Evaluation of quenching agents for residual chlorine and biocides to prevent microbial regrowth would improve sample preservation and prevent degradation of MX-analogues. Evaluating percent recoveries from each processing step based on detection of individual halogenated furanones, rather than by mutagenicity, would also prove more

valuable in the development of an analytical method for the detection of MX-analogues in drinking water.

New Method Development

Identification and Quantification of Standards. Development of a method for the analysis of MX-analogues (Figure 1) in drinking water began by first identifying and quantifying the compounds in synthesized and commercially available standards. The only commercially available MX-analogues were MX, mucochloric acid (MCA), and mucobromic acid (MBA, surrogate standard), from Sigma-Aldrich (St. Louis, MO). The other components were provided in small mg quantities from the labs of individual researchers. Leif Kronberg (Åbo Akademi, Finland) synthesized EMX (75% purity) and ox-EMX (Kronberg et al., 1991). Ramiah Sangaiah (UNC) synthesized MX, red-MX, and ox-MX (Kronberg et al., 1991; Padmapriya et al., 1985). Angel Messeguer (CSIC, Spain) synthesized BMX-1, BMX-2, and BMX-3 (Lloveras et al., 2000). Starting with MX (Sigma-Aldrich), the identities and purities of the compounds were confirmed by ^{1}H and ^{13}C nuclear magnetic resonance, electron ionization and chemical ionization mass spectrometry.

Qualitative and Quantitative NMR. Milligram quantities of MX-analogues (Figure 1 + MBA) were dissolved in deuterated methanol (Aldrich, 99.8 atom %D), and transferred to 5 mm NMR tubes to a height of 60 mm (~1 mL). All spectra were obtained on an Inova 500 MHz NMR instrument. 1,4-Dioxane (Aldrich, 99.8%) was chosen as the internal standard due to its volatility, and ease of removal from the MX analogues after NMR analysis. 1,4-Dioxane interferes with only one chemical shift in MXR. Carbon-13 NMR spectra were obtained for four MX analogues in decoupling mode.

Purity Assay Calculations. Thirty µL of 1,4-Dioxane (density: 1.0337 g/mL) was spiked into 1 mL of deuterated methanol, for a concentration of 30.1 mg/mL in the primary stock solution. Five µL of the primary stock solution was spiked into each NMR sample, which is equivalent to 150.5 µg 1,4-dioxane per sample. The quantitative ^{1}H NMR spectrum of BMX-3 revealed a dioxane peak at δ 3.65 ppm with a peak area equivalent to 8 H's. The peak area of dioxane was then set to 8.00, so that all other areas would be calculated relative to dioxane. The Ring H of BMX-3 at δ 6.35 ppm is equivalent to 1 H with a peak area of 7.03. The weight of BMX-3 in the NMR tube was calculated by Equation 1.

$$W_{unk} = W_{std} \times \frac{N_{std}}{N_{unk}} \times \frac{M_{unk}}{M_{std}} \times \frac{A_{unk}}{A_{std}}$$ (Equation 1, Willard et al., 1988) where

A = peak area
N = number of protons
M = molecular weight
W = weight present.

For BMX-3,

$$W_{BMX\text{-}3} = 150.5\,\mu g \times \frac{8\,H}{1\,H} \times \frac{350.79\,g/mol}{88.11\,g/mol} \times \frac{7.03}{8} = 4.21\ mg\ BMX\text{-}3.$$

The solution in the NMR tube was then transferred to a tared 4 mL amber vial and dried under gentle flow of nitrogen gas. When the deuterated methanol evaporated to dryness, the vial was placed in a vacuum manifold to ensure removal of the solvent. The vial was then weighed on a microscale and the weight of the NMR sample by difference was 5.5 mg. Therefore, BMX-3 is 76% pure as measured by proton NMR. The remaining NMR samples were assessed for purity in the same manner (Table 1). The ox-MX and red-MX standards were prepared without addition of the internal standard dioxane. However, they could still be quantified relative to residual MX remaining in the standard from the synthesis reaction. Ox-MX was found to be 17% pure relative to MX, and red-MX was 88% pure relative to MX, by ^{1}H NMR.

Table 1. Purity of Standards by Quantitative ^{1}H NMR

Compound	Calculated Weight (mg)	Original Weight (mg)	Percent Purity
MX (Sigma)	3.46	5.2	66%
MX ester	1.58	2.64	60%
BMX-1	0.76	4.0	19%
BMX-2	1.06	4.0	27%
BMX-3	4.21	5.5	76%
MCA	4.98	6.0	83%
MBA	6.65	10.4	63%
Ox-MX			17%
Red-MX			88%

The brominated MX-analogues (BMX-1, BMX-2, BMX-3) were synthesized overseas and arrived as one neat 10 mg mixture of BMX-1 and BMX-2, as well as one neat 5 mg BMX-3. Therefore, BMX-1 and BMX-2 had to be separated by high performance liquid chromatographic (HPLC) fractionation (Lloveras et al., 2000). The 10-mg mixture of BMX-1 and BMX-2 was dissolved in 1.5 mL of deuterated methanol (CD_3OD) and the ^{1}H NMR spectrum was obtained by an Inova 500 MHz instrument. The NMR sample was transferred from the NMR tube to a 4 mL amber vial with two successive washes with regular methanol (Burdick & Jackson THM-free methanol). The methanol was evaporated under gentle flow of nitrogen gas. The residue was then diluted to 100 μL and transferred to an HPLC vial with a 350 μL insert. Twenty-five μL aliquots of the BMX mixture were injected onto the Waters HPLC system. The course of the separation was monitored at λ=254 on a photodiode-array detector, using 25:75 acetonitrile (ACN): 0.05 M buffer HCOOH:Et_3N pH 3.2 as the eluent system, at a flow rate of 2.5 mL/min (Beckman Ultrasphere ODS 5 μm x 10 mm x 25 cm). The compounds eluted in the order of, first, an unknown, second, BMX-1, and third, BMX-2. The latter two peak eluates were collected with an automated fraction collector.

Each 35-mL fraction was separately extracted in a 125 mL separatory funnel with two 50 mL aliquots of Ethyl Acetate (Mallinckrodt AR). The aqueous layer was removed

(and stored in the refrigerator in case re-extraction was needed). The organic layer was extracted with 40 mL of brine (DIW saturated with NaCl, Mallinckrodt AR), and the aqueous layer was removed and disposed. The organic layer was dried over a funnel filled with a glass wool plug and ample sodium sulfate (Na_2SO_4, EM Science, Granular), and collected in a round bottom flask. The ~100 mL organic layer was dried down to 1 mL with a rotary evaporator. The remaining 1 mL was loaded onto a preparatory thin-layer-chromatography (TLC) silica plate with a Pasteur pipette and developed for 1 hour with a mobile phase of 1:1 ethyl acetate and hexane (Mallinckrodt AR) in a glass development chamber. BMX-1 gave an R_F value of 0.51, and the R_F of BMX-2 was 0.24.

Compound Identification Confirmation by Direct Probe Mass Spectrometry. The electron ionization mass spectra of MX and red-MX were acquired and confirmed by literature spectra (Kronberg et al., 1991; LaLonde et al., 1990; Padmapriya et al., 1985). The mass spectrum of ox-MX was not previously published, so it is included below (Figure 6). It was found to contain significant contamination from MX (Figure 6, Table 2).

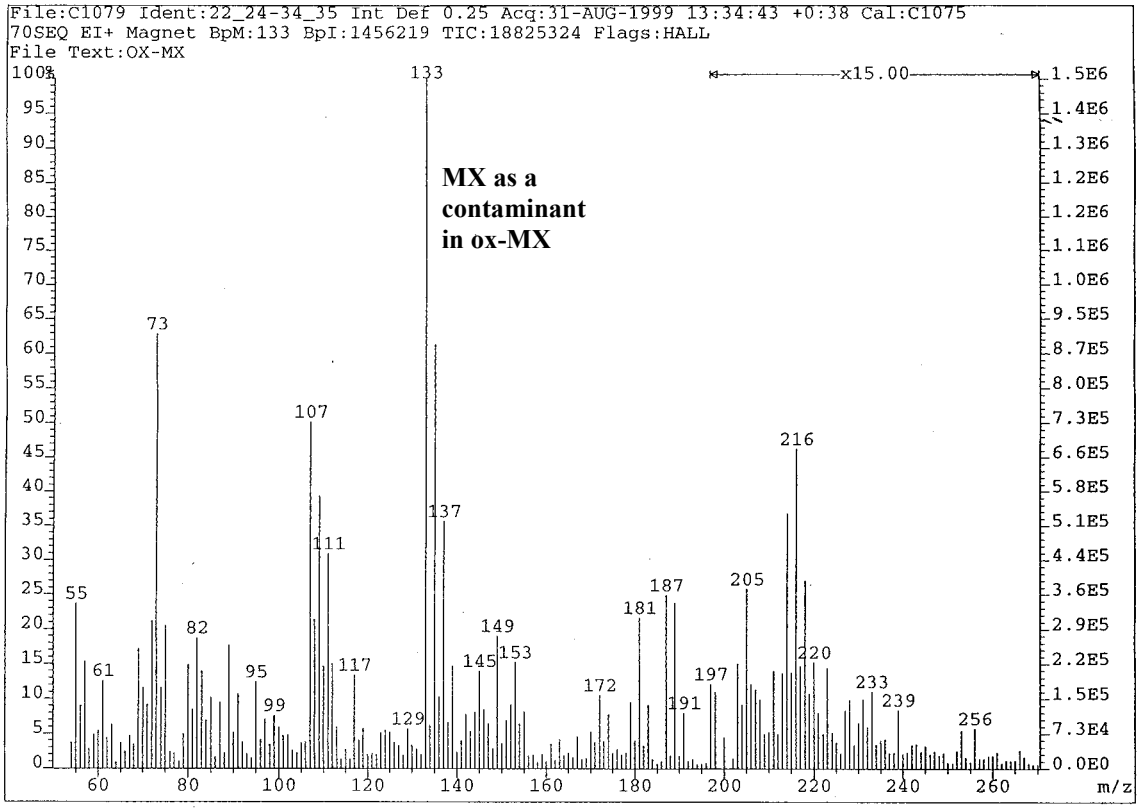

Figure 6. Background-subtracted direct insertion probe EI mass spectrum of synthesized ox-MX (1.81 mg/mL, molecular ion = 232, 17% pure by proton NMR).

Table 2. Ox-MX fragmentation

m/z	Fragment ion
187	$(M\text{-}CO_2H)^+$
133	MX contaminant
107	$C_3HCl_2^+$
73	$C_3H_2Cl^+$

Derivatization of MX-Analogues for GC-ECD and GC/MS Detection. Gas chromatography with electron capture (GC-ECD) and mass spectrometric (GC/MS) detection were chosen as the ideal separation and detection methods for the analysis of MX-analogues because these types of instrumentation are widely used by environmental and water utility laboratories across the United States. However, the majority of the MX-analogues contain one or more hydroxyl groups that can react with unprotected silanol groups on the solid phases of gas chromatographic open tubular columns. Therefore, a methylating agent was chosen to protect the hydroxyl groups of the MX-analogues and allow separation of the MX-analogues on a GC column. The boron-trifluoride methanol complex (BF_3/MeOH, Sigma) was chosen in order to effectively methylate all of the MX-analogues; this is the only methylating agent suitable for ox-MX (Kronberg et al., 1991).

The limiting concentration of BF_3/MeOH was unclear from previous work (Kanniganti et al., 1992), and was evaluated by adding increasing volumes of 14% BF_3/MeOH to a 1 mL solution of MX in methanol (25 μg/L MX/MeOH) (THM-free methanol, Burdick & Jackson). By varying the amount of BF_3/MeOH added, the concentration changed from 7% BF_3/MeOH with a 1 mL addition, to 9% with 2 mL, and 10.5% with 3 mL. Each mixture was sealed with a Teflon-lined, open-top screw cap and heated in a heating block at 70°C (just above the boiling point of methanol, 67°C, to encourage reflux) for 16 hours (Ball, 1998, personal communication). To halt the derivatization reaction after 16 hours, a saturated solution of sodium bicarbonate in deionized water (10% $NaHCO_3$) was added until the pH approached neutral (pH 7). The methylated MX in the neutral solution was then back-extracted with 1 mL of hexane (Ultra-Resi grade 95%, J.T. Baker). The neutral pH of the aqueous fraction ensured that any underivatized MX would remain ionized and dissolved in water, and would not be extracted by hexane. The saturated salt solution (10% $NaHCO_3$), used to neutralize the BF_3/MeOH, has been shown to improve extraction recovery of the esters into hexane (Metcalfe et al., 1966).

When analyzed by GC-ECD on a DB-1701 (30-m x 0.25 mm ID x 0.25 μm film thickness) fused-silica column, the 9% BF_3/MeOH solution gave the largest area response for MXR. Thereafter, a volume ratio of 2:1 BF_3/MeOH to MX/MeOH was utilized for the derivatization step. The final hexane extract was separated on a DB-1701 column with a temperature program of 50°C for 1 min, and 2.5°C/min to 250°C, revealing a retention time of 46.7 min for MXR.

Additional MX-analogues were derivatized with BF_3/MeOH, as outlined above, and analyzed by gas chromatography-ion trap mass spectrometry using both electron ionization (EI) (example in Figure 7, Table 3, ox-MXR) and chemical ionization (CI) modes. The total ion chromatogram and mass spectra obtained for the esterified mucochloric acid revealed two products, MCR *ring* form and MCR *open* form (the methylated 2,3-dichloro-4-oxobutenedioic acid) (Kanniganti et al., 1992; Nawrocki et al., 2000). The two peaks eluted at 12.2 and 20.5 min, on the DB-5 column, with a temperature program of 60°C for 1 min, 2.5°C/min to 250°C, and 250°C for 5 min; injection temperature of 150°C.

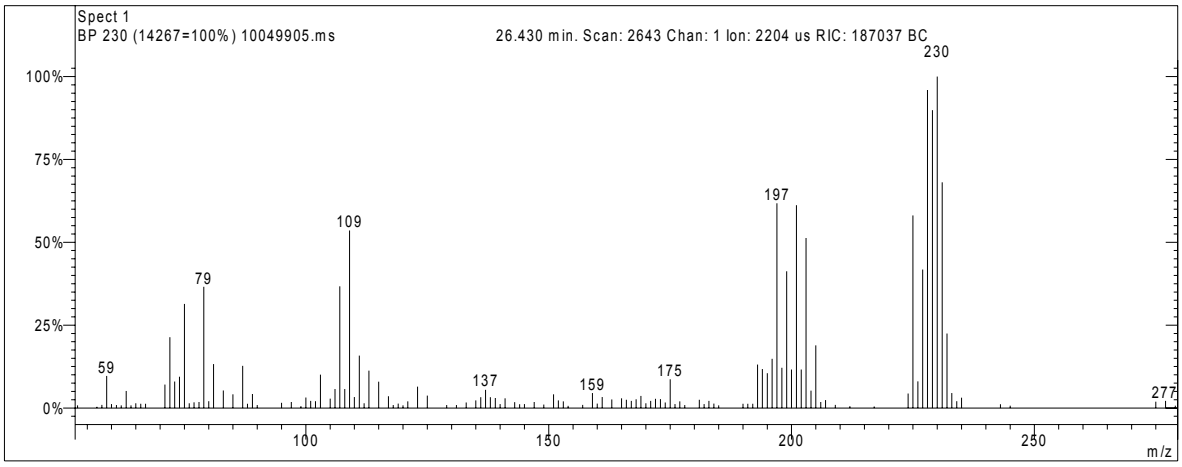

Figure 7. Background-subtracted EI mass spectrum for methylated ox-MX (molecular ion = 260, R_t=26.43 min); agrees with mass spectrum of methylated ox-MX found by Kronberg et al. (1991).

Table 3. Ox-MXR fragmentation

m/z	Fragment ion
229	$(M\text{-}OCH_3)^+$
228	$(M\text{-}CH_3OH)^+$
225	$(M\text{-}Cl)^+$
201	$(M\text{-}CO_2CH_3)^+$
197	$(M\text{-}Cl\text{-}C_2H_4)^+$
109	$C_2H_2O_3Cl^+$
107	$C_3HCl_2^+$
79	CO_2Cl^+

The esterified mucobromic acid also contained two peaks (MBR *ring* and MBR *open* forms) (Backlund et al., 1988; Kronberg et al., 1988; Nawrocki et al., 2000), eluting at 19.17 and 25.73 min. This was also the case for the esterified brominated MX-analogues (BMXR-1 at 25.98 min, BEMXR-1 at 30.70 min, BMXR-2 at 30.14 min, BEMXR-2 at 34.45 min, BMXR-3 at 34.26 min, BEMXR-3 at 37.59 min). The BMX compounds synthesized by Angel Messenguer were not pure. Each one contained three components: an unknown peak, the *ring* form (BMXR) and the *open* form (BEMXR). Identities of these esters were confirmed by spectra in the Ph.D. thesis of Peters (1991).

By GC/MS peak area, red-MX was 66% pure relative to MXR, eluting at 19.08 min, and ox-MXR was 28% pure relative to MXR (Figure 8, Table 4), eluting at 26.43 min. The detector response for red-MX following derivatization was considerably lower due to losses during back-extraction into hexane. Red-MX does not require methylation because it lacks

the hydroxyl group present on the MX ring. The identity of ox-MXR was confirmed by GC/MS (Kanniganti et al., 1992; Kronberg et al., 1991). The mass spectrum of ox-EMXR could not be obtained due to the small amount of available material and detection limit constraints on the Saturn II mass spectrometer. The percent purities of the MXR-analogues are given in Table 5, based on GC/MS peak area.

In order to isolate and quantify EMX, the method required further manipulation. MX was shown previously to isomerize to EMX above pH 4 (Holmbom et al., 1984). Therefore, a pH 6 phosphate-buffered aqueous solution containing MX was monitored over time for production of EMX. Aliquots (1 mL) of this solution were taken at time increments from 10 min to 24 hours, and extracted with methyl *tertiary*-butyl ether (MtBE, OmniSolv grade, EM Science, 1 mL). These MtBE extracts were derivatized with BF_3/MeOH, and extracted with hexane, as outlined above. The hexane extracts were analyzed by GC-ECD and GC/Ion Trap MS on a DB-5 (30-m x 0.25 mm ID x 0.25 μm film thickness, J&W Scientific/Agilent, Folsom, CA) column using a temperature program of 60°C for 1 min, 2.5°C/min to 150°C, and held at 150°C, to encompass the eluting compounds' retention times. Each of the hexane extracts contained three distinct peaks: MXR at 22.85 min, ZMXR at 28.17 min, and EMXR at 29.34 min, as identified by GC/MS (Kronberg et al., 1988). The ratio of MXR to ZMXR to EMXR was 34:15:1, and did not change over the time tested (10 min to 24 hours), as measured by GC-ECD. Therefore, the MX→EMX reaction was not observed at pH 6, unless, of course, the reaction completes in less than 10 min. In subsequent investigations, quantification of EMX was determined against a 2% presence in the MX standard (Table 5). Similarly, quantification of ZMX was determined against a 31% presence in the MX standard.

Derivatization Reaction Time

The optimum derivatization time for MX in the 1-8 hour range was 4 hours with a 65% yield. Aliquots (1 mL) of MX solution (10 μg/mL MX/MeOH) were derivatized with 2 mL of 14%BF_3/MeOH at 70°C for 1, 2, 3, 4, 5, 6, 7, and 8 hours. These results enabled the derivatization time of MX to be reduced from 16 to 4 hours. Then the derivatization time was evaluated for a mixture of other MX-analogues, for 1-8 hours (Onstad and Weinberg, 2001). The mixture contained 250 ng of each MX-analogue dissolved in methanol. Most of the compounds (MX, MCA, MBA, BMX-1, BMX-2, and BMX-3) approached a threshold derivatization efficiency after 3 hours (see Figure 9), with the exception of ox-MX, which will not completely derivatize even after 19 hours. Previous researchers used a derivatization time of 10-16 hours at 70-100ºC in combination with a boron trifluoride methanol complex (Ball, 1998, personal communication; Kanniganti et al., 1992; Kronberg et al., 1991). A derivatization time of 4 hours was chosen for the compounds overall.

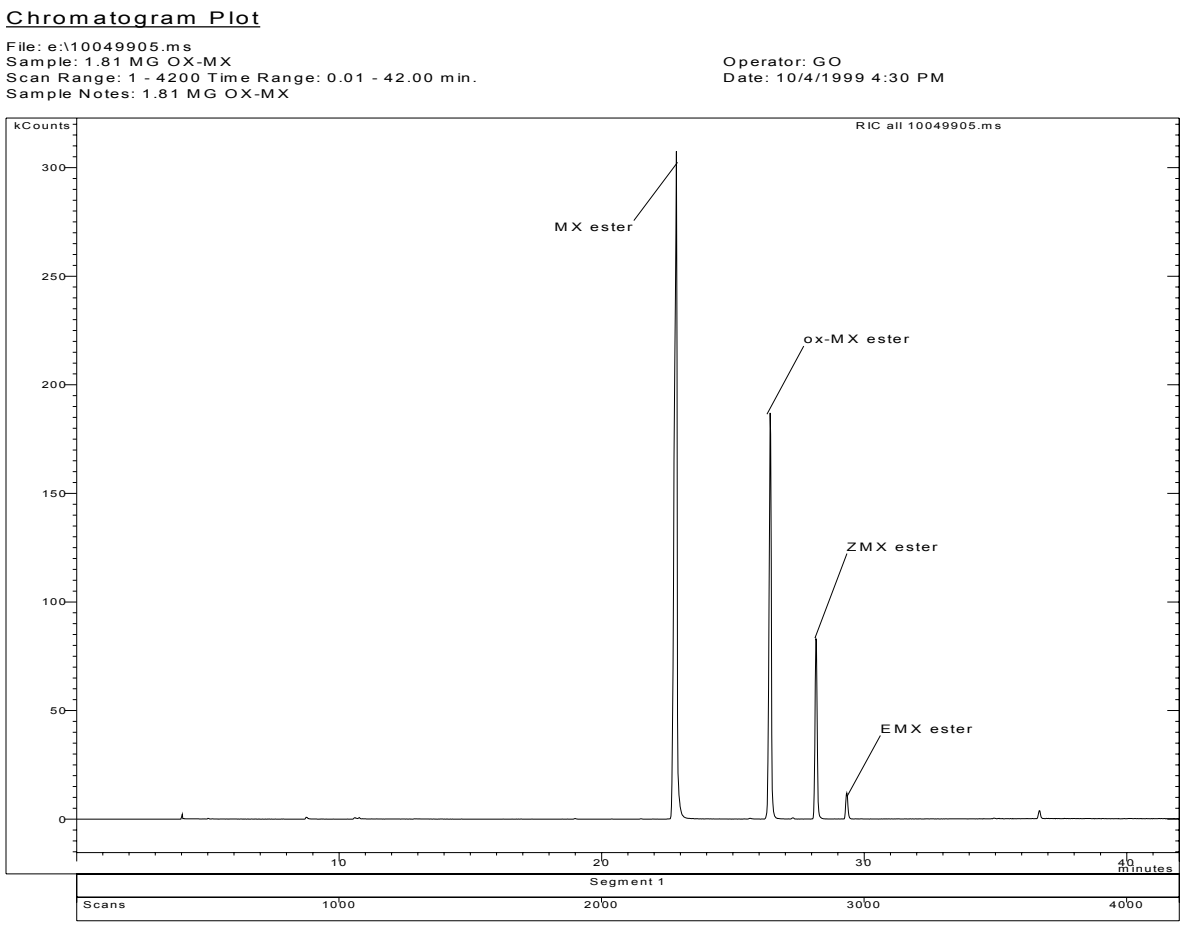

Figure 8. Total ion chromatogram for methylated ox-MX (1.81 mg/mL), with the MX, ZMX and EMX esters in the mixture.

Table 4. Percent Purity of ox-MXR standard

Compound	% TIC	% Area
MXR	52%	58%
Ox-MXR	32%	28%
ZMXR	14%	12%
EMXR	2%	2%

Table 5. Purity of Ester Standards by GC/Ion Trap MS

Compound	Percent purity with respect to components (by area)
MXR	67% MXR, 31% ZMXR, 2% EMXR
Ox-MXR	28% MXR, 58% ox-MXR, 12% ZMXR, 2% EMXR
Red-MX	66% red-MX, 29% MXR, 8% ZMXR
BMXR-1	31% UNK BMX-1, 9% BMXR-1A, 35% BMXR-1B, 25% BEMXR-1
BMXR-2	61% UNK BMX-2, 23% BMXR-2, 16% BEMXR-2
BMXR-3	41% UNK BMX-3, 41% BMXR-3, 18% BEMXR-3
MCR	18% MCR *ring,* 82% MCR *open*
MBR	27% MBR *ring,* 73% MBR *open*

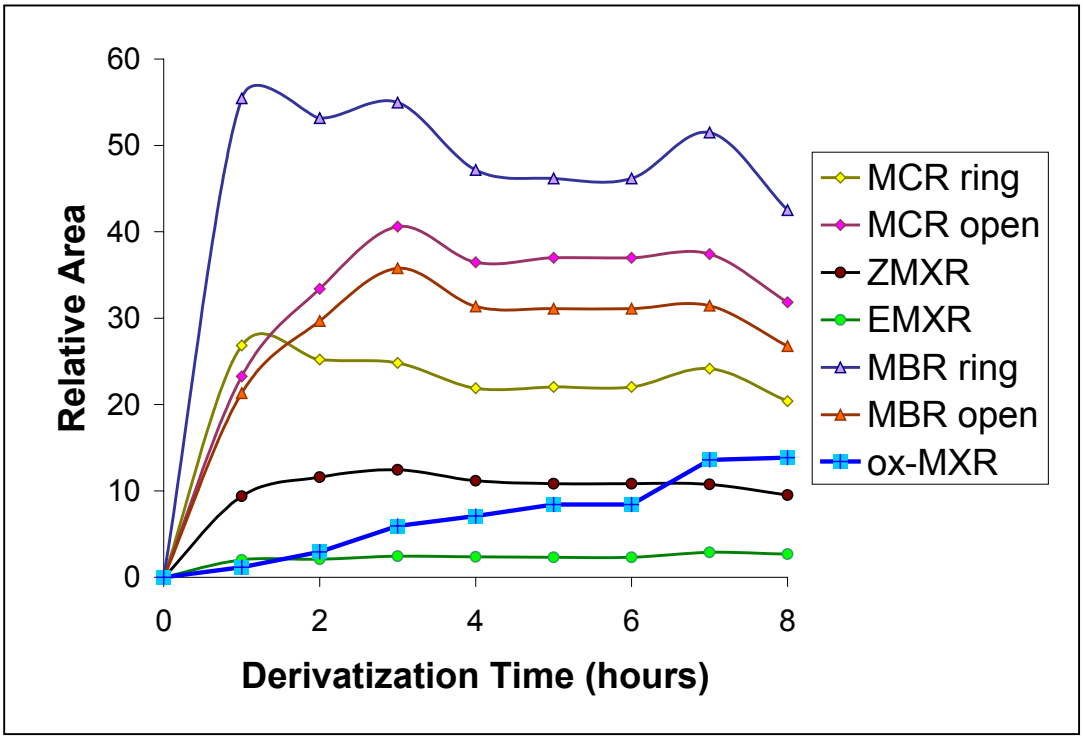

Figure 9. Derivatization of MX-analogues with boron trifluoride/methanol.

Back-Extraction of the MXR-analogues into Hexane

The final step in the analysis was evaluated to determine the recovery of the esterified forms of the MX-analogues during back-extraction from bicarbonate solution to hexane (Onstad and Weinberg, 2001). Synthesized MXR-analogues were dissolved in methanol and spiked into an aqueous sodium bicarbonate solution. Results were attainable for only four of the MX-analogues (Table 6) (red-MX was not extractable by hexane). The equation used to calculate the partition coefficients (K_d) for MXR-analogues between sodium bicarbonate solution and hexane follows (Equation 2):

$$K_d = C_s / C_a \qquad \text{(Eqn.2)}$$

where K_d = partition coefficient at equilibrium
C_s = concentration of MXR-analogue in hexane (ng/mL)
C_a = concentration of MXR-analogue in sodium bicarbonate solution (ng/mL)

MXR and MCR *open* exhibited the best recoveries by hexane extraction, although only 60% on average (E in Equation 3 and Table 6). Hexane only recovered 7% of the original ox-MXR. Red-MX, when included in this mixture, cannot be recovered at all by hexane. Therefore, other extraction processes are being investigated for red-MX that do not require derivatization prior to GC-ECD analysis. One possibility could be to analyze the MtBE extract directly by GC-ECD, after addition of the internal standard (Kronberg et al., 1991). The fraction of the MXR-analogue extracted (E) was calculated using the following equation:

$$E = C_s V_s / \left(C_s V_s + C_a V_a\right) \qquad \text{(Eqn. 3)}$$

where E = the fraction of MXR-analogue extracted
V_s = volume of hexane (mL)
V_a = volume of sodium bicarbonate solution (mL)

The "n for 75%" indicates the number of extractions (n) needed to recover 75% of each MXR-analogue. This value is calculated using the following equation (Equation 4), setting E equal to 0.75:

$$n = \frac{\log(1-E)}{\log\left[1/\left(1+K_d V\right)\right]} \qquad \text{(Eqn. 4)}$$

where $V = V_s / V_a$

By adding another hexane extraction and combining the two hexane extracts, MXR and MCR *open* can be more efficiently recovered from the bicarbonate solution. Two hexane extractions are consistent with previous methods for the esterified MX-analogues (Hemming et al., 1986; Kronberg et al., 1991). Recovery of the brominated MXR-analogues is still under investigation.

Table 6. Partitioning of MXR-analogues into Hexane

Compounds	MXR	MCR *open*	ox-MXR	red-MX
Kd	4.75	8.58	0.29	0.00
E (Recovery)	54%	68%	7%	0%
n for 75%	1.77	1.21	19.95	NA

NA: not applicable

Instrument Detection Limits and Gas Chromatographic Separation

A mixture of esterified MX-analogues was separated on a DB-5 column (60-m, 0.25 mm ID, 0.25 µm film thickness) (Figure 10) with a mild temperature gradient (2.5ºC/min) from 105 to 195ºC, followed by a high temperature gradient (20ºC/min) up to 250ºC (Onstad et al., 2000). A shorter column length (30 m) of the same phase did not allow separation between red-MX and the *open* form of mucochloric acid ester (MCR *open*). Coelution was observed between MX and an unknown component in the standard of BMX-2 (BMX-2 UNK). However, this coelution does not preclude detection of MX, because MX can be quantified by the ZMX peak (#14, Table 7), although, with greater variability. Two peaks are present for BMX-1 *ring*, which could be due to the presence of diastereomers, as the ion trap mass spectra appear identical, and the chromatographic retention times are close. Twelve components in the gas chromatogram are listed in Table 7, in addition to red-MX, the three BMX unknowns and the internal and surrogate standards. Use of an HP 6890 GC fitted with a micro electron capture detector (µ-ECD) enabled instrument detection limits of 1 pg/µL for MXR, MCR, ox-MXR, and red-MX; 16 pg/µL for BMXR-1 and BMXR-3; and 25 pg/µL for BMXR-2, in the final hexane extract.

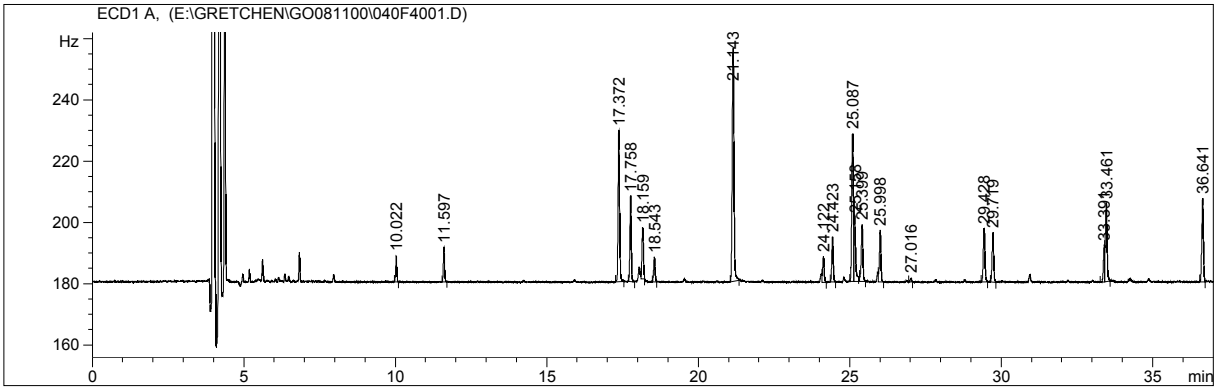

Figure 10. GC-ECD chromatogram of 7 MX-analogues and isomers at 20 pg/µL.

Table 7. Peak identification in GC-ECD trace

Elution Order	Retention Time	Compound
1	10.022	3-Bromochlorobenzene (internal standard, IS)
2	11.597	Mucochloric ester (ring) (MCR *ring*)
3	17.372	unknown component of BMX-1 standard (BMX-1 UNK)
4	17.758	Mucochloric ester (open) (MCR *open*)
5	18.159	Red-MX
6	18.543	Mucobromic ester (ring) (surrogate standard, MBR *ring*)
7	21.143	unknown component of BMX-2 standard (BMX-2 UNK)
8	21.143	MX ester (ring) (MXR)
9	24.122	Ox-MX ester (ox-MXR)
10	24.423	Mucobromic ester (open) (surrogate standard, MBR *open*)
11	25.087	unknown component of BMX-3 standard (BMX-3 UNK)
12	25.158	BMX-1 ester (*ring*) (BMXR-1A)
13	25.399	BMX-1 ester (*ring*) (BMXR-1B)
14	25.998	ZMX ester (ZMXR), an *open* form of MXR
15	27.016	EMX ester (EMXR), an *open* form of MXR
16	29.428	BMX-2 ester (*ring*) (BMXR-2)
17	29.719	BMX-1 ester (*open*) (BEMXR-1)
18	33.391	BMX-2 ester (*open*) (BEMXR-2)
19	33.461	BMX-3 ester (*ring*) (BMXR-3)
20	36.641	BMX-3 ester (*open*) (BEMXR-3)

MX recoveries by other organic solvents, ethyl acetate (EtAc, EM Science, OmniSolv grade) and hexane (Burdick & Jackson, for THM analysis), were compared to MtBE using the 10:2 aqueous solution (100 ng/mL MX/DIW) to organic solvent extraction ratio, and a single extraction. Ethyl acetate (94% recovery) recovered similar amounts of MX as MtBE (83%), while hexane (7%) was relatively unsuccessful at recovering MX from the aqueous solution. The high recoveries of MX (83% MX with MtBE vs. 58% in previous experiment) can be explained by the doubling of the derivatization solvent ratio to LLE extraction solvent (2 mL of 14%BF_3/MeOH to 500 μL of LLE solvent). Thereafter, the LLE extraction solvent was reduced to 500 μL with nitrogen (N_2) gas prior to addition of the derivatization agent. MtBE was chosen as the better extracting solvent over EtAc, because MtBE can be obtained from manufacturers at a higher level of purity; the GC-ECD trace of EtAc contained several contaminant peaks in the vicinity of the MXR elution time.

Liquid-liquid extraction was applied to other MX-analogues, and MtBE was evaluated for recovery of MCA, red-MX, MBA, MX and ox-MX from an aqueous solution (1 ng/mL each in DIW), using the 20:4 extraction ratio, and triplicate extractions. MtBE recovers 40-90% of the MX-analogues (Table 8). This translates to a detection limit of 4-9

pg/µL on column, or 200-450 ng/L in a 20 mL drinking water sample. Red-MX and ox-MX apparently were not recoverable with LLE. ZMX and EMX did not give reproducible area counts for quantitation. Although the LLE recoveries were good for MCR, MBR and MXR, there still existed the need for recovery of the other MX-analogues and preconcentration to achieve lower ng/L levels in drinking water.

Table 8. Percent recoveries of MX-analogues at 1 ng/mL by LLE

Compounds	Percent Recoveries
MCR ring	40%
MCR *open*	57%
red-MX	1%
MBR ring	93%
MXR	81%
ox-MXR	0%
MBR *open*	87%

The MtBE extraction efficiency of MX-analogues from water was next evaluated by comparing recoveries after the addition of salt (granular sodium sulfate, EMScience) or acid [sulfuric acid (Aldrich) to pH 2] (Onstad and Weinberg, 2001). Each extraction was of a 20-mL deionized water sample spiked to 5 µg/L with the MX-analogues. Two standard mixes were evaluated separately, to prevent co-elution on the gas chromatogram, the first one containing MX, ox-MX, and BMX-3, and the second one containing MCA, BMX-1, and BMX-2. Percent recoveries were calculated relative to the GC responses of derivatized standard mixes (Table 9). The MX-analogues were recovered poorly in the control (28 ± 25%), with only three compounds yielding higher that 50% (MXR, ZMXR, and BEMXR-1). The salting-out approach did not improve extraction efficiency relative to the control (16 ± 17%). Acidification to pH 2 improved the MtBE extraction efficiency of both the *open* and *ring* forms of the MX-analogues (74 ± 10%).

Table 9. Extraction Efficiencies of MX-analogues

Compound	Control	Salt	Acid
MCR *ring*	16%	0%	82%
MCR *open*	11%	3%	66%
MXR	61%	39%	89%
ox-MXR	0%	13%	64%
ZMXR	55%	40%	73%
EMXR	12%	14%	61%
BEMXR-1	41%	31%	73%
BEMXR-2	53%	0%	75%
BEMXR-3	0%	0%	87%
average	28%	16%	74%
std dev	25%	17%	10%

Solid Phase Extraction

Solid phase extraction (SPE) was evaluated as a viable method of preconcentration and an alternative method of extraction to LLE. The octadecyl silane phase (C18, J.T. Baker) was compared to LLE for recovery of MX from a 10-mL aqueous solution (100 ng/mL MX/DIW). The aqueous sample was passed through the SPE column at a rate of < 5 mL/min, and the solid phase was dried using a vacuum. When eluted with 1 mL of methanol, the C18 column recovered only 25% of MX in aqueous solution.

Using the method development guidelines of Thurman and Mills (1998), different solid phases and elution solvents were first compared for the recovery of a mixture of MX-analogues made in the elution solvent, and then solid phase recoveries of a mixture of MX-analogues spiked into deionized water and tap water were determined. Two different solid phases, C18 (3 mL, 500 mg) and polyamide (DPA-6S, Supelco, 6 mL, 500 mg) were each washed with MX-analogue solutions (40 ng/mL chlorinated MX-analogues) made separately in methanol (Mallinckrodt AR Anhydrous), MtBE, and 14% BF_3/MeOH (Table 10), to determine whether there would be irreversible retention of the target analytes on the solid phase if these were the eluting solvents used in the SPE process. The BF_3/MeOH esterifying reagent dissolved the polyamide (DPA-6S) phase, and created large air pockets, therefore preventing further investigation of this combination. The BMX compounds were not included in this preliminary study. The percent recovery results follow.

Table 10. Percent recovery of MX-analogues from C_{18} and DPA-6S

Compounds:	**MCR *ring***	**MCR *open***	**red-MX**	**MBR *ring***	**MXR**	**ox-MXR**	**MBR *open***	**ZMXR**	**EMXR**
C18 spk/MtBE	29%	49%	0%	3%	38%	2%	51%	62%	62%
C18 spk/MeOH	108%	59%	0%	102%	122%	70%	56%	78%	148%
C18 spk/BF3/MeOH	60%	53%	0%	63%	65%	0%	29%	48%	70%
DPA-6S spk/MtBE	1%	2%	0%	1%	0%	0%	0%	0%	0%
DPA-6S spk/MeOH	0%	0%	0%	0%	8%	6%	0%	0%	0%

Methanol was chosen to be the best solvent for partitioning of the MX-analogues off of the C18 solid phase extraction columns (average 83% recovery). BF_3/MeOH was the second best solvent for C18 SPE (average 42% recovery), without heating, during derivatization. MtBE gave similar recoveries when applied to C18 SPE (average 36 % recovery). The MX-analogues preferentially partitioned onto the DPA-6S SPE columns using methanol or MtBE (average 0% recovery). The spiked BF_3/MeOH degraded the DPA-6S phase on contact; this is due to the derivatization reaction which releases

hydrofluoric and boric acids. All calculated average percent recoveries were weighted down by zero recovery of red-MX in all cases. For compounds containing *open* and *ring* forms (MXR, MBR, MCR), the *open* forms were retained by the solid phase much more than the *ring* forms (~100% recovery of *ring* vs. ~60% *open* on the C18 spk/MeOH). This was also evident for ox-MXR. The C18 reverse phase proved to be the most effective phase for recovery of the MX-analogues (80-100% recovery of select MX-analogues).

Solutions of MX-analogues in deionized water (100 mL volumes at 1 µg/L MX-analogues/DIW) were then evaluated for recovery by C18 solid phase, with less favorable results. Table 11 highlights the recoveries of MX-analogues under neutral (no alteration, NA) and low pH (acidified to pH 2, AD) conditions, as well as percent breakthrough of columns in tandem (breakthrough from top column was detected in bottom column). Recovery of the MX-analogue standard solution (MeOH Mtx) from C18 solid phase was reevaluated, this time including the BMX compounds. In this case the average percent recovery of the MeOH Mtx was 50-60%, much lower than the above 80-100%. Solid phase extraction was very poor with respect to the BMX compounds, both in the NA and AD solutions. Acidification helped to increase the recovery of the MX-analogues. However, the pH decrease also caused the *ring* forms of the MX-analogues to predominate.

Table 11. Recovery of the MX-analogues from spiked DIW by SPE

Sample label:	**Mtx-NA top**	**Mtx-NA bottom**	**Mtx-AD Top**	**Mtx-AD bottom**	**MeOH Mtx**
Compounds					
MCR *ring*	ND	ND	28%	22%	64%
MCR *open*	ND	ND	ND	ND	53%
red-MX	ND	ND	ND	ND	ND
MBR *ring*	ND	ND	41%	39%	64%
MXR + UNK BMX-2	7%	ND	54%	29%	52%
ox-MXR	ND	ND	26%	ND	46%
MBR *open*	ND	6%	ND	ND	62%
BMXR-1A	ND	>100%	ND	ND	>100%
BMXR-1B	ND	ND	>100%	ND	>100%
ZMXR	ND	ND	ND	ND	54%
EMXR	ND	ND	16%	ND	40%
BMXR-2	>100%	83%	>100%	ND	>100%
BEMXR-1	ND	ND	ND	ND	57%
BEMX-2	ND	ND	6%	ND	65%
BMX-3	ND	ND	ND	ND	ND
BEMX-3	ND	ND	ND	ND	42%

ND: not detected (below 5% recovery), NA: not acidified, AD: acidified to pH 2

A number of other solid phases (3 mL, 500 mg) were then compared to C18 for effective recovery of MX (Table 12). An aqueous solution (260 ng/L MX and 100 ng/L MBA in DIW) was prepared and passed through Cyclohexyl (J.T. Baker), Cyano (J.T. Baker), C8 (Phenomenex Strata), C18E (Phenomenex Strata), and C18 (J.T. Baker) in 250 mL quantities, and results were compared to blanks, both in duplicate. Each column was eluted twice with 500-µL aliquots of methanol. The methanol eluents were derivatized, neutralized, and hexane-extracted before analysis by GC-ECD. None of the solid phases recovered greater amounts of MX than C18 had previously recovered (25%) from spiked DIW. For this reason, SPE was not considered as a practical alternative preconcentration method to LLE for the MX-analogues.

Table 12. Comparison of SPE phases for MX recovery from DIW

Solid Phase	MX Recovery
Cyclohexyl	16%
Cyano	0%
C8	9%
C18E	15%
C18	6%

Method Calibration Curves

The liquid-liquid extraction method was applied to acidified (pH 2), 100 mL samples that were spiked with all of the MX-analogues, except ox-EMX (Figure 1) (Onstad and Weinberg, 2001). The chlorinated tap water samples were quenched of residual chlorine with ammonium sulfate (Mallinckrodt) prior to extraction. The combined 50 mL MtBE extracts (2 x 25 mL MtBE) were reduced to 500 µL with nitrogen gas (UHP, 99.999%). After derivatization of the MtBE extract and neutralization, the final hexane extract (1 mL) recovered only ~60% of the MXR-analogues, considering the results of the partition experiments above. Linearity was observed for MX and MX-analogues in deionized and chlorinated tap waters only at ng/L levels. Example calibration curves are shown in Figures 11 and 12 (MX) and Figures 13 and 14 (MCA). Recoveries of MX and MCA were greatly reduced in the chlorinated tap water samples (Figures 11 and 12), when the detector response was expressed as the ratio of MX or MCA areas to the internal standard (HCB). However, the recoveries were more similar when the detector response was expressed as the ratio of MX or MCA areas to the surrogate standard (MBA) area (Figures 13 and 14). Reliable data is obtainable down to 50 ng/L MCA and 75 ng/L MX by liquid-liquid extraction (100:1 concentration factor) when 100 mL is used as the sample volume.

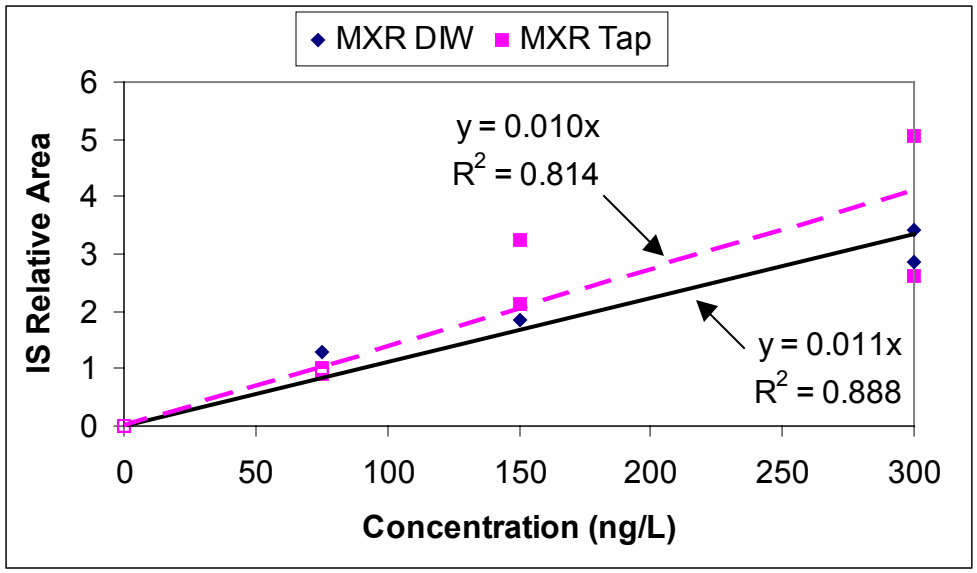

Figure 11. MX Calibration Curve, using area relative to internal standard.

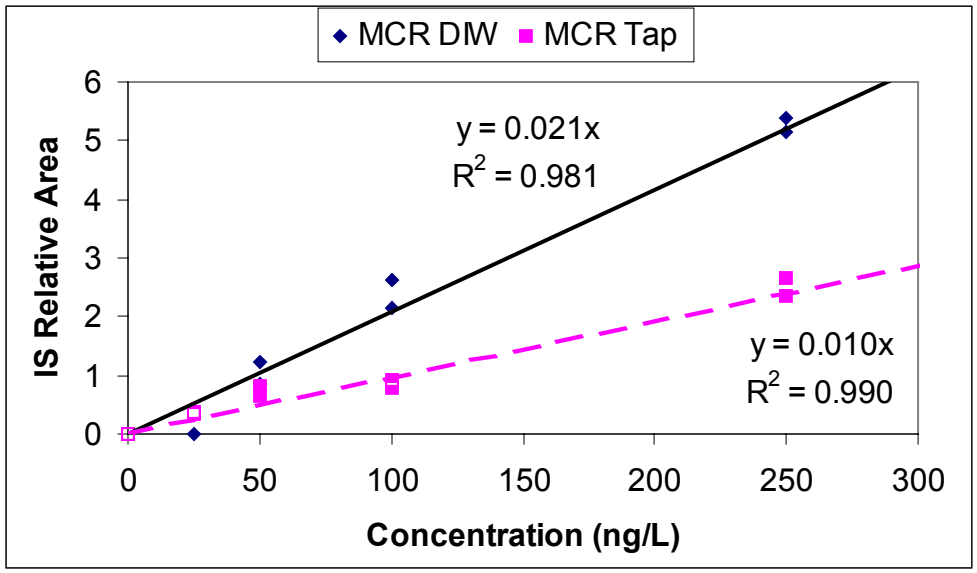

Figure 12. MCA Calibration Curve, using area relative to internal standard.

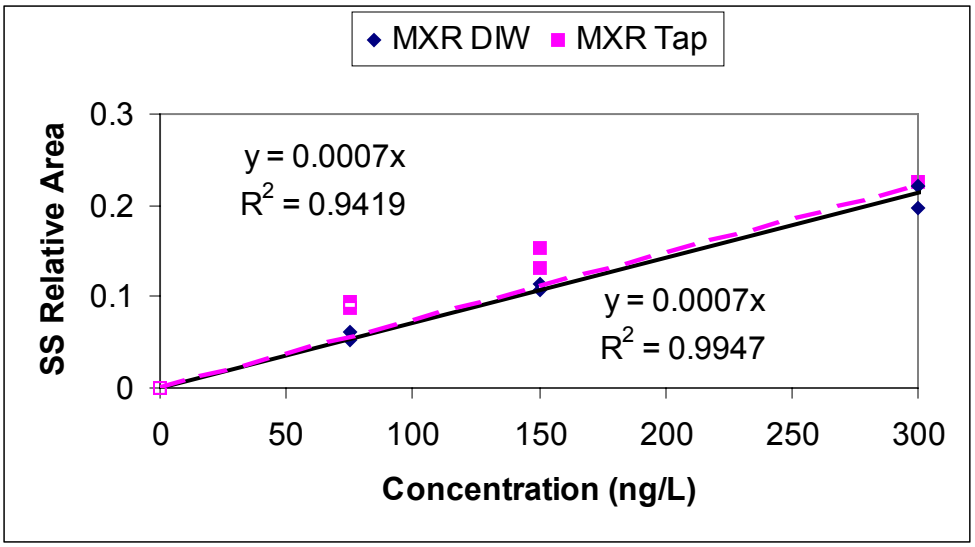

Figure 13. Calibration curve for MX, using area relative to surrogate standard.

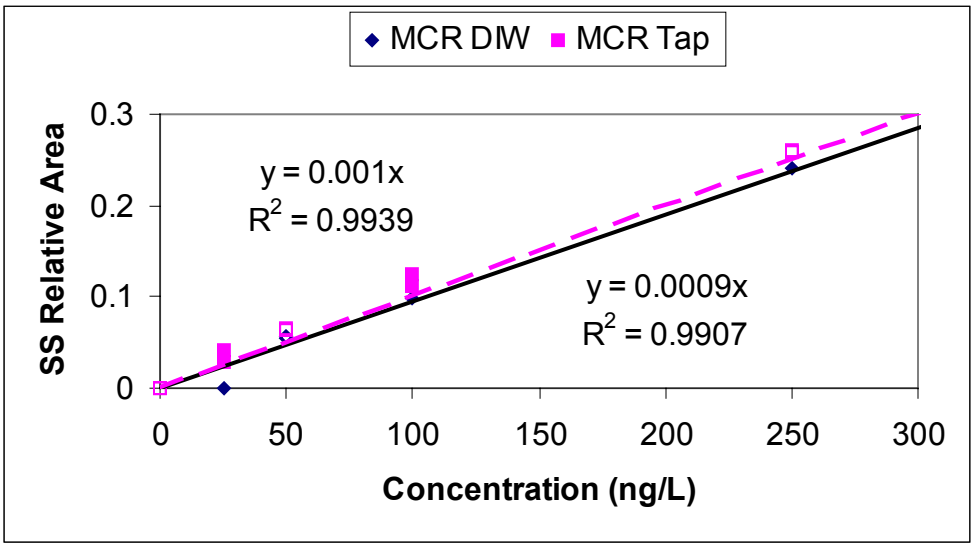

Figure 14. Calibration curve for MCA, using area relative to surrogate standard.

Stability in Aqueous Solutions

In order to stabilize the levels of MX in samples upon collection, they must be quenched of residual chlorine to prevent further production or degradation of MX by chlorine, treated with a biocide to prevent microbial degradation of MX, acidified to pH 2 in order to prevent conversion of MX to *open* forms (ZMX and EMX) and degradation at high pH, and stored at low temperatures (less than or equal to 4°C) to prevent thermal degradation of MX.

Holding temperature of samples was evaluated by storing an aqueous solution (100 ng/mL MX/DIW) at room temperature (25°C) and in a refrigerator (4°C). The samples were extracted after 24 and 48 hours, using LLE at a 10:2 extraction ratio with MtBE. MX was more stable at the lower temperature; at 4°C, 63% MX was recovered, while at 25°C, only 40% MX was recovered. MX recoveries for the two storage temperatures did not change between 24 and 48 hours.

The stability of MX and MCA in tap water samples was then monitored over 14 days to determine the appropriate holding time for samples (Onstad et al., 2000). Previous attempts to determine holding time utilized the biocide sodium azide (NaN_3) in combination with a variety of chlorine quenching agents (ammonium sulfate, *L*-ascorbic acid, sodium sulfite, and sodium bisulfate). However, the MX-analogues could not be recovered by extraction, due to the reaction of sodium azide with the furanone rings in MX-analogues (Beccalli et al., 2000). Therefore, the biocide was removed from the procedure. In this case, a 10 L sample of chlorinated tap water was spiked with MX and MCA to a concentration of 500 ng/L. The water was transferred to 250 mL bottles and quenched of residual chlorine with aqueous ammonium sulfate solution (100 µL of 40 mg/mL $(NH_4)_2SO_4$) or a combination of ammonium sulfate and sulfuric acid.

The samples were stored at 4°C and extracted in duplicate on days 0, 1, 2, 4, 7, and 14. Prior to extraction, each 250-mL sample was spiked with the surrogate standard (MBA) to a concentration of 500 ng/L. The samples containing only ammonium sulfate as the quenching agent needed to be acidified prior to extraction (to pH 3), while the other samples were already acidic (also pH 3). Method calibration samples at concentrations of 0 and 500 ng/L for MX-analogues in deionized water were extracted each day of the study, in order to calculate concentrations of the MX-analogues in the tap water samples. The MtBE extracts were reduced from 100 mL to 500 µL with rotoevaporation and nitrogen gas. After derivatization of the MtBE extract and neutralization, the final combined 2 mL hexane extract (2 x 1 mL hexane) was reduced to 250 µL with nitrogen gas and then spiked with an internal standard, hexachlorobenzene (HCB). This process created a concentration factor of 1000.

The first-order plots show that the combination of ammonium sulfate and acid for quenching stabilized the MX in the tap water samples only slightly longer than ammonium sulfate alone (Figures 15 and 16). The first-order degradation rate constants are very similar, as well ($k \sim 0.077$ days^{-1}, $t_{1/2}=9.0$ days). This agrees with rates of hydrolysis at pH 7.0 measured by Croué and Reckhow (1989) at 20ºC, $k = 0.9 \pm 0.5 \times 10^{-6}$ s^{-1} (~0.07 days^{-1})

and $t_{1/2}$ ~ 8.9 days. The MCA components coeluted with components in the tap water samples and their stability could not be evaluated in this study. The immediate degradation of MX in tap water samples calls for rapid sample extraction and processing upon receipt of samples.

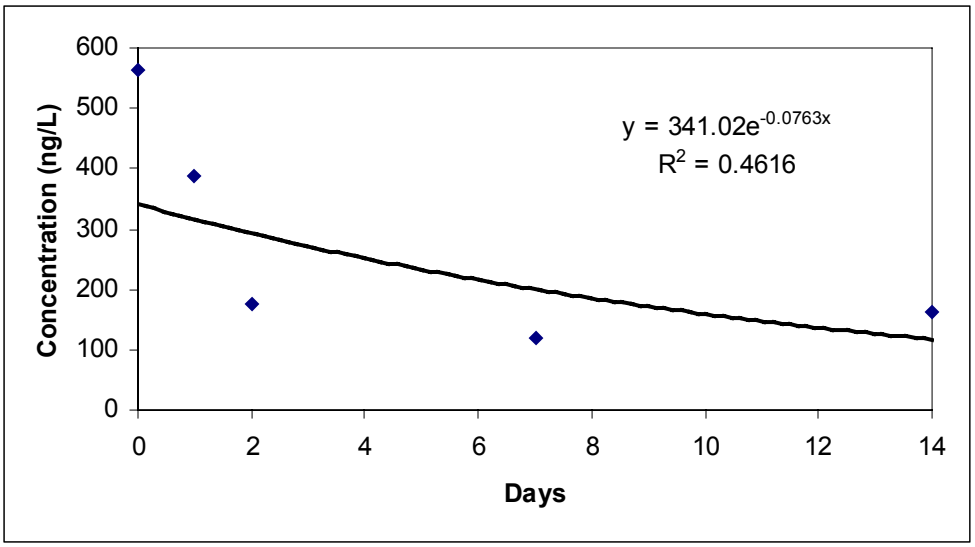

Figure 15. Degradation of MX in chlorinated tap water quenched with ammonium sulfate.

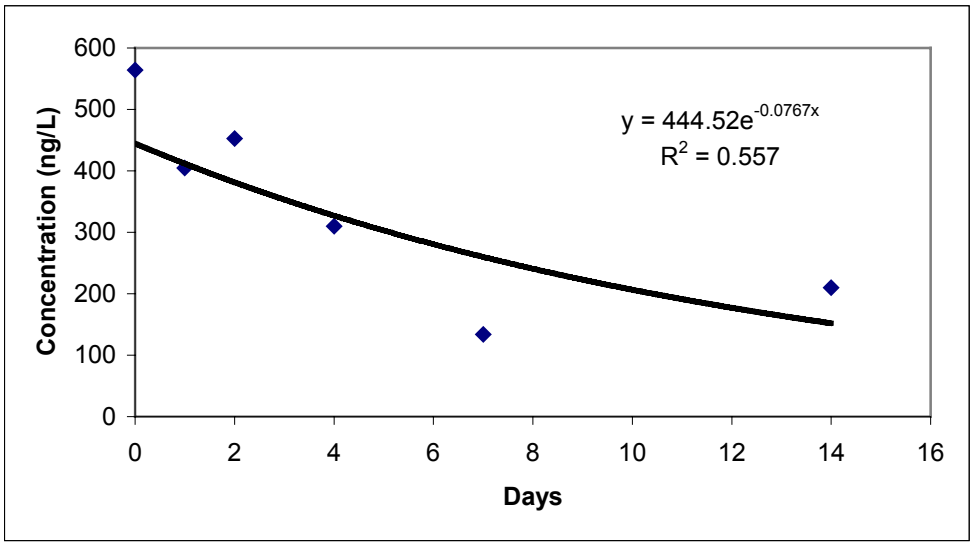

Figure 16. Degradation of MX in chlorinated tap water quenched with ammonium sulfate and preserved with sulfuric acid.

Final Method for Occurrence Study Drinking Water Samples.

The final optimized method developed for the MX analogues is shown in the first part of this chapter (**Method Summary**).

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CARBONYL, HALOACID, HALOACETATE, AND HALOACETAMIDE METHODS

Methods for carbonyl, haloacetate, and haloacetamide target DBPs were developed at the University of North Carolina (UNC). A listing of these DBPs is presented in Table 1. For many of the targeted species, no chemical standards were commercially available. Therefore, synthesis was required for many. Proton nuclear magnetic resonance spectroscopy (NMR) and gas chromatography (GC) with ion trap mass spectrometry (MS) detection were used to confirm the identity and establish purities for these synthesized standards. The standards were stored at –15°C and periodically reassessed for purity. Extraction methods developed included liquid-liquid extraction (LLE) and solid phase extraction (SPE), which were used in combination with different derivatization techniques (e.g., methylation or pentafluorobenzylhydroxylamine [PFBHA] derivatization) and GC with electron capture detection (ECD) or mass spectrometry (MS) (Table 1). Liquid chromatography (LC) with electrospray ionization (ESI)-MS was also investigated for two of the target DBPs, but quantitative methods at the low µg/L detection limits were effected through the use of gas chromatography. The stability of these DBPs in water was also investigated

Table 1. Target carbonyl, haloacid, haloacetate, and haloamide compounds[1]

Compound	Abbreviation	Source of Standard	Purity	Analytical Method
3,3-dichloropropenoic acid	DCPA	Synthesized at UNC	>95% by NMR	LLE – diazomethane
Dimethylglyoxal (2,3-butanedione)	23BD	Aldrich	97%	PFBHA-LLE
Chloroacetaldehyde	CA	ChemService and Aldrich	50% solution in water	PFBHA-LLE
Bromochloroacetaldehyde	BCA	Can Syn	35%	LLE, PFBHA-LLE
Dichloroacetaldehyde	DCA	TCI America	>95% by GC/EI-MS	LLE, PFBHA-LLE
Bromochloromethyl acetate	BCMA	Supelco	>99.99%	LLE
2-Chloroacetamide		Aldrich	98%	LLE
2,2-Dichloroacetamide		Aldrich	98%	LLE
2-Bromoacetamide		Aldrich	98%	LLE
2,2-Dibromoacetamide		Sigma-Aldrich	98%	LLE
2,2,2-Trichloroacetamide		Aldrich	99%	LLE
Trans-2-hexenal	TH	Acros	99%	PFBHA-LLE, SPE-ESI
5-Keto-1-hexanal	5KH	Majestic Research	~20%	PFBHA-LLE, SPE-ESI
Cyanoformaldehyde-oxime	CNF	Can Syn	51%	LLE
6-Hydroxy-2-hexanone	6HH	Majestic Research	>95%	PFBHA-LLE, SPE-ESI

[1]Abbreviations: Can Syn: Synthesized by Can Syn Chem Corp (Toronto, ON, Canada); TCI America (Portland, Ore.); Aldrich Chemical Co. (St. Louis, Mo.); Acros Organics (Pittsburgh, PA); Majestic Research: Synthesized by Majestic Research (Athens, GA).

SAMPLE COLLECTION

Amber glass bottles (20 mL for carbonyl, haloacetate, and haloacetamide samples; 250 mL for haloacid samples) containing a quenching agent and labeled according to sample site and location, quenching agent added, and date were sent in coolers to each drinking water utility for sampling. Samples were collected headspace-free in these vials by staff at the water utilities. Travel blanks were prepared in the same manner, but were pre-filled with deionized water and capped with no headspace. All bottles for the same sample location and site were individually wrapped in bubble wrap and packaged together and labeled with the sample site and location. Bubble-wrapped bottles were then packed into a padded cooler along with a check-list of bottles sent and ice packs. Once samples were collected at the utility, they were shipped back to UNC overnight.

CARBONYL METHOD

Figure 1 provides of summary of the procedure used to quantify the carbonyl DBPs in drinking water samples. Methods published by Yu et al. (1995) and the U.S. EPA (Method 556) served as the basis for the method used here.

Concentrations of stock solutions prepared are summarized in Table 2. Dilutions were made using methanol (Dilution I and II) or deionized water (DIW) (Dilution III). Solutions of the surrogate standard, 4-fluorobenzaldehyde, were made up in methanol, and solutions of the internal standard (IS), 1,2-dibromopropane, were made up in hexane. Dilution III solutions could be used for 2-3 days. PFBHA solutions were prepared fresh for each derivatization/extraction. Stock solutions of all compounds, internal standard and surrogate standard and their dilutions were stored at $4^{o}C$ when not in use. Calibration curves were created using different concentration ranges (in the low μg/L range) for each DBP (Table 3).

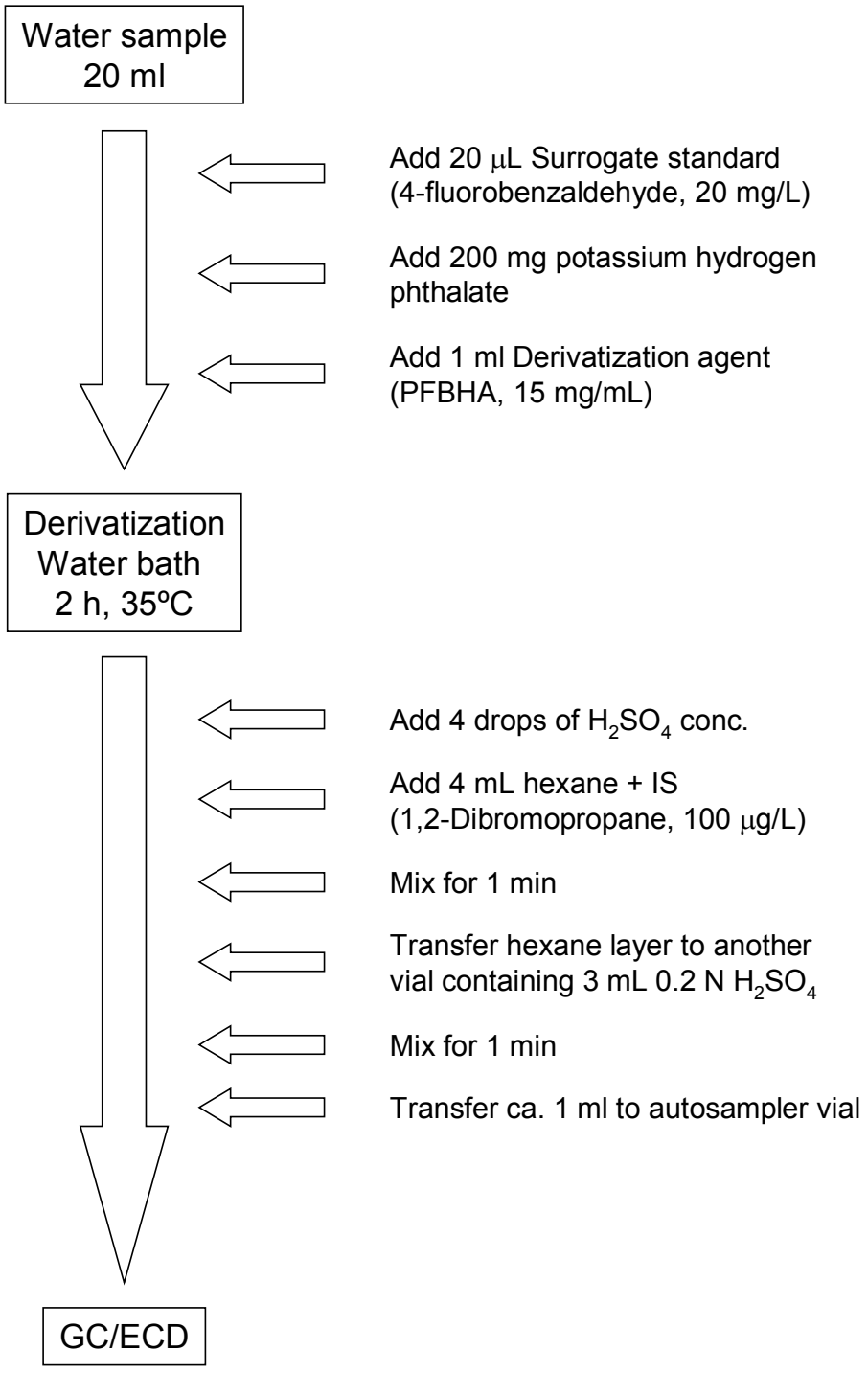


Figure 1. Summary of procedure used to quantify carbonyl DBPs in water.

Table 2. Carbonyl Stock Solutions and Dilutions

Compound	Dilution I [a]	Dilution II [a]	Dilution III
	Conc. (g/L MeOH)	*Conc (mg/L MeOH)*	*Conc ($\mu g/L$ H_2O)*
Chloroacetaldehyde	12.035	120.35	1203.50
Bromochloroacetaldehyde + Dichloroacetaldehyde	0.242 0.345	9.68 13.80	96.80 138.00
Dichloroacetaldehyde	2.156	86.24	862.40
Tribromoacetaldehyde	26.825	10.73	107.30
Trans-2-hexenal	8.3	9.96	99.60
6-Hydroxy-2-hexanone	3.204	51.26	512.60
5-Keto-1-hexanal	1.106	11.06	110.60
2,3-Butandione	10.111	10.11	101.11
Cyanoformaldehyde-oxime	0.956	9.56	95.6
4-Fluorobenzaldehyde (Surrogate Standard)	235.44	23.544	
1,2-Dibromopropane (Internal Standard)	939.85	9.3985	

[a] Solutions of the internal standard were made in hexane

Table 3. Concentrations used for calibration curves (solutions in deionized water)

CA	BCA	DCA	TBA	TH	23BD	5KH	6HH	CNF
1.204	0.097	1.000	0.107	0.100	0.101	0.111	0.513	2.88
2.407	0.194	2.001	0.215	0.199	0.202	0.221	1.025	5.8
6.018	0.484	5.002	0.537	0.498	0.506	0.553	2.563	14.4
12.035	0.968	10.004	1.073	0.996	1.011	1.106	5.126	28.8
24.070	1.936	20.008	2.146	1.992	2.022	2.212	10.252	57.6

Derivatization and Extraction

Briefly, the pentafluorobenzylhydroxylamine (PFBHA) derivatization procedure was carried out as follows. Twenty mL of each drinking water sample was measured and placed into a 40-mL vial (2 vials per sample). Four 20-mL vials of one sample were also collected from each treatment plant to determine recoveries. Twenty mL of each calibration standard was also measured and placed into 40-mL vials (2 vials per sample). Twenty µL of the surrogate solution (23.5 mg/L of 4-fluorobenzaldehyde) was then spiked into each calibration and aqueous sample, and approximately 200 mg of potassium hydrogen phthalate was added to samples for pH adjustment. One mL of freshly prepared PFBHA (15 mg/mL in deionized water) was then added to each sample, and samples were placed in a water bath at 35^{o}C for 2 hours. After cooling to room temperature, 4 drops of concentrated sulfuric acid (approximately 0.05 mL) was added to prevent the extraction of the unreacted PFBHA reagent, and 4 mL of the internal standard solution (9.4 mg/L in hexane) was added and mixed for 1 min using a vortex mixer. The aqueous and hexane layers were allowed to separate, and the hexane layer was transferred to a separate 20-mL vial that contained 3 mL of 0.2 N sulfuric acid, and was mixed for 1 min using a

vortex mixer. Finally, a disposable pipet was used to draw off the hexane layer into a labeled 1.8-mL autosampler vial. Prior to analysis by GC-ECD, samples were stored in the freezer covered with aluminum foil.

GC-ECD Analysis

GC analyses were carried out on a Baity GC-3 gas chromatograph. Injections of 1 μL of each extract were introduced via a splitless injector onto a DB-1 column (30-m, 0.25 mm ID, 0.25 μm film thickness; J&W Scientific/Agilent, Folsom, CA). The GC temperature program consisted of an initial temperature of 50°C, which was held for 1 min, followed by an increase at a rate of 4°C /min to 250°C, followed by an increase at a rate of 3°C /min to 280°C, which was held for 3 min. The injector and the detector were controlled at 150 and 280°C, respectively. Prior to analyzing the real drinking water extracts, the internal standard solution (in hexane) and the pure hexane used to prepare this solution were analyzed as blanks.

Results

The retention times obtained for the carbonyl standards are shown in Table 4. Two isomers were formed for the PFBHA derivatives—*syn* and *anti*. When these isomers separated by GC, both retention times are given below. Figure 2 shows a representative GC chromatogram, which was used for one of the calibration points. Practical quantitation limits obtained using this method are listed in Table 5, along with typical coefficient of variations for triplicate analyses.

Table 4. Retention times for PFBHA-derivatized DBPs

Compound	Abbrev.	Retention time (min)	
		DB-1	HP-5MS
Chloroacetaldehyde	CA	30.39	18.54
Dichloroacetaldehyde	DCA	32.37 32.64	20.55 20.84
Bromochloroacetaldehyde	BCA	35.14 35.50	23.70
Cyanoformaldehyde	CFA	28.23 28.35	17.37
Trans-2-hexanal	TH	37.26 37.46	25.74
6-Hydroxy-2-hexanone	6HH	39.47 39.90	27.77 28.10
5-Keto-1-hexanal	5KH	39.14 39.65	
2,3-Butanedione	23BD	31.57	39.34
4-Fluorobenzaldehyde (Surrogate)	4FBA	41.38 41.69	29.91 30.09
1,2-Dibromopropane (IS)	12DBP	13.44	4.14

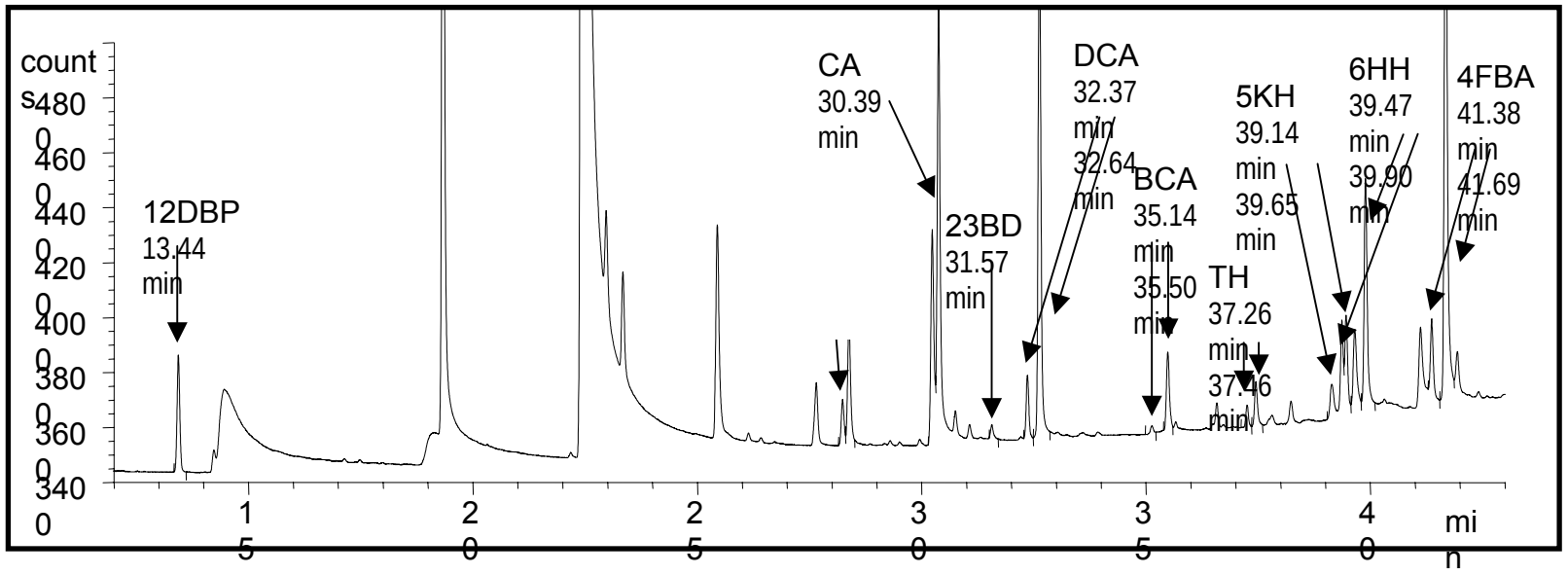


Figure 2. GC-ECD chromatogram showing the different carbonyl-PFBHA derivatives, along with the internal standard (1,2-dibromopropane [2DBP]) and surrogate standard (4-fluorobenzaldehyde [4FBA]). Abbreviations given in Table 1.

Table 5. Practical quantitation limits (PQLs) for carbonyl DBPs

Compound	PQL (μg/L)
Chloroacetaldehyde	0.2
Dichloroacetaldehyde	0.4
Bromochloroacetaldehyde	0.3
Cyanoformaldehyde	3.0
Trans-2-hexanal	0.3
6-Hydroxy-2-hexanone	0.3
5-Keto-1-hexanal	0.8
2,3-Butanedione	0.3

Stability of DBPs

In order to determine an appropriate sample handling procedure, a variety of quenching agents were assessed over a 7-day holding time. Although sodium sulfite appeared to maintain levels of carbonyl DBPs over the 14-day period, it was not chosen as the quenching agent because it is capable of participating in side reactions with other precursors to generate the DBPs studied here. Therefore, for the sake of consistency with other methods used for this study, ammonium sulfate, which also adequately preserved the DBPs over the 14-day period, was selected as the quenching agent for these compounds.

Compound Notes

Haloacetaldehydes. PFBHA derivatization in water generated a consistent 85% conversion of chloro- and dichloroacetaldehyde to the corresponding oximes in a variety of matrices. For the measurement of bromochloroacetaldehyde, dichloroacetaldehyde was found to be a major contaminant in the synthesized product; therefore, the product generated by PFBHA derivatization contained a mixture of 35% bromochloroacetaldehyde and 38% dichloroacetaldehyde. These "standards" were used to quantify the conversion of the aldehyde to the oxime during *in situ* derivatizations in water. Derivatizations showed a consistent 75% conversion. The sum of the *syn* and *anti* isomers used for quantitation of bromochloroacetaldehyde in water.

Cyanoformaldehyde. While the PFBHA oxime standard of this species was synthesized and successfully characterized, many attempts at the synthesis of the target aldehyde were unsuccessful. Consequently, only semi-quantitative analysis of this compound could be made.

Trans-2-hexenal. Both *syn* and *anti* oxime isomers were formed by PFBHA derivatization, and the sum of these peaks was used to quantify *trans*-2-hexenal in water.

6-Hydroxy-2-hexanone. Both *syn* and *anti* oxime isomers were formed by PFBHA derivatization, and the sum of these peaks was used to quantify *trans*-2-hexenal in water.

5-Keto-1-hexanal. Both *syn* and *anti* oxime isomers were formed by PFBHA derivatization, and the sum of these peaks was used to quantify *trans*-2-hexenal in water.

2,3-Butanedione (dimethyl glyoxal). Matrix effects suppressed the ability of the diketone to form a di-derivatized oxime. However, quantitation was possible by calibrating using both the mono- and di-oximes and summing their concentration for the overall concentration of 2,3-butanedione in the original water sample.

3,3-DICHLOROPROPENOIC ACID METHOD

Liquid-liquid extraction (LLE) and diazomethane derivatization were used with GC-ECD detection to quantify 3,3-dichloropropenoic acid (DCPA) in drinking water samples (a modified EPA Method 552 approach). A practical quantitation limit (PQL) of 0.3 μg/L was obtained.

Extraction and Derivatization

Samples were equilibrated to room temperature; two duplicate 20-mL samples were used to analyze for DCPA. Calibration standards were prepared in deionized water at concentrations of 1.9, 4.75, 9.5, 19, and 47.5 μg/L. Twenty mL of each of the two duplicate samples was measured into 40-mL vials, and 50 μL of the surrogate solution (2,3-dibromopropanoic acid, 20 mg/mL) was added to each sample. Concentrated sulfuric acid (1.5 mL) was then added, vials were cooled to room temperature, and 4 mL of the internal standard (100 μg/L in MtBE) was added to each sample. Approximately 6 g of sodium sulfate was added to each vial and was mixed by vortex for at least 1 min. The upper ether layer was then transferred to a 2-mL volumetric flask, magnesium sulfate was added, and flasks were cooled in the refrigerator for 10 min.

Cold diazomethane solution (225 μL, previously prepared according to a slight modification of the method of Glastrup (1998)), was added to each flask and returned to the refrigerator for 30 min. Following this period, flasks were gently removed from the refrigerator and allowed to come to room temperature for 15 min. The presence of a yellow color should remain (indicating the presence of an excess of diazomethane reagent). A small scoop of silicic acid was then added to each sample to quench the excess diazomethane, and 10-15 min was allowed for the solid to settle. The upper ether layer was ten transferred to labeled autosampler vials for GC-ECD analysis. If samples could not be analyzed immediately, autosampler vials containing extracts were stored in the freezer.

GC-ECD Analysis

GC analyses were carried out on a Hewlett-Packard Model 6890 gas chromatograph (Hewlett-Packard/Agilent, Folsom, CA). Injections of 1 μL of each extract were introduced via a splitless injector onto a HP5-MS column (30-m, 0.25 mm ID, 0.25 μm film thickness; J&W Scientific/Agilent, Folsom, CA). The GC temperature program consisted of an initial temperature of 37^{o}C, which was held for 1 min, followed by an increase at a rate of 5^{o}C /min to 280^{o}C, which was held for 30 min. The injector and the detector were controlled at 180 and 297^{o}C, respectively. Prior to analyzing the real drinking water extracts, the internal standard solution (1,2-dibromopropane, 200 mg/L in MtBE) and the pure MtBE used to prepare this

solution were analyzed as blanks, surrogate standards were analyzed for retention time checks, calibration curve samples were analyzed in duplicate, and the internal standard was analyzed once more. Following the analysis of samples (in order of increasing concentration), the internal standard was analyzed again.

Stability

3,3-Dichloropropenoic acid showed good stability in water. Degradation was not detected when ammonium sulfate was used to quench residual chlorine, nor when the aqueous sample was stored for up to 14 days at 14^{o}C.

HALOACETATE METHOD

Bromochloromethylacetate was the only haloacetate DBP targeted in this study. A pure standard was obtained from Supelco and checked for purity using NMR and GC/MS. A liquid-liquid extraction (LLE)-GC-ECD method similar to that of EPA Method 552.2 was used for quantifying bromochloromethylacetate in water, except that hexane was used in place of MtBE as the extraction solvent. LLE with hexane was found to provide a more consistent and higher recovery (92%) than MtBE (75%). No sample pretreatment or derivatization was necessary for this compound. The practical quantitation limit (PQL) for this compound with a 1:5 concentration factor was determined to be 0.3 μg/L.

Extraction

Samples were equilibrated to room temperature; two duplicate 20-mL samples were used to analyze for bromochloromethylacetate in water. Calibration standards were prepared in deionized water at concentrations of 0.3, 1.0, 5.0, 10.0, and 25.0 μg/L generating a calibration curve with a median regression coefficient (r^2) of 0.998. Twenty mL of each of the two duplicate samples was measured into 40-mL vials, 4 mL of the extracting solvent (hexane) and 100 μg/L internal standard (1,2-dibromopropane) dispensed, and approximately 6 g of sodium sulfate added to each vial, which was then capped and mixed by vortex for at least 1 min. The upper organic layer was then transferred to a 1-mL autosampler vial for analysis by GC-ECD. Spike recoveries were assessed on the plant effluent or average distribution system samples through the addition of 5 μg/L of standard. Typical spike recoveries in these samples fell in the range 80-110% for all samples analyzed in this project. For a single set of triplicate, spiked samples, the coefficient of variation was in the range of 6-10%. All plant samples were collected in vials containing ammonium sulfate to quench residual chlorine. During method development it was observed that the presence of a chloramine or chlorine dioxide residual had no effect on the levels of bromochloromethylacetate spiked into plant waters, provided the samples were stored within 24 hours of collection at 4^{o}C and subsequently analyzed within 14 days. Chlorine-quenched samples (with ammonium sulfate) could be held under similar conditions without compromising sample integrity.

Analysis

The GC-ECD conditions were as follows: a 30-m DB-5 column (J&W Scientific/Agilent, Folsom, CA) with dimensions 0.25 mm I.D. and 0.25μm film thickness) was operated under the following oven temperature program: initial temperature of 50 °C held for 1 min, followed by a temperature gradient of 4°C/min to 250°C, which was held for 3 min. The injector was operated in the splitless mode at a temperature of 180°C, while the μECD was held at a temperature of 300°C. The retention time of the target compound under these conditions (and carrier gas flow-rate of 1 mL/min) was 6.1 min and was well resolved from other co-extracted neutral DBPs, such as trihalomethanes.

HALOACETAMIDE METHODS

The haloacetamides included in this study are listed in Table 6. Several approaches were attempted for these compounds including silylation, a novel liquid chromatography (LC)/MS method, a method involving the conversion of haloacetamides to their corresponding haloacetic acids by acid-catalyzed hydrolysis, and a direct liquid-liquid extraction-GC-ECD method. The silylation method, as described in a paper by Le Lacheur et al. (1993) resulted in a practical quantitation limit of 10 μg/L. The novel LC/MS method in conjunction with solid-phase extraction also showed relatively high detection limits (>20 μg/L). The hydrolysis approach appeared to be the most promising method when initially tested on standards in deionized water, but when tested using real drinking water samples containing natural organic matter, it resulted in the formation of additional halogenated by-products. Finally, a direct LLE with gas chromatography (GC)-electron capture detection (ECD) proved to be the best method to use for quantifying the haloacetamide DBPs for this Nationwide Occurrence Study.

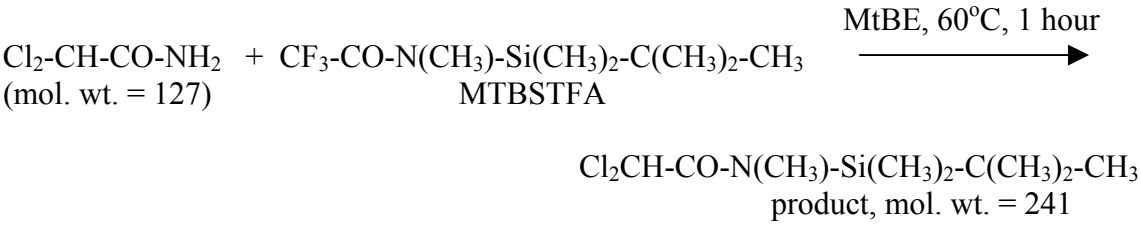
Table 6. Listing of haloacetamides included in this study

Compound	Supplier & cat. #	Final conc. of stock solution (g/L)	Retention Time By GC-ECD
Trichloroacetamide	Aldrich	0.98	25.821
Dibromoacetamide	SALOR(Aldrich)	1.08	27.226
Dichloroacetamide	Aldrich	1.01	21.799
Monobromoacetamide	Aldrich	1.02	22.84
Monochloroacetamide	Aldrich	0.98	17.55

Silylation Method

This method was initially tested using one of the halacetamides--dichloroacetamide. Three dichloroacetamide/MtBE solutions were used: 108, 54 and 1.08 mg/L. One mL of each solution was treated with 100 μL of N-methyl-N-(*tert*-butyldimethylsilyl)trifluoroacetamide (MTBSTFA) and sonicated at 60°C for 1 hour. The solution was then cooled to room

temperature and stored at -20°C until analyzed by GC-ECD using a DB-5 column (J&W Scientific/Agilent, Folsom, CA). The reaction is shown below.



Silyl derivatives were made at four different concentrations of dichloroacetamide in MtBE for use as standards. In a typical experiment, a known amount of dichloroacetamide in 2 mL MtBE was measured into a 4-mL vial. Then, 100 µL of the silylating agent MTBSTFA was injected and the vial kept at 45°C for 2 hours. After cooling, the sample was analyzed by GC-ECD and GC/MS using a 30-m, 0.25 mm, 0.25 µm DB-5 column (J&W Scientific/Agilent, Folsom, CA). The operating conditions were as follows: carrier gas flow rate was 1.2 mL/min, initial oven temperature 50°C for 1 min then 4°C/min to 250°C; with ECD, the splitless mode injector temperature was 180°C and detector temperature was 300°C; with ion trap MS, initial injector temperature was 50°C for 1 min then rapid increase to 250°C. The trap manifold was set at 180°C and transfer line at 280°C. Emission current was 10 µA, mass scan range was from 50-650 Da, and electron multiplier voltage was 1500 V.

The silyl-dichloroacetamide derivative eluted at approximately 15.5 min by GC/MS. Figures 3 shows the electron ionizaton (EI) mass spectrum for the silyl-dichoroacetamide derivative.

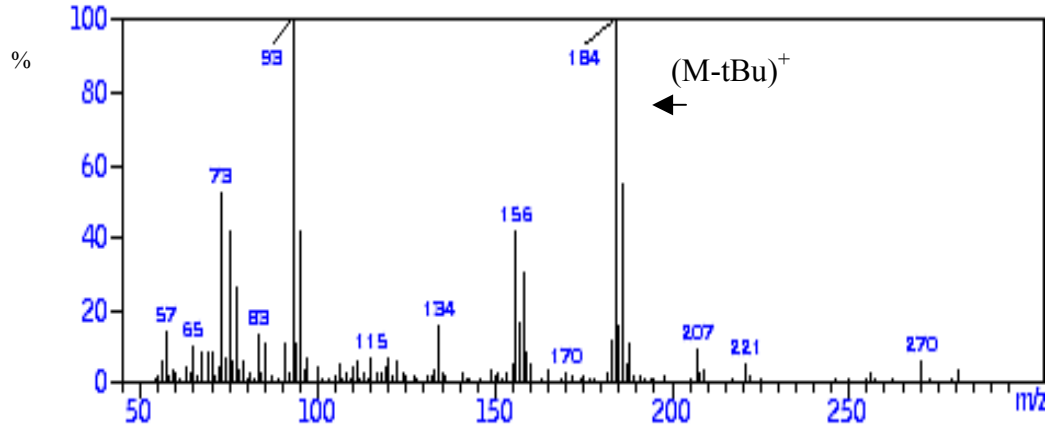


Figure 3. EI mass spectrum of silyl-dichloroacetamide.

Recovery of Dichloroacetamide from Deionized Water. Six concentrations of dichloroacetamide in deionized warer were used. Ten mL of each solution was saturated with sodium sulfate in a 40-mL vial. Five mL of MtBE containing 100pg/μL dibromopropane (internal standard) was added and shaken well to extract the dichloroacetamide. The ether layer was transferred to another vial and dried over anhydrous magnesium sulfate thoroughly before silylation. MTBSTFA (100μL) was injected into each of the vials and kept at 50°C for 1 hour. The solution was then cooled to room temperature and transferred to a GC vial for analysis. The recoveries compared to the standards were very low (4-20%) and suggested that, at least without additional preconcentration, the application of this method for the analysis of dichloroacetamide in water would be limited to a practical quantitation limit of 10μg/L.

Because the recoveries were poor with this method, direct determination of dichloroacetamide from water by solid phase extraction was also attempted, but was not successful.

Acid-Catalyzed Hydrolysis Method

Another method investigated was the acid-catalyzed hydrolysis method. This method involves the acid-catalyzed hydrolysis of the haloacetamide to the corresponding haloacetic acid, as shown below for dichloroacetamide:

$$CHCl_2CONH_2 + H_2O \rightarrow CHCl_2COOH + NH_3$$

The accepted method (EPA Method 552) for haloacetic acids could then be applied before and after hydrolysis to determine the amount of this compound accounted for by the haloacetamide.

For the analysis of the haloacetic acids (EPA Method 552), an aqueous sample was treated with concentrated sulfuric acid, saturated with salt, extracted with MtBE and methylated with diazomethane and determined as its ester. Assuming that the low molecular weight amide may undergo acid-catalyzed hydrolysis readily with concentrated sulfuric acid and the heat generated during the addition, this assumption was tested by making fairly concentrated solutions of dichloroacetamide in deionized water and subjecting to the procedure for the analysis of dichloroacetic acid. This procedure produced a recovery of 38 % for dichloroacetamide.

In order to optimize the method, experiments were carried out to determine the effect of different acid concentrations on the degree of dichloroacetamide hydrolysis. The following scenarios were investigated on a 20 mL aqueous sample for a 2 hour reaction: at ambient temperature (23^{o}C), no acid was compared to the addition of 4 mL sulfuric acid; at a water bath temperature of 80^{o}C, no acid was compared to 4 and 6 mL of sulfuric acid. A 200 μg/L solution of dichloroacetamide was used, and if the conversion were 100 %, 201.5 μg/L of dichloracetic acid would be generated. Results shown in Table 7 reveal an optimum conversion with the addition of 4 mL sulfuric acid at 80^{o}C.

Using the 80°C – 4 mL acid scenario, tests were then made to determine whether the reaction time could be reduced without significantly impacting recovery. The results are shown in Table 8.

Table 7. Impact of different reaction conditions on the hydrolysis of dichloroacetamide to dichloroacetic acid (DCAA)

Sample	DCAA measured (µg/L)	% Conversion
Ambient no acid	23.31	11.57
Ambient – 4 mL acid	151.2	75.04
80°C – no acid	115.3	57.22
80°C – 4 mL acid	**195.7**	**97.12**
80°C – 6 mL acid	146.0	72.46

Table 8. Impact of different reaction times on the hydrolysis of dichloroacetamide to dichloroacetic acid (DCAA) using 4 mL acid at 80°C

Reaction time (hours)	DCAA measured (µg/L)	% Conversion
0	55.4	27.49
0.5	175.9	87.30
1	**183.4**	**91.02**
2	184.4	91.51
3	179.4	89.03
4	177.5	88.09

It was apparent that a 1 hour reaction would suffice. Using this optimized set of reaction conditions, dichloroacetamide solutions in a concentration range from 0 to 200 µg/L were taken through the hydrolysis process and the resultant equivalent amount of DCAA calculated. A plot of these values shown in Figure 4 indicates an average 82% conversion using a linear regression.

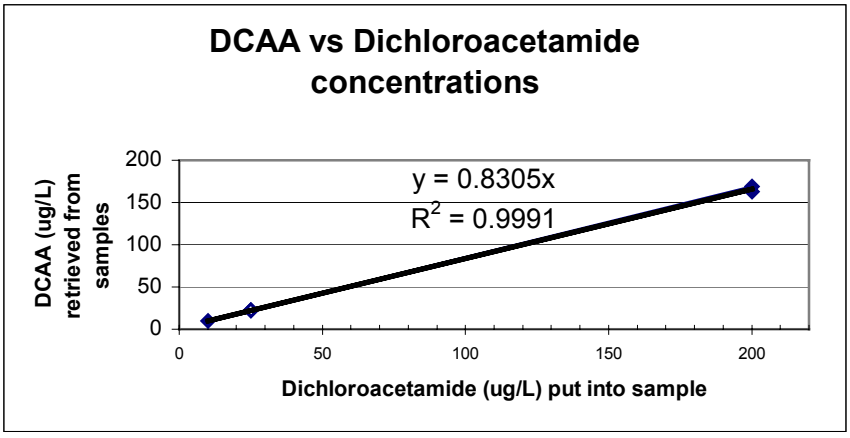


Figure 4. Formation of DCAA from dichloroacetamide over a wide concentration range.

LLE-GC-ECD Method

A final method, involving a simple liquid-liquid extraction (LLE) and GC-ECD analysis proved to be the best method to use for this study. A 100 mL aliquot of 200 μg/L dichloroacetamide in deionized water was prepared by diluting 1 mL of 20 mg/L dichloroacetamide in MtBE to a final volume of 100 mL with deionized water. Four 20 mL aliquots were measured into clean 20 mL vials with Teflon-lined screw caps. Four mL of MtBE and the internal standard (100 μg/L of 2,3 dibromopropane in MtBE) were added to two of the aliquots, while 4 mL of ethyl acetate (EtAC) was added to the two remaining aliquots. Each vial was vortexed for 1 min and the solvent layer allowed to separate for five min. The extracts were compared to a standard of dichloracetamide at the 100% recovery level of 1 mg/L. A 1-mL sample of the organic layer was then analyzed by GC-ECD under the following conditions:

GC Column: 30-m, 0.25 mm ID, 0.25 μm film thickness HP5-MS (Hewlett-Packard/Agilent, Folsom, CA); oven temperature program - initial temperature: 37°C, held for 1 min; 5°C/min increase to 280°C. The injector and detector temperatures were 180 and 300°C, respectively, and the injector was operated in the splitless mode. The recoveries of each sample are shown in Table 9.

Table 9. Recovery of dichloroacetamide by liquid-liquid extraction from deionized water

Sample	Extraction solvent	Retention time (min)	Peak area	Expected peak area	Recovery (%)
1	MtBE	10.521	7737.71	33255	23.27
2	MtBE	10.521	7509.28	33255	22.58
3	EtAC	10.550	19798	33255	59.53
4	EtAC	10.552	19163.5	33255	57.63

Based on the percent recoveries, ethyl acetate appeared to be a better solvent for extracting dichloroacetamide from water. This approach was then expanded for the other haloacetamides listed in Table 6. The statistical evaluation of this method is presented in Table 10. The linear calibration range extended from 1 to 50 μg/L, and water samples were spiked at 5 μg/L.

Table 10. Statistical evaluation of LLE method for haloacetamides in water

Compound	PQL (μg/L)	Average % CV at 1 μg/L	Average Spike Recovery (%)
Trichloroacetamide	0.1	8.4	95
Dibromoacetamide	0.1	6.5	90
Dichloroacetamide	0.1	5.4	104
Monobromoacetamide	0.1	10.3	88
Monochloroacetamide	0.1	11.3	78

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BROADSCREEN GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) METHODS

Sample Concentration

All water samples (39 L) were concentrated by adsorption on resins (Amberlite XAD, Supelco). Details about the preparation and cleaning of these resins can be found elsewhere (Richardson et al., 1994). Water samples were acidified to pH 2 by the addition of hydrochloric acid prior to passage through the columns containing a combination of resins (XAD-8 over XAD-2). A maximum ratio of 770:1 (v/v) of water to resin was used to maximize the adsorption of organic compounds and to minimize breakthrough. The columns were eluted with ethyl acetate, and residual water was removed from the ethyl acetate eluents by using separatory funnels to drain off the water layers, followed by the addition of sodium sulfate. Samples were further concentrated by rotary evaporation (to approximately 5 mL), followed by evaporation with a gentle stream of nitrogen (to a final volume of 1 mL).

Raw, untreated water was collected at each sampling to enable the distinction of chemicals that were formed as disinfection by-products (DBPs) in the treatment process from chemical pollutants that were already present in the raw water. In addition to the raw water controls, four blanks were also analyzed: (1) ethyl acetate passed through the XAD resins and concentrated in the same manner as the treated samples; (b) deionized, distilled water passed through the XAD resins and concentrated; (c) deionized, distilled water treated with chlorine and concentrated; and (d) deionized, distilled water treated with chloramine and concentrated. The latter two blanks were done to determine whether there were any artifacts due to reaction of secondary disinfectants with the ethyl acetate or with resin impurities. As compared to the raw water samples and the treated samples, these blanks contained relatively few compounds.

Derivatizations

Methylation derivatizations with boron trifluoride in methanol were used to aid in identifying carboxylic acids (Kanniganti et al., 1992), and pentafluorobenzylhydroxylamine (PFBHA) derivatizations were used to identify polar aldehydes and ketones (Sclimenti et al., 1990).

GC/MS Analysis

High-resolution GC/electron ionization (EI)–MS and GC/chemical ionization (CI)–MS analyses were performed on a hybrid high-resolution mass spectrometer (VG 70-SEQ, Micromass, Inc.) equipped with a GC (Model 5890A, Hewlett-Packard-Agilent). The high-resolution mass spectrometer was operated at an accelerating voltage of 8 kV. Low-resolution analyses were carried out at 1000 resolution and high-resolution analyses at 10,000 resolution. Positive CI experiments were accomplished by using methane gas. Injections of 1–2 μL of the extract were introduced via a split/splitless

injector onto a GC column (DB-5, 30-m × 0.25-mm ID, 0.25-µm film thickness, J&W Scientific-Agilent). The GC temperature program consisted of an initial temperature of 35ºC, which was held for 4 min, followed by an increase at a rate of 9ºC/min to 285ºC, which was held for 30 min. Transfer lines were held at 280ºC, and the injection port was controlled at 250ºC. Duplicate analyses were also carried out with the GC injection port held at 140ºC to enable the analysis of trihalonitromethanes (THNMs). In previous work, THNMs were found to decompose at temperatures higher than 170ºC (Chen et al., 2002).

Chemical Standards

The following chemicals were prepared synthetically and provided by Can Syn Chem. Corp. (Toronto, ON, Canada): dichloroiodomethane, bromochloroiodomethane, iododibromomethane, diiodochloromethane, diiodobromomethane, 2,2-dibromopropanoic acid, 3,3-dibromopropenoic acid, cis-2,3-dibromopropenoic acid, tribromopropenoic acid, 2-bromobutanoic acid, cis-2-bromo-3-methylbutenedioic acid, trans-2,3-dibromobutenedioic acid, bromonitromethane, dichloronitromethane, bromochloronitromethane, bromodichloronitromethane, 1,1-dibromopropanone, 1,1,1-tribromopropanone, 1,1-dibromo-3,3-dichloropropanone, 1,3-dibromo-1,3-dichloropropanone, and 1,1,3-tribromo-3-chloropropanone. 1,1,3,3-Tetrabromopropanone and dibromonitromethane were prepared synthetically and provided by Majestic Research (Athens, GA). These chemicals were used to confirm tentative identifications made by mass spectrometry. All other chemicals used for broadscreen analyses were purchased at the highest level of purity from Aldrich, Chem Service, and TCI America.

Identification of DBPs

For qualitative identification work, the criteria used for listing an identified compound as a DBP was its presence in the treated-water samples in quantities at least 2–3 times greater than in the untreated, raw water (as judged by comparing GC peak areas). It was important to distinguish a compound as a DBP, even if small amounts of the compound were present in the raw water, because many compounds that are common pollutants (or natural contaminants in water) have also been proven to be DBPs.

GC/MS chromatograms were carefully analyzed for the presence of chemicals that were produced in the treated samples. Each mass spectrum was carefully background-subtracted to remove closely eluting or co-eluting peaks, after which the NIST, Wiley, and Athens-EPA mass spectral library databases were searched for a match of the unknown's mass spectrum. Several common DBPs, such as haloacetic acid methyl esters, could be quickly identified through a library database match using the large NIST (>100,000 spectra) and Wiley databases (>200,000 spectra). In addition, the user library database created at the USEPA laboratory in Athens, GA (>200 spectra, mostly DBPs) also enabled a rapid identification of many less common DBPs, such as 1,1,3,3,-tetrabromopropanone and bromochloroiodomethane. Even with a definitive library match, however, these identifications are listed as tentative until a match of the unknown's GC retention time could be made with an authentic chemical standard. Only

when both the mass spectrum and the retention time matched were the DBPs listed as 'confirmed'.

Despite the large size of the library databases and the user library that had been created at the USEPA-Athens, there were many new DBPs identified in this study that required significant interpretation to enable their identification. This process involved an initial study and interpretation of the low resolution GC mass spectrum. Ion fragments and losses from the molecular ion were studied to postulate a tentative structure. The presence or absence of the molecular ion was determined, and CI-MS was used when the molecular ion was not present or to confirm a molecular ion that was present. Next, high resolution EI-MS analyses were made, which allowed the mass-to-charge (m/z) ratio of an ion to be determined to 3 decimal places. For example, by low resolution mass spectrometry, a molecular ion can only be assigned a nominal mass (e.g., m/z 200). With high resolution mass spectrometry, this ion can be measured with greater accuracy (e.g., m/z 200.012). With this exact mass, generally a single empirical formula (number of carbons, hydrogens, oxygens, nitrogens, etc.) can be assigned to the ion. High resolution EI-MS was used not only for the molecular ions, but also for the fragment ions, which generally reduced the number of possible empirical assignments from 6-8 to one.

Once the empirical formulas were known, functional groups could be postulated and overall structures assigned. All possible isomers were considered when making these tentative assignments. When it was not possible to choose a particular isomer as the correct assignment for the unknown DBP, an attempt was made to purchase or obtain a synthetically produced, authentic chemical standards of all the possible isomers so that a definitive match could be made (of both mass spectra and retention time). When the identification of a compound was confirmed through the analysis of an authentic chemical standard, it was denoted in italics in this report. All other DBP identifications should be considered tentative.

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Mass Spectra of Newly Identified DBPs

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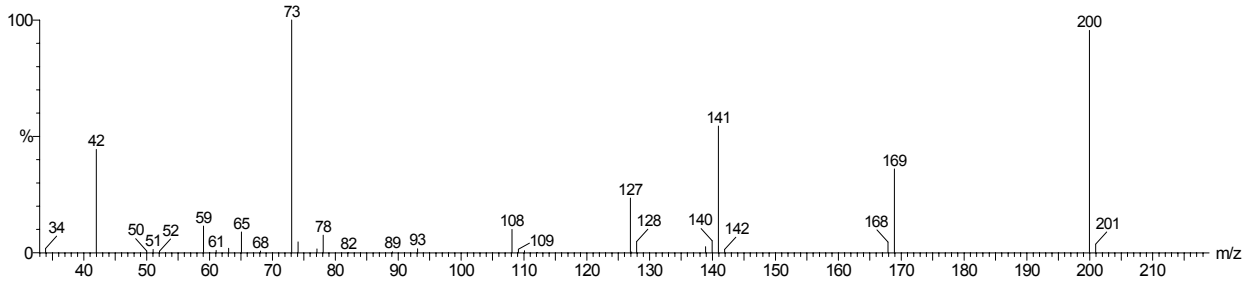

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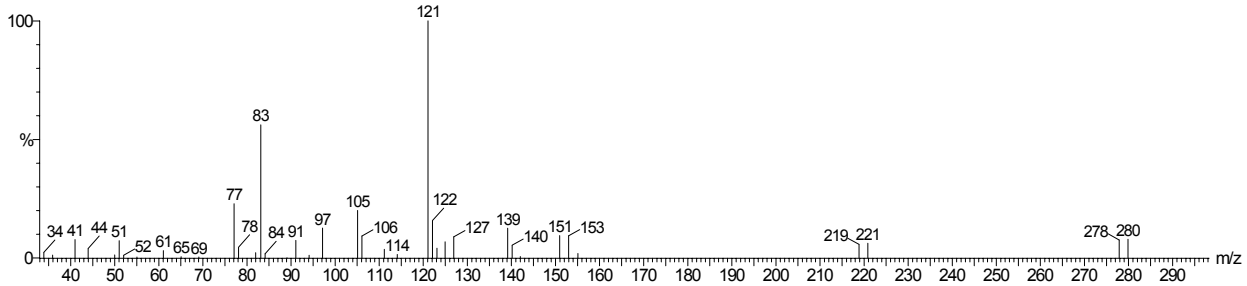

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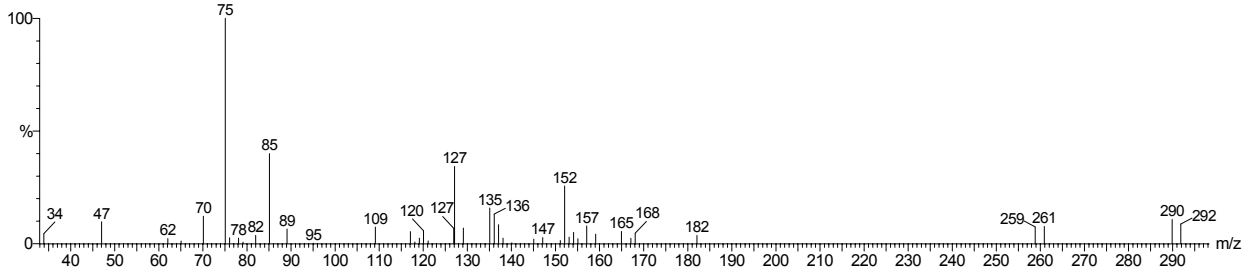

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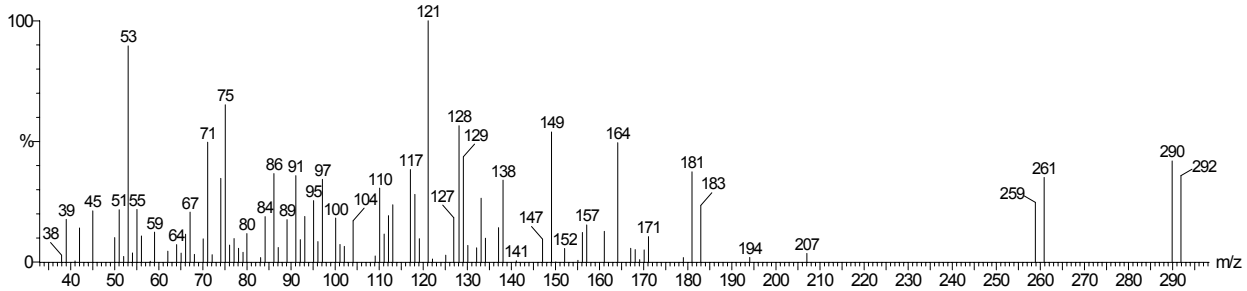

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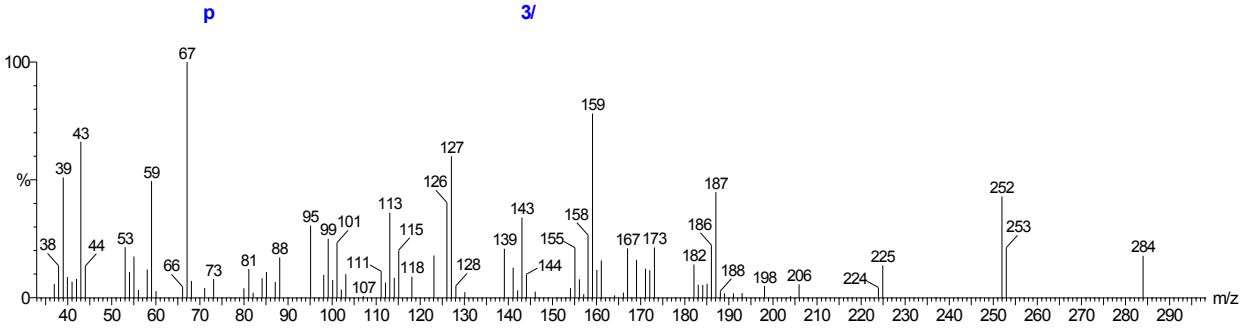

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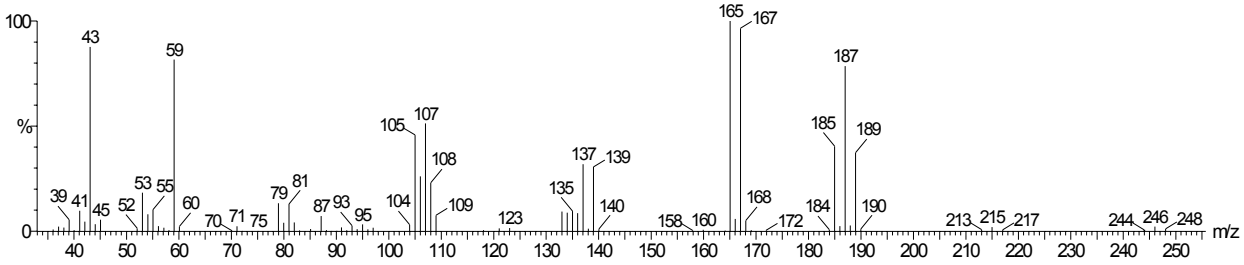

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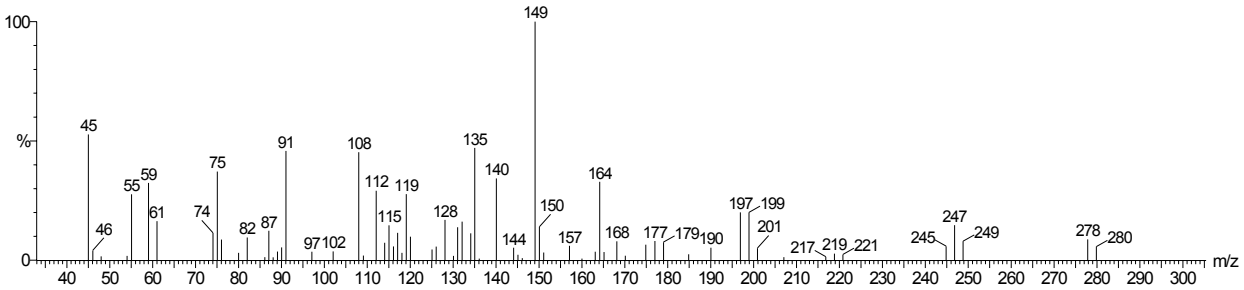

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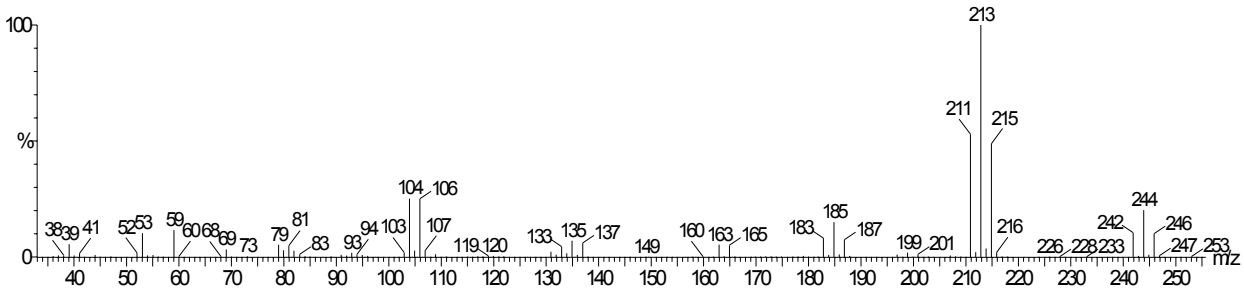

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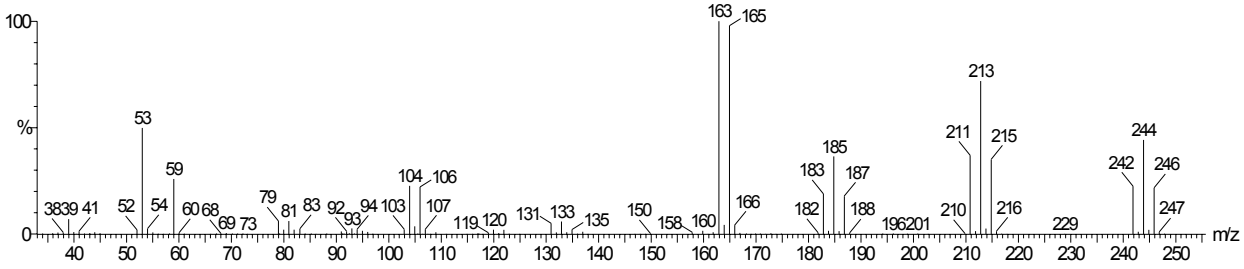

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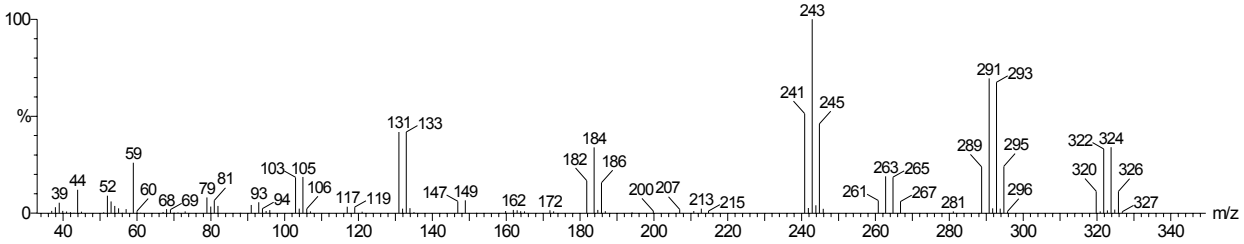

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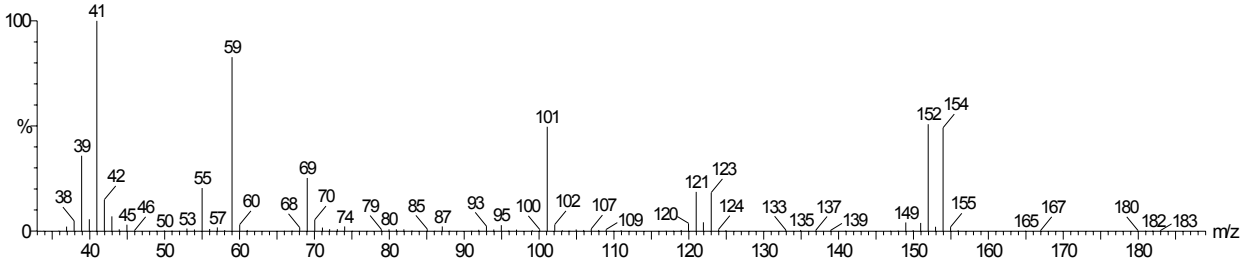
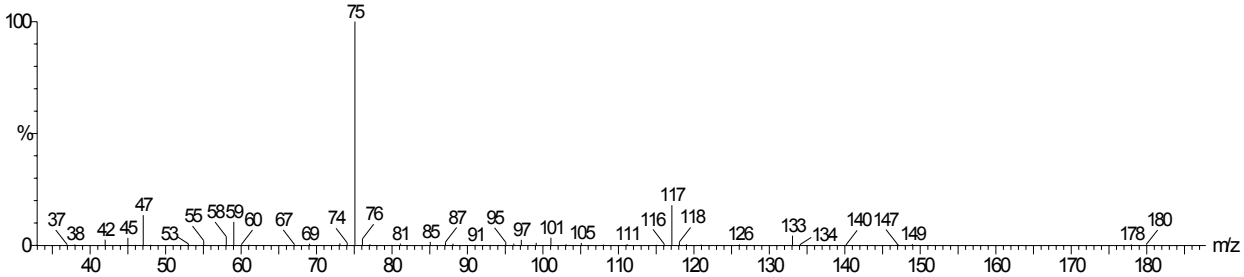
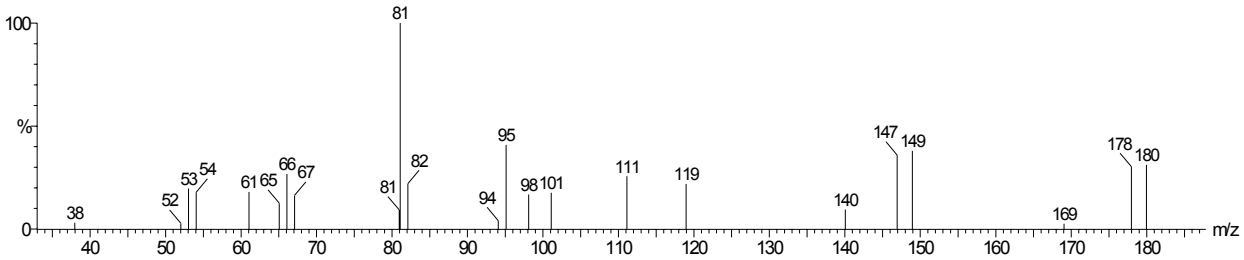


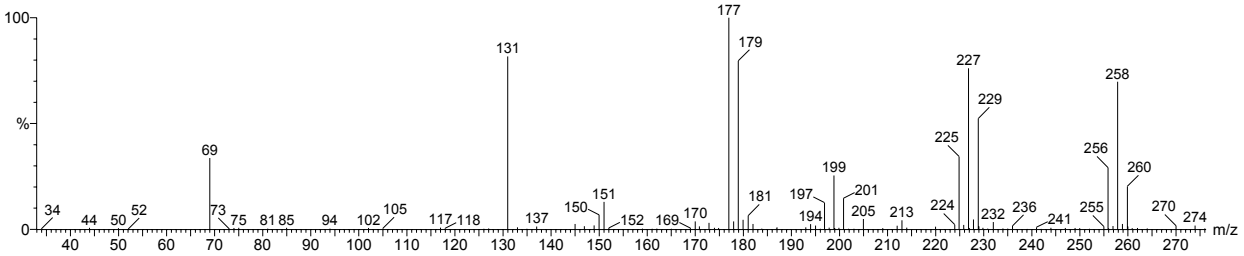
trans-4-Bromo-2-butenoic acid methyl ester



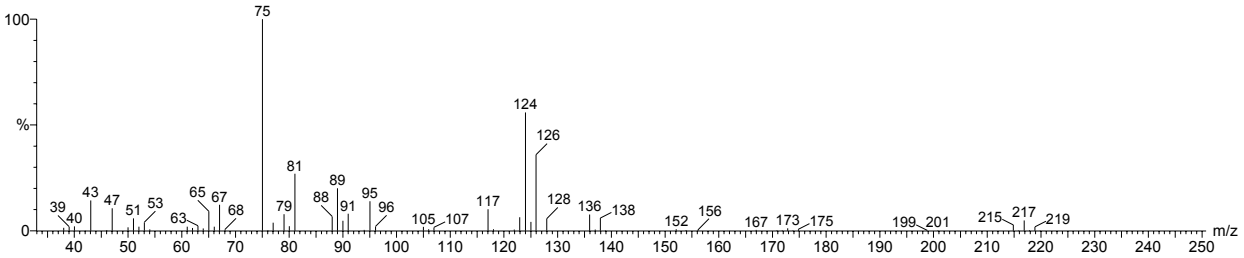
cis-4-Bromo-2-butenoic acid methyl ester



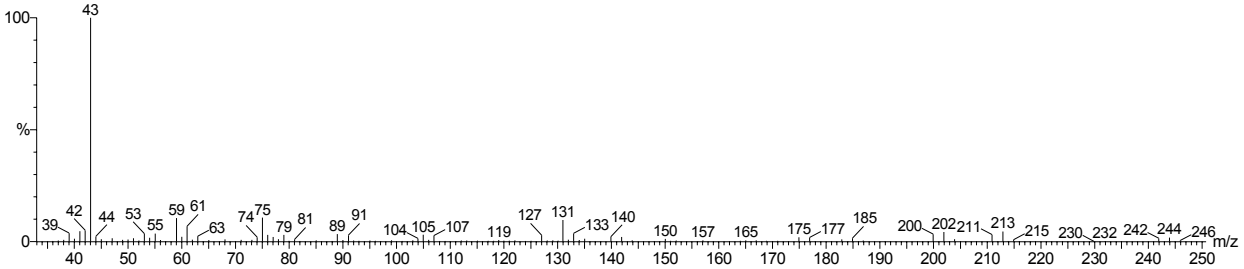
2,3-Dibromo-2-butenoic acid methyl ester



Bromodichlorobutenoic acid methyl ester

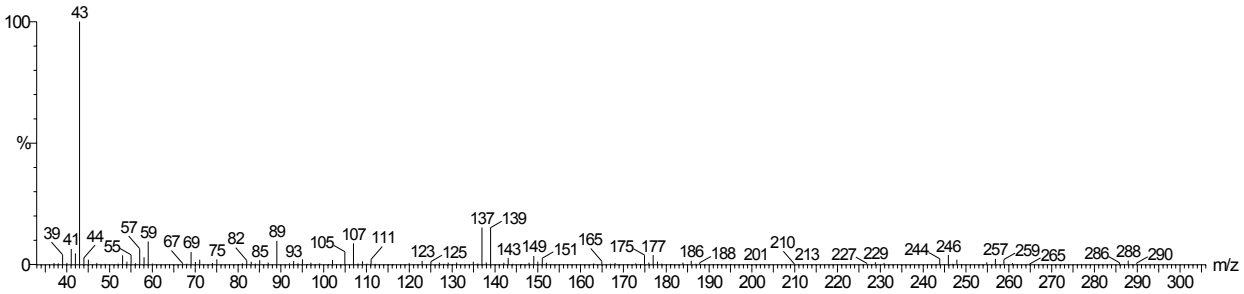


Bromochloro-4-oxopentanoic acid methyl ester

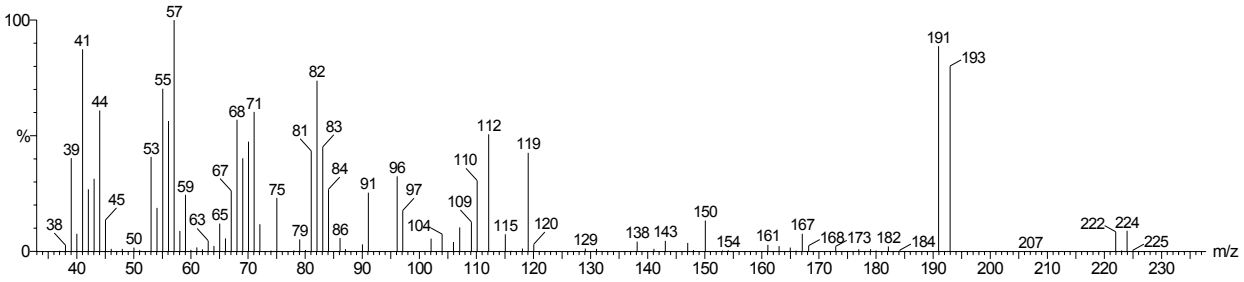


Dibromo-4-oxopentanoic acid methyl ester

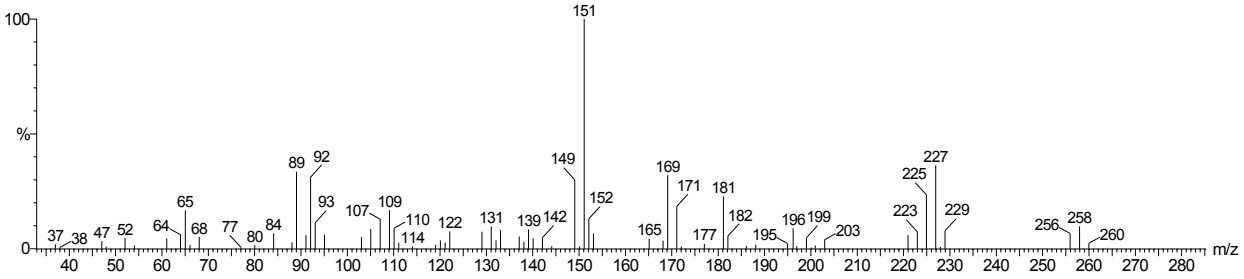
(01)



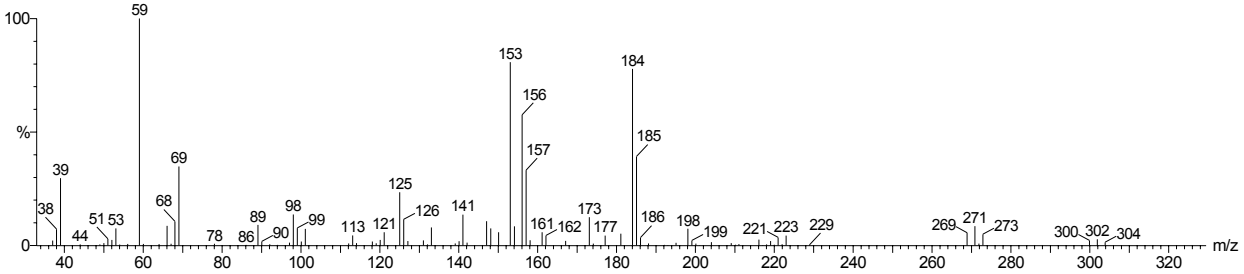
Bromoheptanoic acid methyl ester



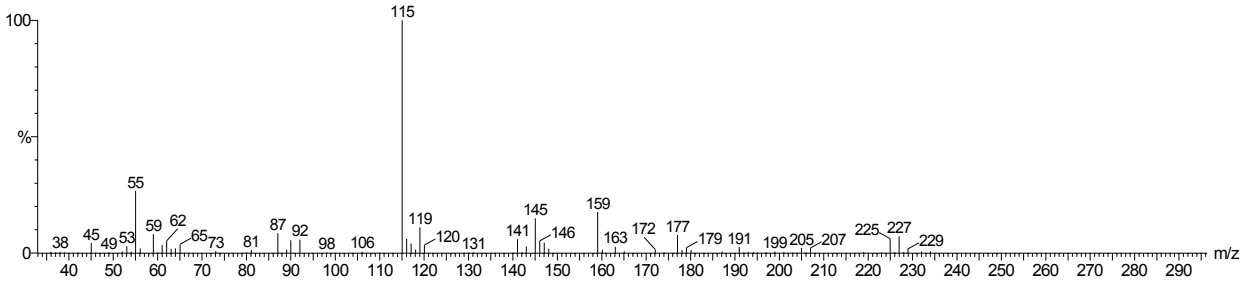
Bromochloroheptanoic acid methyl ester (2nd isomer)



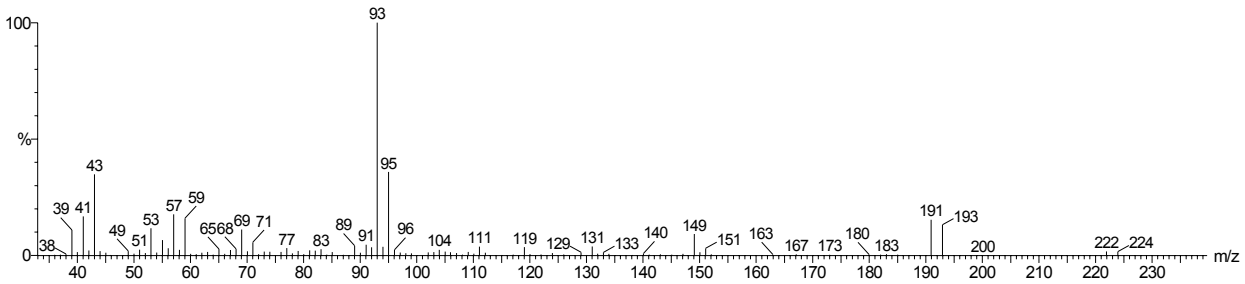
Dibromoheptanoic acid methyl ester



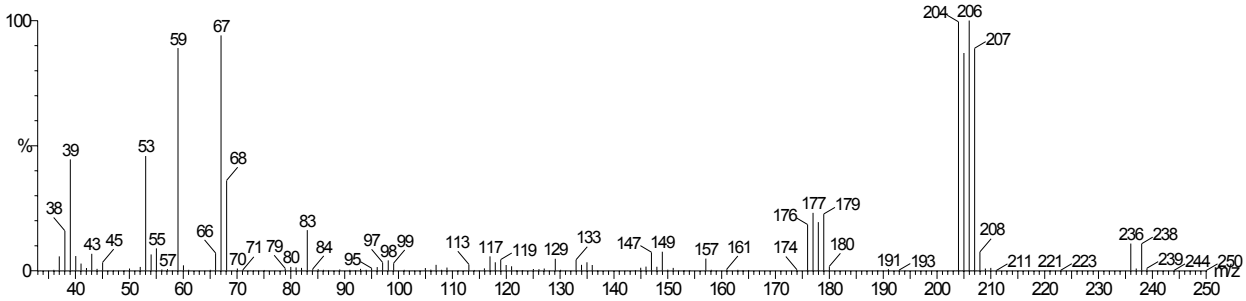
Bromochlorononanoic acid methyl ester



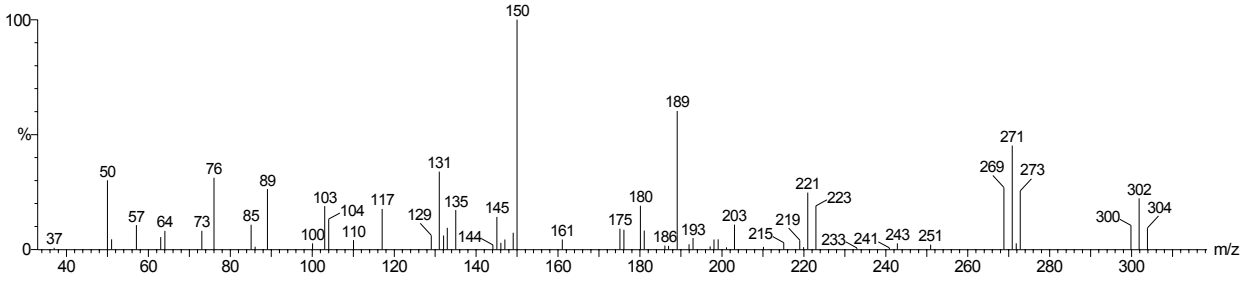
2-Bromobutenedioic acid dimethyl ester



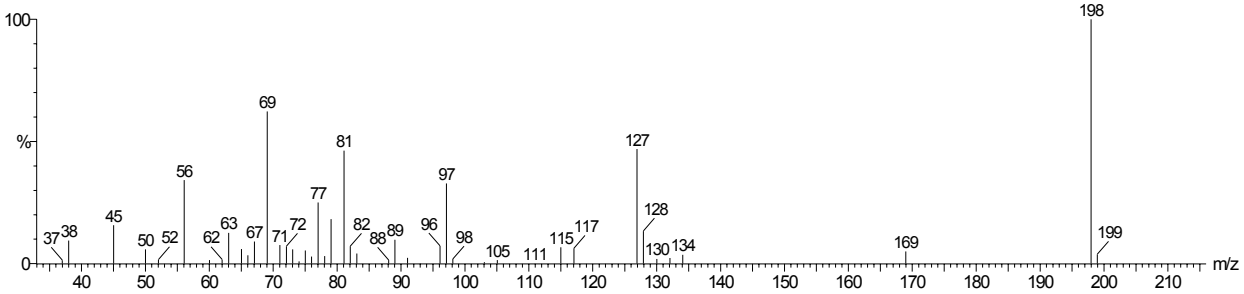
cis-2-Bromo-3-methylbutenedioic acid dimethyl ester



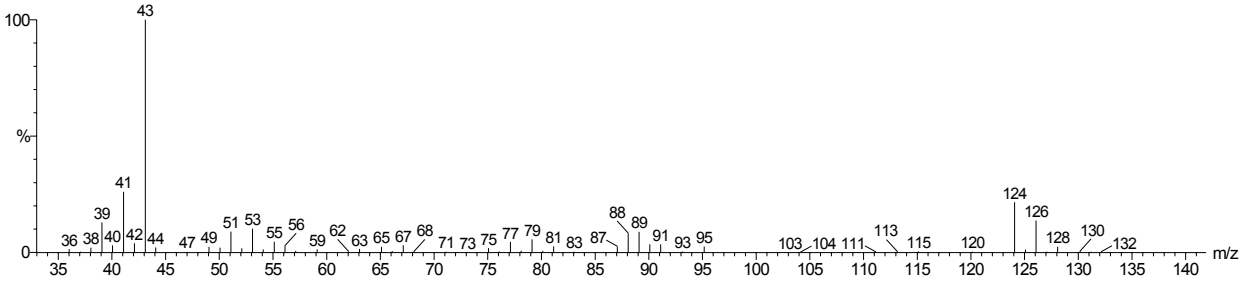
trans-2,3-Dibromobutenedioic acid dimethyl ester



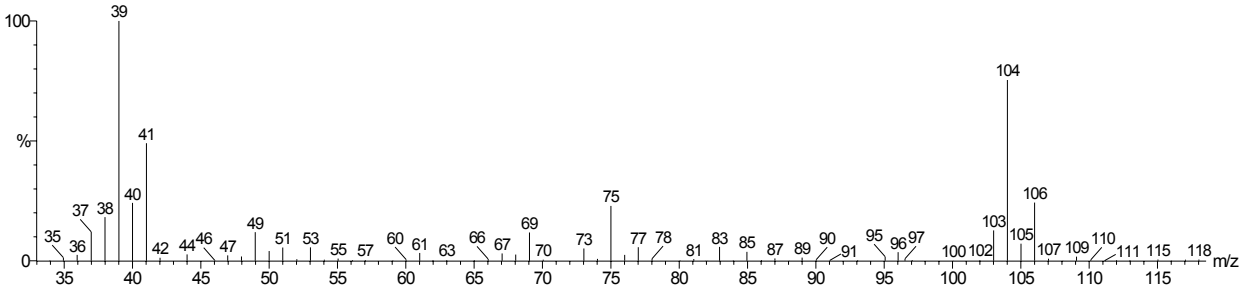
Iodobutanal



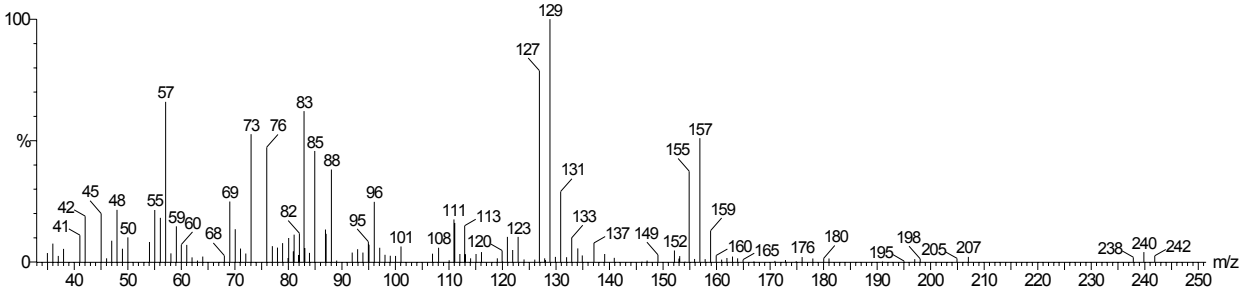
Dichloropropenal



4-Chloro-2-butenal

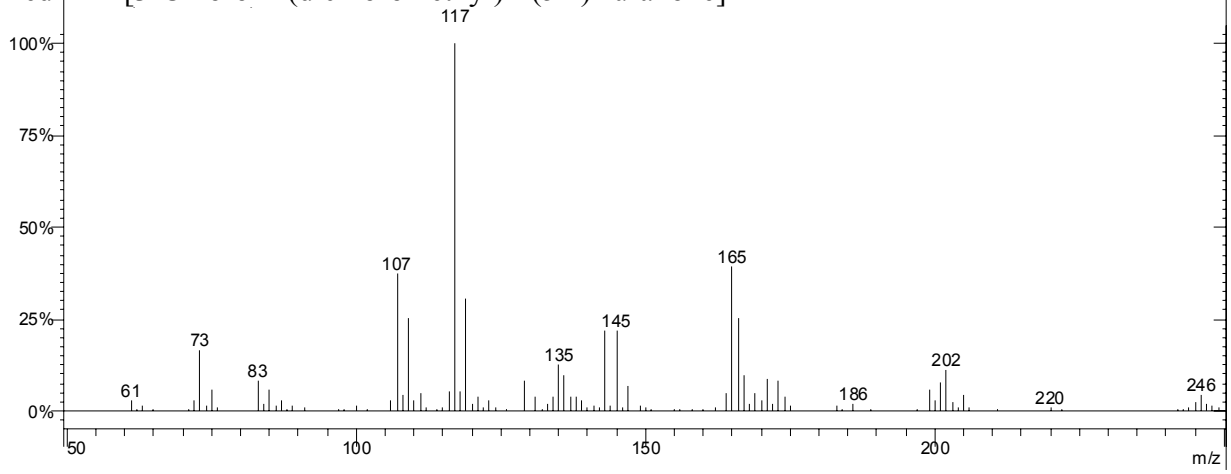


1-Bromo-1,3,3-trichloropropanone

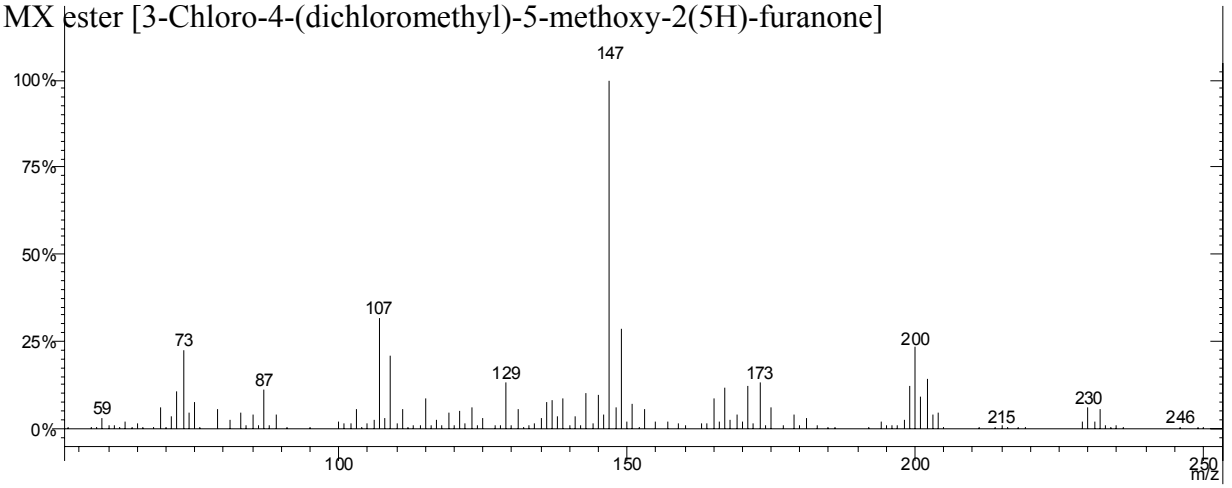


Ion Trap Mass Spectra (EI) of Halogenated Furanone Standards

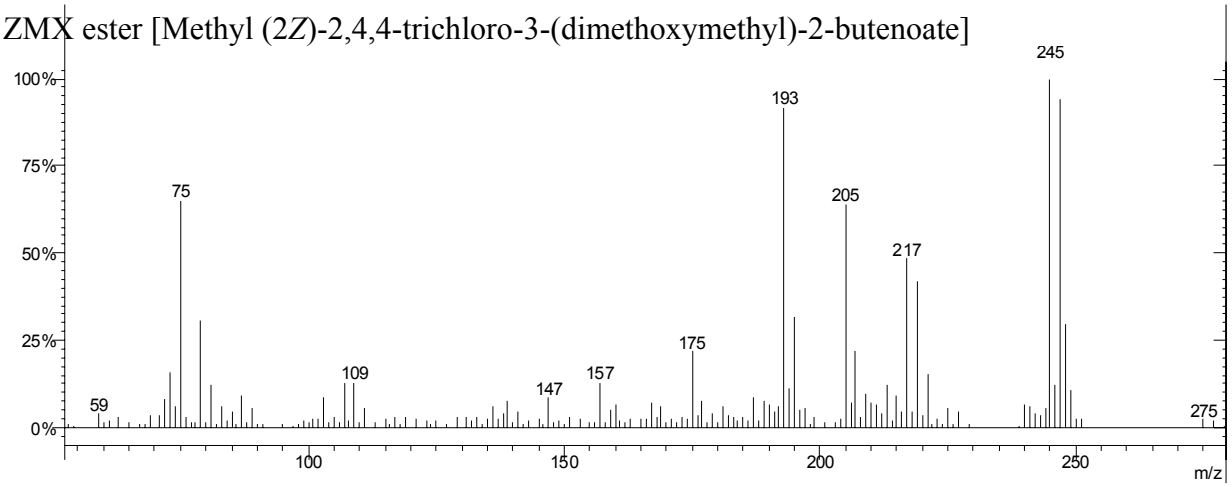
Red-MX [3-Chloro-4-(dichloromethyl)-2(5H)-furanone]



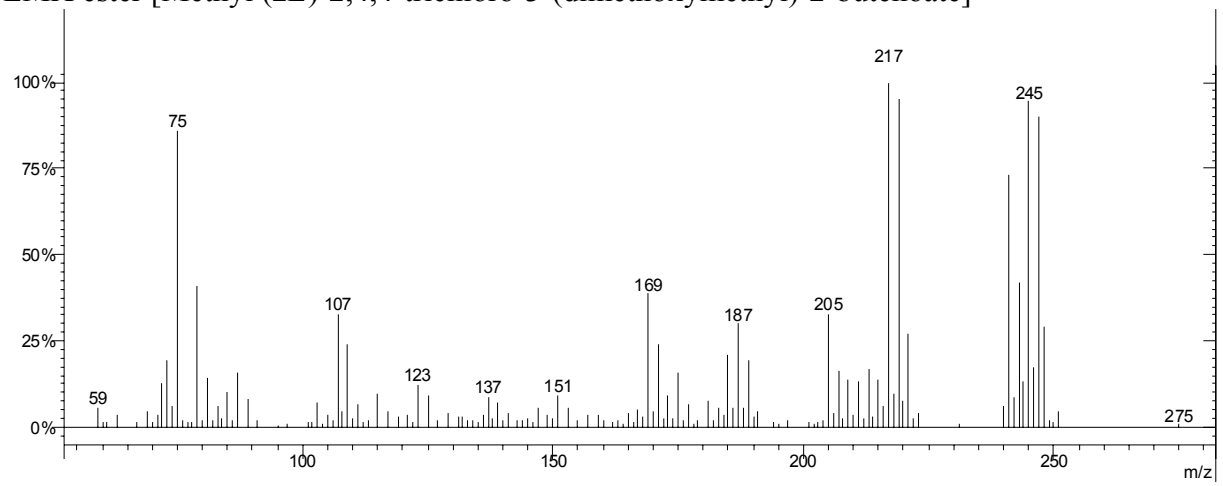
MX ester [3-Chloro-4-(dichloromethyl)-5-methoxy-2(5H)-furanone]



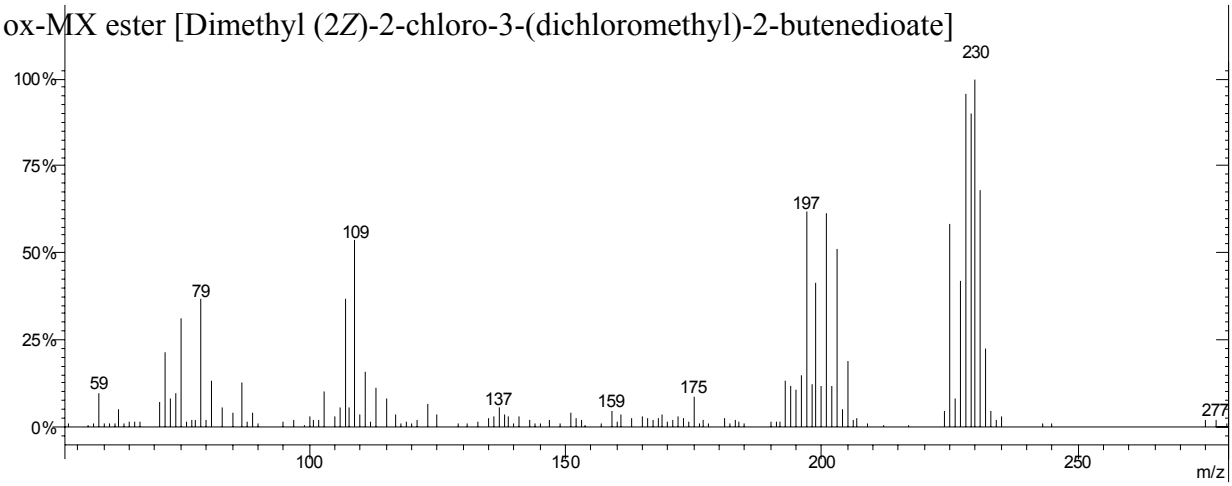
ZMX ester [Methyl (2*Z*)-2,4,4-trichloro-3-(dimethoxymethyl)-2-butenoate]



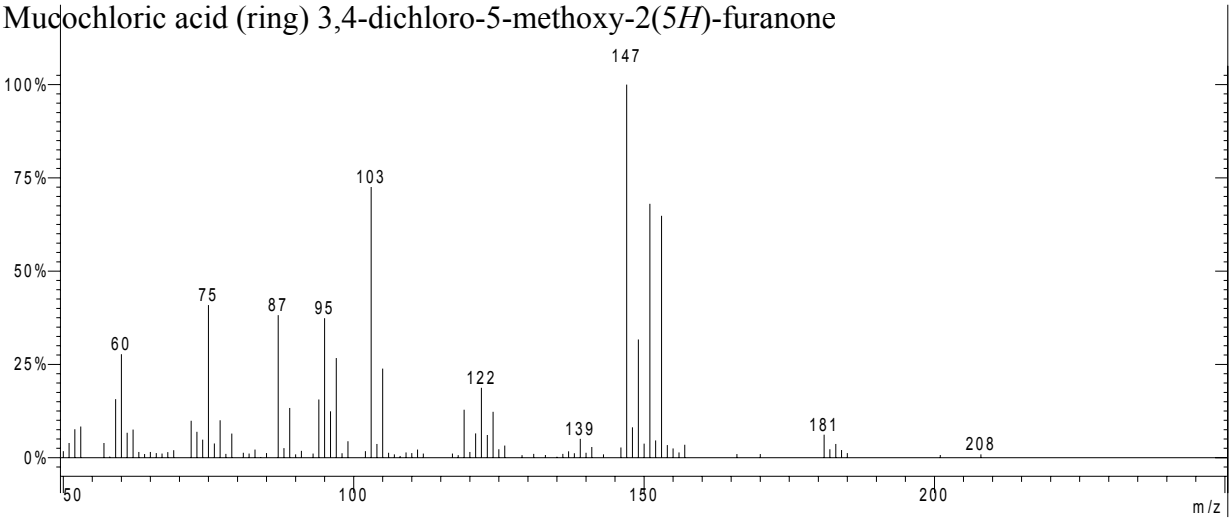
EMX ester [Methyl (2*E*)-2,4,4-trichloro-3-(dimethoxymethyl)-2-butenoate]



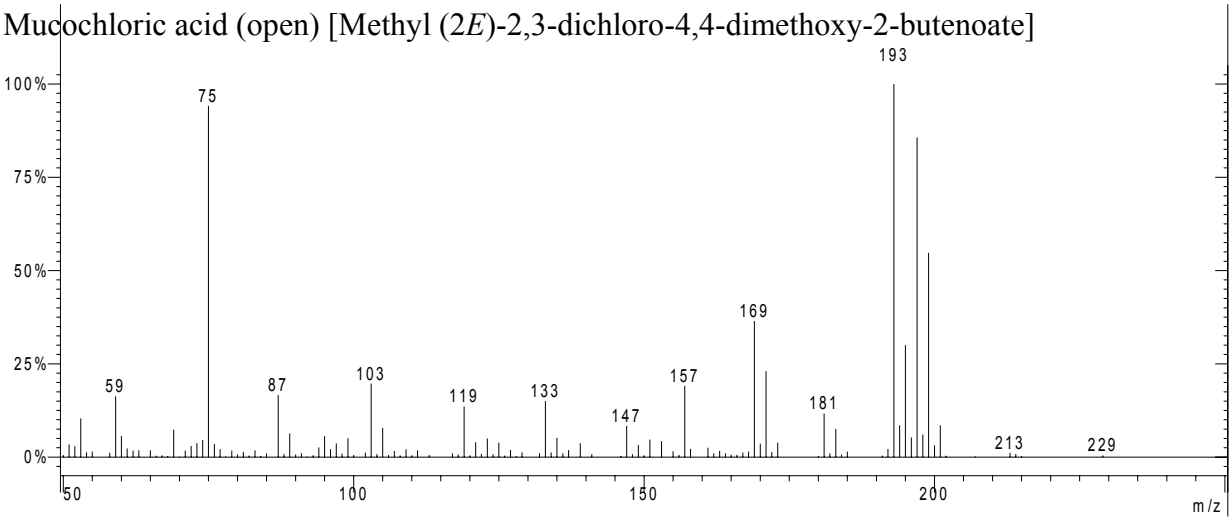
ox-MX ester [Dimethyl (2*Z*)-2-chloro-3-(dichloromethyl)-2-butenedioate]



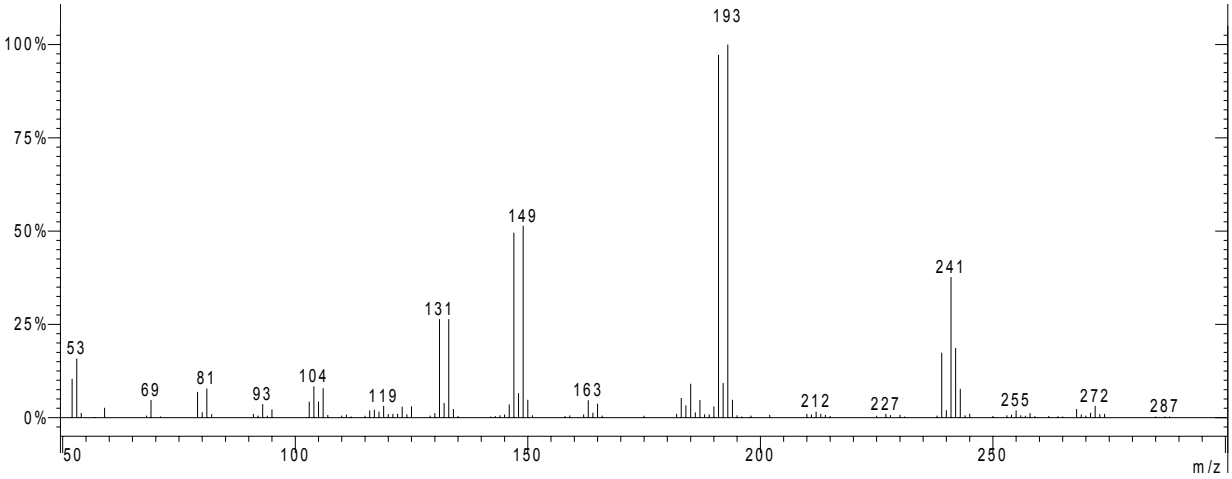
Mucochloric acid (ring) 3,4-dichloro-5-methoxy-2(5*H*)-furanone



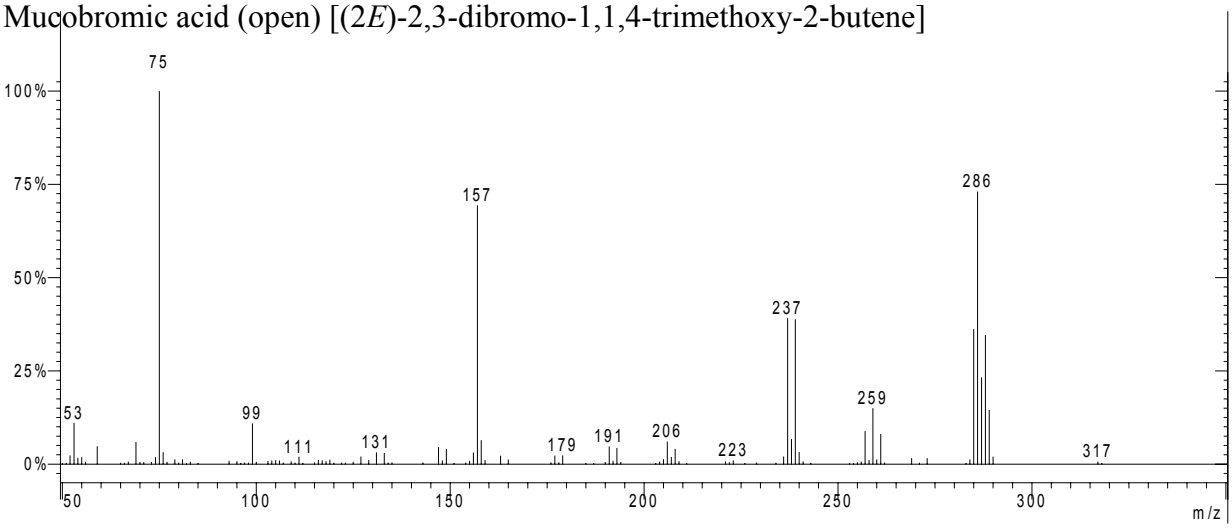
Mucochloric acid (open) [Methyl (2*E*)-2,3-dichloro-4,4-dimethoxy-2-butenoate]



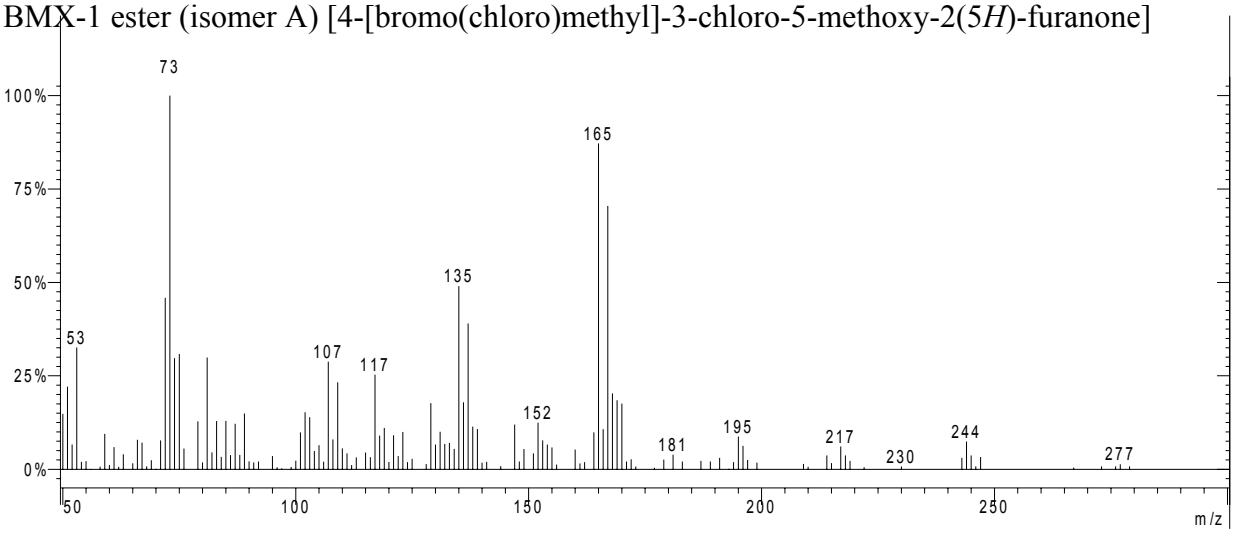
Mucobromic acid (ring) [3,4-dibromo-5-methoxy-2(5*H*)-furanone]



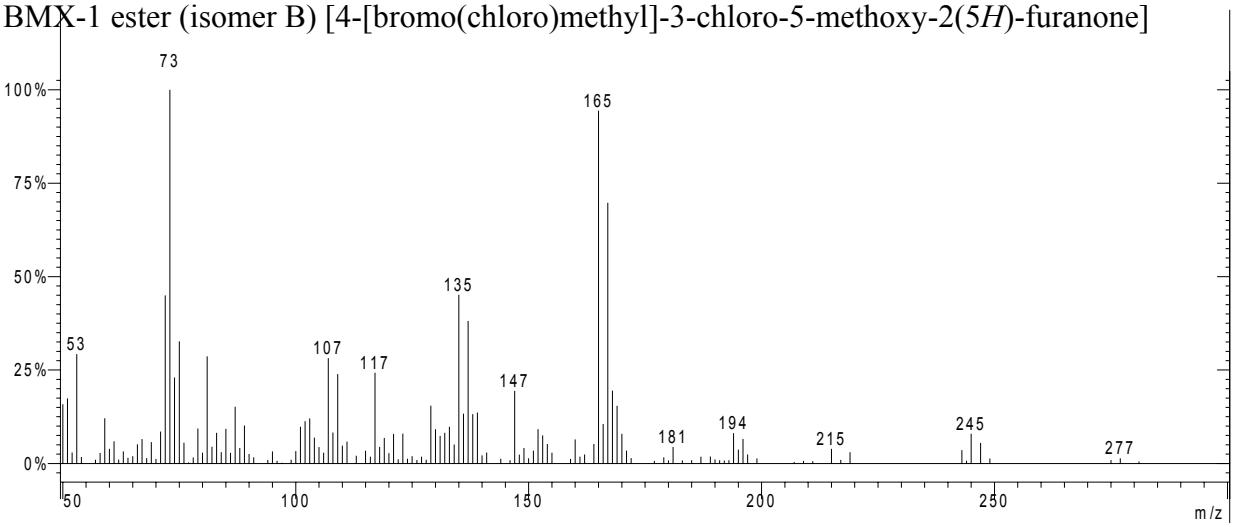
Mucobromic acid (open) [(2*E*)-2,3-dibromo-1,1,4-trimethoxy-2-butene]



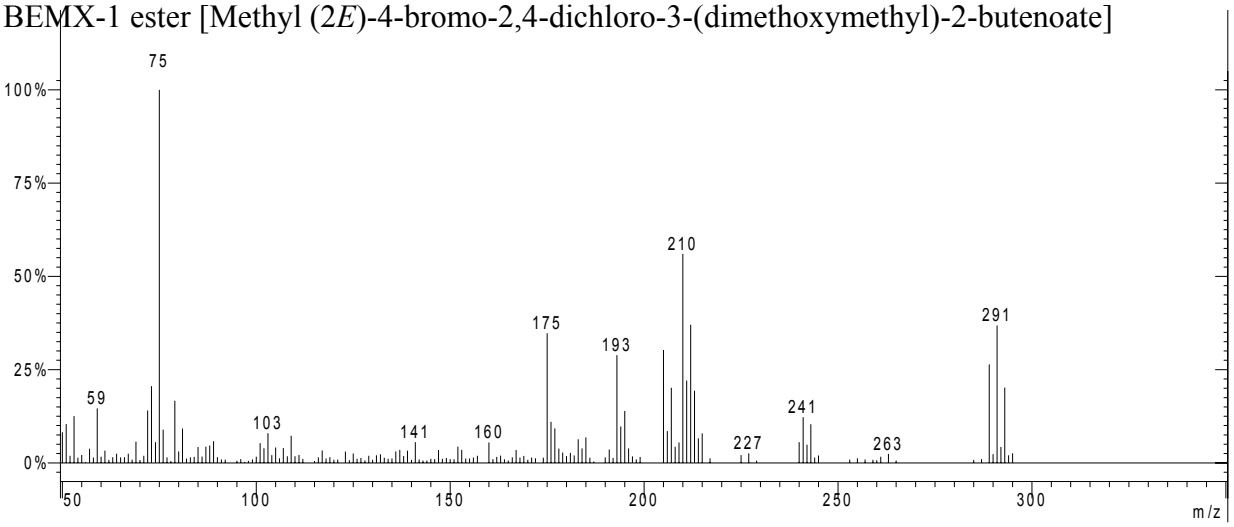
BMX-1 ester (isomer A) [4-[bromo(chloro)methyl]-3-chloro-5-methoxy-2(5*H*)-furanone]



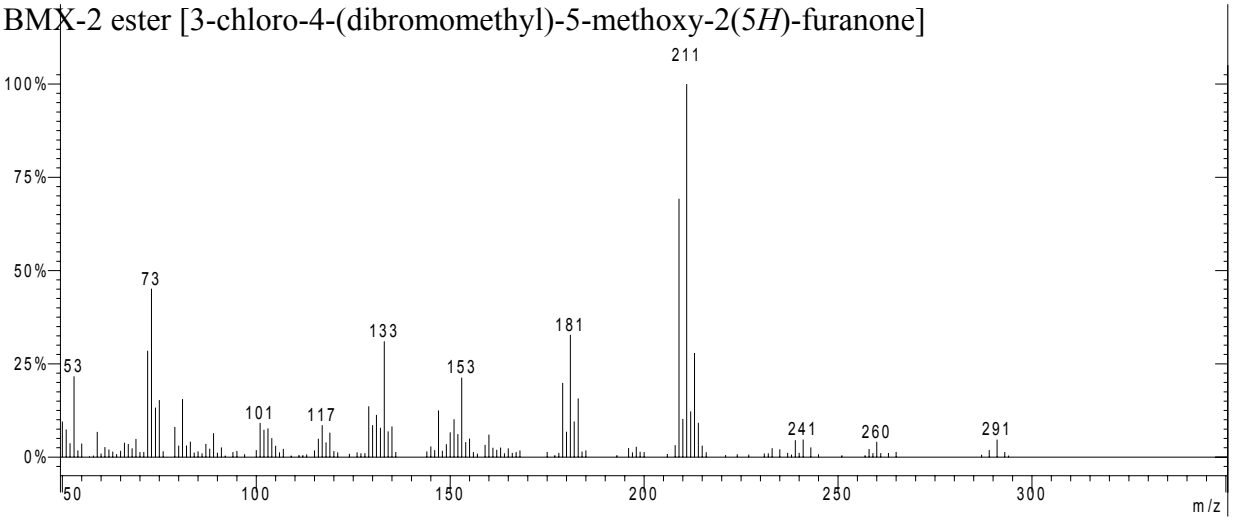
BMX-1 ester (isomer B) [4-[bromo(chloro)methyl]-3-chloro-5-methoxy-2(5*H*)-furanone]



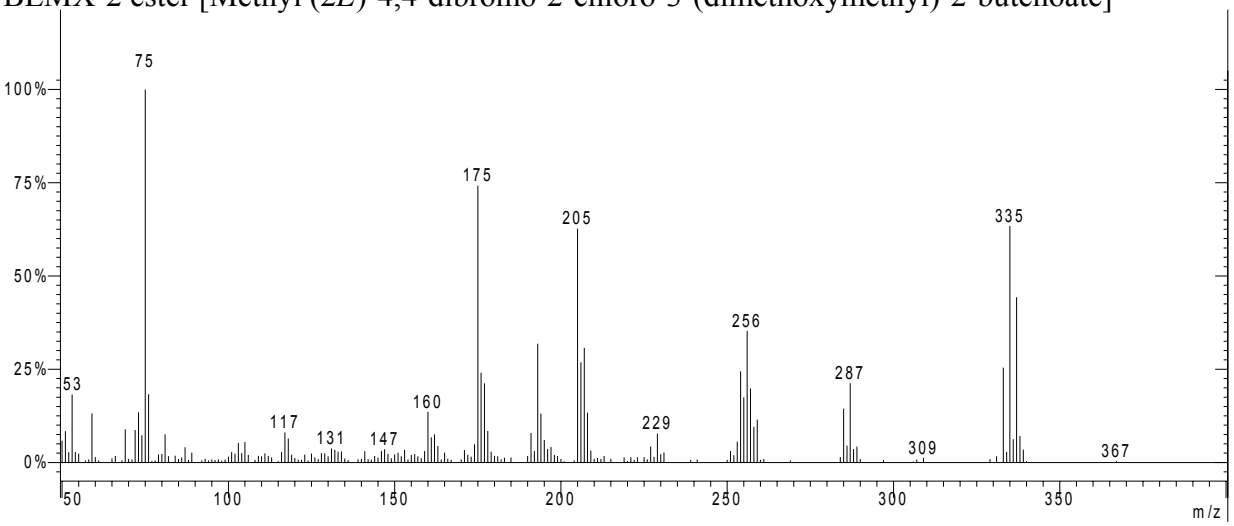
BEMX-1 ester [Methyl (2*E*)-4-bromo-2,4-dichloro-3-(dimethoxymethyl)-2-butenoate]



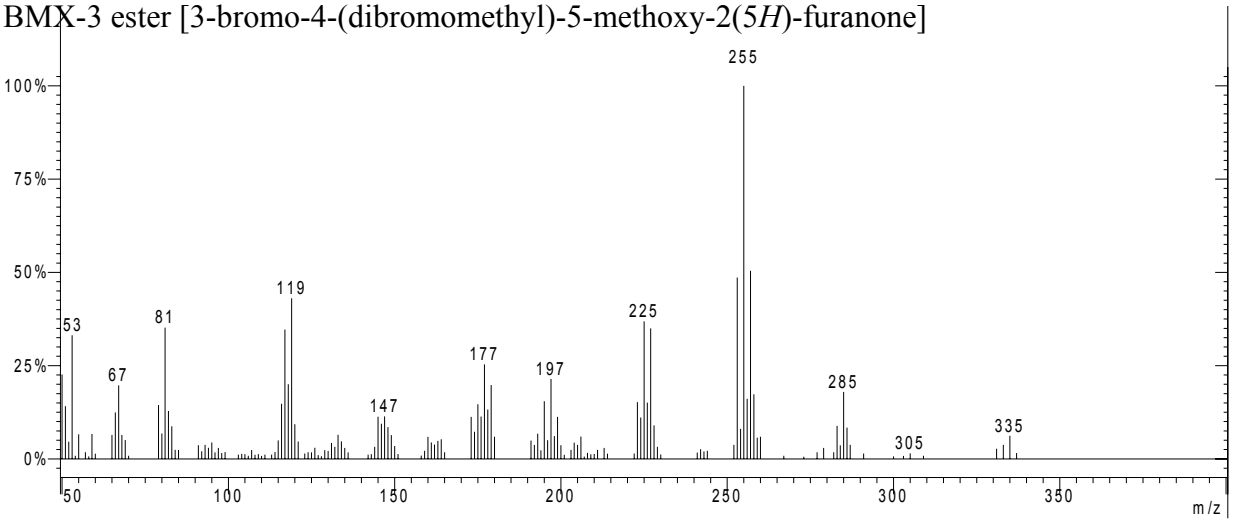
BMX-2 ester [3-chloro-4-(dibromomethyl)-5-methoxy-2(5*H*)-furanone]



BEMX-2 ester [Methyl (2*E*)-4,4-dibromo-2-chloro-3-(dimethoxymethyl)-2-butenoate]



BMX-3 ester [3-bromo-4-(dibromomethyl)-5-methoxy-2(5*H*)-furanone]



BEMX-3 ester [Methyl (2*E*)-2,4,4-tribromo-3-(dimethoxymethyl)-2-butenoate]